


Divalent Cobalt and Copper Coordination Complexes of κ^2 -*N*, *O*-Derivatives of (*Z*)-1-*R*-2-(2'-oxazolin-2'-yl)-eth-1-en-1-ates: Structure and Reactivity Patterns

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Abstract: The synthesis and characterisation of a small library of Co and Cu derivatives (29 examples) incorporating the (*Z*)-1-*R*¹-2-(4',4'-*R*²-2'-oxazolin-2'-yl)-eth-1-en-1-ate (**L**: *R*¹ = alkyl or aryl; *R*² = H or Me) skeleton is described. This work includes six new derivatives of "Tohda's Ligands". In the case where *R*² = H, solid-state stable Co(II) materials of formula Co(κ^2 -*N*,*O*-**L**)₂ could, in some cases, be obtained following base-induced deprotonation of **L**+**H** and treatment with hydrated CoX₂ salts. These complexes display redox induced solution decomposition behaviour giving Co(κ^2 -*N*,*O*-**L**)₃ as one isolable product. Stable Cu(II) complexes could only be obtained in the case of for *R*¹ = Ph and *R*² = H. In the case of *R*² = Me, distorted tetrahedral Co(II) compounds (also Co(κ^2 -*N*,*O*-**L**)₂) are obtained as above (twelve examples). Square planar derivatives of Cu(II), of similar stoichiometry, are likewise isolated (eleven new examples). In contrast to the *R*² = H reactions, all of these latter materials were found to be air-stable in solution or the solid phase. In total, 18 complexes have been characterised by single crystal X-ray diffraction. Molecular modelling (PM6(tm) and DFT) are also used to elucidate the molecular properties of selected complexes. Only a single Co complex (*R*¹ = *t*-butyl and *R*² = Me) of the library displays reversible one-electron redox properties.

Introduction

Ligand design remains one of the cornerstones of coordination chemistry and the subsequent applications of these complexes into fields such as homogeneous catalysis, materials science and metal-based drug strategies.^[1-6] In this regard, our research interests are primarily focused on the use of azole heterocycles for a variety of topics within coordination chemistry. These areas include fundamental structural studies,^[7-10] metal-mediated polymerization,^[11] catalysts for selective C-C bond formation (e.g., Suzuki-Miyaura coupling),^[12, 13] and medicinal chemistry.^[17] Recently, we have turned our attention to a class of azole metal-binding agents that we call *Tohda's Ligands* (Figure 1).^[28-31]

<Insert Figure 1>

These organics have been investigated in some detail by Yasuo Tohda since 1984 and indeed random related examples of this general structural class have been studied since the 1970s.^[28-43] The compounds themselves exist in the solid-state in the *enamine* form (Figure 1: centre) and in some cases equilibrate in solution to include the *keto* isomer (Figure 1: right).^[28-31, 32, 37, 43] This aspect depends on both the solvent and the nature of the *R* / *R*' groups.^[28-40] Protonation at the *N*-atom leads to complete conversion to the *keto* tautomer.^[43] The presence of base typically leads to H⁺ loss and the formation of a reactive *enolate*.^[28-42] Despite the fact that these materials have been studied for many years, there are only a few reports of metal chelation by these reagents and their analogues.^[41-43] Sometime ago, we briefly reported on such a Cu(II) example of formula *bis*-([*Z*]-1-phenyl-2-{4',4'-dimethyl-2'-oxazolin-2'-yl}eth-1-en-1-ate)copper(II), i.e., complex **3aa**: Figure 2).

<Insert Figure 2>

This material, with an unusual highly distorted arrangement of bonding atoms around the metal centre, is produced *via* deprotonation of (*Z*)-1-phenyl-2-(4',4'-dimethyl-2'-oxazolin-2'-yl)eth-1-ol (i.e., **1aa**: Scheme 1) in aq. EtOH solutions containing hydrated Cu(NO₃)₂.^[43]

<Insert Scheme 1>

The degree of distortion, as measured by Houser's τ_4 parameter, is 0.441.^[44] This places the ligand binding set close to an atypical seesaw disposition around Cu. The suggestion therein is that these enolate sources may provide a gateway to some very unusual coordination complexes. Such a situation we have

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already probed in the chemistry of four-coordinate Ni(II).^[45] These Group 10 compounds likewise reveal uncommon bonding modes at the Ni centres. In addition, these materials have been shown to be useful polymerization catalysts when employing alkyl Al reagents as co-promoters.^[45] Four-coordinate divalent Cu(II) and related Co(II) ligand complexes have historically provided many important examples of both structural (*i.e.*, tetrahedral [Tet], square planar [SqP], *etc.*) and electronic in nature (*e.g.*, d^9 metal-based valence electron count; *Jahn-Teller* effects). These works provided key benchmark examples with respect to bonding models such as those based on the Crystal and Ligand Field theories.^[46-50] In this report, we detail the synthesis, properties and structural characterization of a large library of Cu(II), Co(II) and Co(III) materials containing ligands derived from **1a-c** and **1aa-1ll** (Scheme 1). We further examine their subtle structural nuances with respect to the complexes themselves and other related ligand systems.

Results and Discussion

Syntheses and Structural Aspects

Previously described enolate precursors **1a**, **1b**, **1aa**, **1bb** and **1dd** – **1hh** (Scheme 1) were synthesized using literature preparations as described by Tohda *et al.*,^[18-21] Pittman and co-workers,^[23, 25, 28-32] or the methodologies of Meyers.^[22] Novel materials **1c**, **1cc**, **1ii**, **1jj**, **1kk** and **1ll** were synthesized using adaptations of the above protocols (see Experimental Section).

Compounds **1a** – **1c** represent amongst the most simple of this class of potential enolates and present a mix of EWG character (**1c**) and EDG properties (**1b**) on the aromatic system. Oxazoline metal-binding agents that are unsubstituted at ring position-4 are generally less common in the literature. This is due to the fact that the 4,4-dimethyl analogues are generally more stable and can be easier to synthesise. Their mono-substituted 4-R (chiral) partners are routinely used in *enantio*-selective catalysis and hence represent another large sub-class of these ligands.^[43, 51-61] We first turned our attention to coordination complexes of the ligand precursors **1a** – **1c** with divalent Co and Cu metal centres. Previous work on Ni(II) systems had revealed that coordination is facilitated by the addition of base to a Ni(II) salt; hence, we employed a similar tactic here.^[45] Thus, treatment of solutions (EtOH / MeOH) of cobaltous chloride or nitrate with **1a** – **1c**, in the presence of excess of NEt_3 , were found to be optimal to give the corresponding $\text{Co}(\text{1-H})_2$ complexes (**2a** – **2c**; Scheme 2 and Experimental Section).

<Insert Scheme 2>

Yields ranging from 39 to 85% for **2a-c** were noted. These compounds vary in colour from orange to red; a situation not atypical for 4-coordinate (*pseudo*-tetrahedral) Co(II) systems.^[1-2, 4-6, 47-49, 62-70] The three materials are air-stable in the solid state although less so in solution (*vide infra*). Characterisation of these paramagnetic complexes by elemental analysis, IR and UV-Vis spectroscopy was consistent with the $\text{Co}(\text{1-H})_2$ formulation (Experimental Section). Unfortunately, extensive recrystallisation

experiments only yielded X-ray quality material for **2a**. Single crystal diffraction study of this complex (ESI and Scheme 3; left) reveals a mononuclear Co material with the expected $\kappa^2\text{-N,O}$ bonding motif of the resulting ligand *bis*-enolates. A slightly distorted tetrahedral arrangement of bonding atoms around the metal is noted ($\tau_4 = 0.829$).^[44] Bond lengths and angles of the ligand framework are typical^[43, 45] and the Co–O and Co–N interactions are also of normal length for enolates and oxazolines bound to formally Co^{2+} , respectively.^[26, 41, 63-77] A useful structural comparison can be made to the species *bis*-(2-[2'-oxazolin-2'-yl]phenolato)cobalt(II). This material features very similar bonding parameters ($\tau_4 = 0.829$; Co– $\text{N}_{\text{av}} = 1.961$ Å; Co– $\text{O}_{\text{av}} = 1.936$ Å).^[77]

<Insert Scheme 3>

As noted above, solutions (*e.g.*, CH_2Cl_2) of **2a-c** are unstable over several days at ambient temperatures in open air. The mixtures of both complexes **2a** and **2b** noticeably darkened in colour and began to precipitate black-green coloured materials. Solutions of **2c** also showed similar aspects as above but in this case no pure compounds could be obtained from the solutions. Evaluation of the products of the **2a** and **2b** solution chemistry (IR and NMR spectroscopy; elemental analyses) all strongly suggest that the new materials (**4a** and **4b**, respectively) are the result of both formal metal oxidation and somewhat unusual bidentate ligand exchange processes. Hence, complexes of general formula $\text{Co}(\text{1-H})_3$ have been formed. In all three cases, no other products, such as those of complimentary reduction chemistry, could be isolated. Fortuitously, isolated materials **4a** and **4b** were suitable for X-ray diffraction study (ESI and Scheme 3: centre and right). These complexes feature two *trans*-disposed N_{ox} donors, two *trans*- $\text{O}_{\text{enolate}}$ atoms and a *trans*- $\text{N}_{\text{ox}}, \text{O}_{\text{enolate}}$ pair. This arrangement is therefore a *mer-mer* disposition of like-donor atoms around a distorted octahedral Co centre. Structural aspects of the enolate ligands are typical as are the Co–N and Co–O bond lengths.^[7, 20, 26, 51, 55-62, 78, 79]

Complimentary reactions of **1a** – **1c** with copper(II) salts were overall less fruitful. Enol source **1c** did not lead to the formation of an isolable Cu(II) complex using any typical metal precursors (hydrated CuX_2 ; X = Cl, Br, I, BF_4). Similar attempts with **1b** gave only insoluble material that did not give logical elemental analysis data; these may represent mixtures and / or compounds sensitive to decomposition. Only **1a** gave an isolable complex (**3a**) using hydrated CuBr_2 (70%) as Cu^{2+} source. Data obtained from this material are fully consistent with a complex of stoichiometry $\text{Cu}(\text{1a-H})_2$ (Experimental Section). Unfortunately, X-ray quality sources of this compound were not subsequently forthcoming. We therefore examined the hypothesised mononuclear complex *via* molecular modelling (Density Functional Theory [DFT]: M11-L basis set employing the 6-311+G(2df, 2p) level of theory; ESI) to compare it to known complex **3aa** (Figure 2).^[43] A schematic representation of one possible conformer of a calculated gas phase molecule of **3a** is shown in Figure 3. These data indicate lower distortion from idealised SqP when compared to **3aa**; calculated **3a** yields a τ_4 value of 0.014. This is more representative with respect to the large number of SqP and slightly distorted SqP $\text{Cu}(\kappa^2\text{-N,O-L})_2$

complexes that have been reported.^[41, 51, 80-123] The former of these are species often lie on a crystallographic centre of inversion (hence $\angle\text{O-Cu-O} = \angle\text{N-Cu-N} = 180^\circ$). Many of the previously reported examples contain Schiff base or similar ligands that form six-membered rings incorporating the Cu centre.^[80-123] Of particular relevance to this study is the SqP complex *trans*-Bis[(S)-2-(4-ethyl-4,5-dihydro-1,3-oxazol-2-yl)phenolato- κ^2 -N,O]copper(II), reported by Liu and co-workers in 2007.^[123] It should be noted that there are examples, although a limited number, of seesaw oriented complexes of Cu (*cf.* **3aa**) of this type.^[124-128] Not surprisingly, distorted tetrahedral Cu(II) examples are predictably more rare when one considers the formal d^9 electronic configuration at Cu.^[129]

<Insert Figure 3>

We then turned our attention to the more sterically bulky 4',4'-dimethyl enol sources **1aa** – **1II**. This was due to a combination of the observed inherent instability of the Co materials (oxidation; ligand exchange), the issues with the production and isolation of stable Cu derivatives in general (*vide supra*) and the generally more facile isolation of the ligands themselves.^[28-37]

Compounds **1aa** – **1II** were all found (Experimental section) to give acceptable yields (56 – 99%) of air-stable Co(II) complexes of general formula $\text{Co}(\text{I} - \text{H})_2$ (*i.e.*, complexes **2aa** – **2II**; Scheme 3). These complexes vary in colour from orange to pink to red depending on the nature of the various R groups. Ligand exchange and / or spontaneous solution redox induced decomposition processes are not observed with these materials; a situation in sharp contrast to that of **2a** – **2c** (*vide supra*). Characterisation of nine of these complexes by single crystal X-ray diffraction reveal surprisingly little structural variability (ESI and Scheme 4). All crystallographically characterised materials are found to be mononuclear formally Co(II) compounds with the typical κ^2 -N,O bonding mode of the enolates derived from **1aa** – **1II**. The coordination geometry around the Co metal centres is distorted tetrahedral in nature as the τ_4 values for complexes **2aa** – **2II** are found in the somewhat limited 0.779 to 0.833 range for the nine crystallographically characterised examples (ESI).

<Insert Scheme 4>

In a similar synthetic fashion as above, Cu(II) analogues **3aa** - **3II** (Scheme 4) were produced from the appropriate ligand precursors. Synthetic yields were variable and range from 40% (**3hh**) to 96% (**3bb**). All Cu materials were dark to black-green in colour and are air-stable in both solution and the solid-state. In addition to the previously reported^[43] X-ray data for **3aa**, diffraction studies were carried out on complexes **3cc** – **3gg** and **3II** (Schemes 4 and 5). In contrast to the Co materials above, these Cu examples show a fair degree of structural variability. The materials range from idealised SqP for **3ff** and **3II** ($\tau_4 = 0.00$: centre of inversion) to quite distorted seesaw shaped geometries around the metal, *e.g.*, **3aa**: $\tau_4 = 0.442$ ^[43], **3cc** ($\tau_4 = 0.478$), **3dd**: $\tau_4 = 0.527$), **3ee** ($\tau_4 = 0.497$: average of two unit cell molecules) and **3gg** ($\tau_4 = 0.375$). We further explored the particular ligand

geometry for **3II**, as an *anti*-disposition of naphthyl groups is noted in the solid-state form (*vide supra*). Due to the large number of atoms in **3II**, modelling at the M-11L DFT level of theory (*vide supra*) was deemed too computationally demanding and thus simpler semi-empirical (PM6[tm]) and DFT (B3LYP: 6-31+G*) models were used. Intriguingly, both methods (gas phase) suggest the *syn*-form as the lower energy isomer, as opposed to the crystallographically observed *anti*-form (PM6[tm]: $\Delta\Delta H_f = -0.38$ kJ/mol [anti – syn]; DFT: $\Delta E = >20$ kJ/mol: ESI). The latter DFT model also suggesting significant deviation from the observed SqP geometry for the *syn*-isomer (ESI). We therefore attest that the ligand arrangement and SqP solid-state form observed in isolated **3II** may be due to packing forces.

<Insert Scheme 5>

Our reasoning for the production of the materials described above stems from our long standing interest in both fundamental structural elucidation^[7-10, 42-43] and catalysis^[8, 13, 17, 20-23] with azole-containing transition metal (TM) complexes. Divalent Co and Cu compounds are well-known precursors for selective olefin polymerisation, in some cases under Atom Transfer Radical Polymerisation (ATRP) conditions.^[130-132] A common pre-requisite for such activity is a low energy barrier to reversible redox cycling involving the metal M (*e.g.*, $\text{M}^{2+} \rightleftharpoons \text{M}^{3+} + e^-$ or $\text{M}^{2+} + e^- \rightleftharpoons \text{M}^+$). We therefore investigated the electrochemical properties of complexes **2a** – **2c**, **2aa** – **2II** and **3aa** – **3II** to access this potential. Much to our surprise, only one of the plethora of derivatives (**2ee**: $E_{1/2} = 1.01$ V) displayed fully reversible one-electron solution redox behaviour. The majority of the other complexes showed quasi-reversible redox chemistry that invariably leads to complex decomposition after a single redox event (ESI).^[132-137] The $-\text{CX}_3$ derivatives **2gg** and **2hh** displayed behaviour consistent with complete destruction under electrochemical conditions, possibly due to the formation of halogen-based radicals. Generally, $E_{1/2}$ values follow a Hammett type relationship with respect to the electronic nature of R in the coordinated (*Z*)-1-R-2-(2'-oxazolin-2'-yl)-eth-1-en-1-ate skeleton (ESI). Future work will entail an investigation of **2ee** as a potential mediator of polymerisation and related C-C activation chemistry.

Conclusions

The first investigation of the *Tohda* ligands (**LH**), including six novel examples, with divalent Co and Cu metal precursors has been carried out from a coordination chemistry perspective. Mononuclear complexes of general formula $\text{M}(\kappa^2\text{-N,O-L})_2$ are easily obtained in the presence of NEt_3 using common hydrated MX_2 derivatives. Thirteen Co and six Cu complexes have been further characterised by single crystal X-ray diffraction. The Co materials invariably display distorted tetrahedral geometry around the metal centre in contrast to the Cu derivatives which exhibit square planar or seesaw type geometries around Cu. Stability is greatly enhanced by the presence of methyl substitution on

oxazoline ring position-4. In the absence of such groups, Cu materials could not be obtained in pure form; the isolated Co complexes have been shown to undergo oxidative ligand exchange and decomposition processes in air to yield Co(κ^2 -N,O-L)₃ derivatives (two examples: X-ray). Only a sole Co complex, **2ee**, was found to display completely reversible solution redox behaviour (*i.e.*, $\text{Co}^{2+} \rightleftharpoons \text{Co}^{3+} + e^-$) in contrast to all other complexes studied. This investigation, in combination with the sole previous Cu example, represent the first systematic examination of Tohda's ligands with Groups 9 and 11 metal centres. This work has revealed a rich coordination chemistry with these ligands and provides good background for our continued studies in this realm of inorganic synthesis. Applications of these materials in catalysis will be presented in due course.

Experimental Section

General Considerations

All reagents, solvents and deuterated solvents were obtained from commercially available sources. Dry solvents were dispensed from an Mbraun solvent purification system immediately before use. Thin layer chromatography (TLC) was performed on aluminum backed sheets pre-coated with silica F254 (0.25 nm thick; Silicycle) adsorbent eluting with the specified solvent system used. Column chromatography was carried out on 250-400 mesh size silica gel, eluting with a solvent system as described. Nuclear Magnetic Resonance spectra (¹H: 400 MHz; ¹³C{¹H}: 101 MHz; ¹⁹F{¹H}: 376 MHz) were obtained from CDCl₃ solutions on Bruker Avance II AC-400 spectrometer operating at 300K. Signals were calibrated based on solvent residual for ¹H ($\delta_{\text{H}} = 7.26$ ppm: CHCl₃) and central ¹³C resonance ($\delta_{\text{C}} = 77.17$ ppm: CDCl₃). Proton and carbon assignments were made using a variety of 2D-NMR experiments (COSY, HSQC, HMBC). Infrared spectra were obtained from an Agilent Cary 630-FTIR Spectrometer in open air. Cyclic voltammetry data was collected using a Metrohm μ -Autolab Type III potentiostat / galvanostat. All solvents were degassed prior to analysis by cyclic voltammetry. UV-Vis absorption profiles were collected using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer with a cuvette with a path length of 1 cm using DCM as solvent. Molar extinction coefficients were calculated using the Beer-Lambert law. Melting points were determined in open air, in triplicate and are uncorrected. The growth of all metal complex single crystals was carried out in either a 1:1 mixture of DCM / MeOH or by slow diffusion of Et₂O into CHCl₃ solutions of the complexes, whereas crystal growth of all organic compounds was carried out by slow evaporation of neat acetone mixtures. X-ray diffraction data were acquired as previously described.^[17, 20, 43, 45, 137] Molecular calculations, using semi-empirical PM6(tm)^[26, 138-139] and Density Functional Theory (DFT)^[141], were carried out using the *Spartan 16.0* suite of programs.^[140] The latter calculations involved initial structural optimisation using the PM6(tm) followed by DFT optimization (M11-L / 6-311+G(2df, 2p) or B3LYP / 6-31+G*).^[137-141] Zero-point energy and vibrational analyses were also conducted to indicate that a ground state conformer on the potential energy surface had been realised.^[9, 12, 17, 26, 43] Elemental analyses were performed by Atlantic Microlabs (Norcross, GA, U.S.A.). Compounds **1a**, **1b**, **1aa**, **1bb** and **1dd** – **1hh** and **3aa** ($\mu_{\text{eff}} = 1.48$ B.M.: see ESI) were synthesized as described previously.^[28-31, 32-37, 43] In this regard, C₇H₈ was used *in lieu* of benzene for the purposes of general re-crystallization for all organic compounds.

Ligand Precursor Syntheses

(Z)-1-(3,4-dichlorophenyl)-2-(oxazolin-2'-yl)eth-1-en-1-ol (**1c**)^[142]

A sample of 2-methyl-2-oxazoline (2.00 mL, 2.01 g: 23.4 mmol) was dissolved in THF (45 mL) and subsequently 3,4-dichlorobenzoyl chloride (10.6 g, 50.7 mmol) and NEt₃ (10.0 mL: 71.8 mmol) was added. The mixture was then heated to reflux temperature for 3 h. The solution was cooled (RT) and then filtered. The organic solution was then evaporated to remove volatile components (rotary evaporation). To the resulting solids was added *d*-H₂O (75 mL) and then the solution was washed with CHCl₃ (75 mL). The organic components were then collected and washed with a 10 % aq. solution of Na₂CO₃ (1 × 100 mL). Sodium sulphate was then added, the contents stirred (10 min.), then the mixture filtered and then any volatile constituents were removed (rotary evaporation). The resulting white powders were then further treated with 1.5 M methanolic KOH (25 mL), with stirring, for 2 h. The reaction mixture was then filtered and evaporated to dryness (rotary evaporation). The gel-like mixture was separated via column chromatography eluting with a solvent mixture of 1/3 acetone / *n*-hexanes to collect a pale yellow solid (0.11 g: 2%). Mp.: 153 – 155°C. TLC: 45 % EtOAc/*n*-hexanes *R*_f = 0.07. ¹H NMR: $\delta_{\text{H}} = 3.83$ (t, *J* = 8.5 Hz, 2H), 4.52 (t, *J* = 8.5 Hz, 2H), 5.53 (s, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.65 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 9.94 (s, 1H). ¹³C NMR: $\delta_{\text{C}} = 43.2, 67.8, 74.2, 126.2, 129.1, 130.3, 132.7, 134.7, 140.0, 171.2, 184.9$. Elemental Analysis (%) calc'd. (found) for C₁₁H₉Cl₂NO₂·0.25(H₂O): C 50.31 (49.92); H 3.65 (3.39); N 5.33 (5.25).

(Z)-1-(3,4-dichlorophenyl)-2-(4',4'-dimethyloxazolin-2'-yl)eth-1-en-1-ol (**1cc**)

A flask was charged with 2,4,4-trimethyl-2-oxazoline (3.00 mL, 23.5 mmol), THF (50 mL), and NEt₃ (10.0 mL, 71.7 mmol). After allowing the solution to cool to 0°C, 3,4-dichlorobenzoyl chloride (10.9 g, 52.1 mmol) in THF (25 mL) was added *via* addition funnel. The mixture was set to reflux for 3 hours. The solution was cooled (RT) and filtered to remove salts. Following filtration, the volatile components were removed from the solution *via* rotary evaporation. To the resulting pale yellow coloured solids, *d*-H₂O (75 mL) was added then the solution was extracted with CHCl₃ (75 mL). The organic components were then washed (10 % aq. Na₂CO₃: 1 × 100 mL). Solid Na₂SO₄ was then added, the contents stirred, then the mixture filtered and the volatile constituents were removed *via* a rotary evaporator. The resulting white powder was recrystallized with a 1:2 mixture of toluene-hexane. Isolation by filtration revealed a pale yellow coloured fluffy solid, **Int-cc** (6.7 g: 63%). Mp: 79–82°C. TLC (20% EtOAc / *n*-hexanes: v/v): *R*_f = 0.16. ¹H NMR: $\delta_{\text{H}} = 1.66$ (s, 6H), 4.38 (s, 2H), 4.93 (s, 1H), 7.21-7.23 (m, 1H, Ar-*H*), 7.36-7.38 (m, 1H, Ar-*H*), 7.54-7.65 (m, 3H, Ar-*H*), 7.85 (m, 1H, Ar-*H*). ¹³C NMR: $\delta_{\text{C}} = 22.8, 63.4, 79.9, 85.2, 126.2, 128.1, 129.2, 130.3, 130.9, 131.1, 132.6, 133.8, 133.9, 135.8, 137.8, 139.6, 161.5, 166.2, 184.1$. In a 50 mL round-bottom flask, KOH (2.14 g, 37.5 mmol, 1.5 M) was dissolved in MeOH (25 mL) at RT. After fully dissolved, the intermediate amide compound **Int-cc** from above (1.04 g, 2.19 mmol) was added to the mixture and this was then stirred (19 h) at RT. Volatile components were then removed by rotary evaporation. The resulting white solids were diluted with *d*-H₂O (25 mL) and washed with DCM (1 × 25 mL). Organic constituents were washed once more with water (50 mL). Sodium sulphate was then added to the isolated organic layers, the mixture filtered and any volatiles removed *via* a rotary evaporator. The target product was thereafter collected as a white, needle-like solid of **1-cc** (0.53 g: 84%). Mp: 119–121°C. TLC (20% EtOAc/*n*-hexanes): *R*_f = 0.14. ¹H NMR: $\delta_{\text{H}} = 1.43$ (s, 6H), 4.16 (s, 2H), 5.46 (s, 1H), 7.44 (d, *J* = 8.25 Hz, 1H), 7.65 (dd, *J* = 1.75, 8.25 Hz, 1H), 7.92 (d, *J* = 1.75 Hz, 1H), 9.91 (s, 1H). ¹³C-NMR: $\delta_{\text{C}} = 27.1; 58.7; 73.9; 79.1; 126.0; 128.9; 130.1; 132.4; 134.4; 139.9; 169.8; 184.5$. MS-EI (*m/z*) calc'd (found): [M]⁺ = 286.12 (286.1). Elemental Analysis (%): calc'd. (found) for C₁₃H₁₃Cl₂NO₂: C 54.57 (54.50); H 4.58 (4.51); N 4.89 (4.85).

(Z)-1-(3-chloro-4-methylphenyl)-2-(4',4'-dimethyloxazolin-2'-yl)eth-1-en-1-ol (**1ii**)

In an identical manner to **1cc**, the intermediate amide was **Int-ii** was isolated as a pale-yellow-coloured powder (3.8 g; 68%). Mp.: 142–145°C. TLC (20% EtOAc/*n*-hexanes: v/v): R_f = 0.53. ^1H NMR: δ_{H} = 1.65 (s, 6H), 2.28 (s, 3H), 2.43 (s, 3H), 4.35 (s, 2H), 4.97 (s, 1H), 7.03 (d, J = 1.5 Hz), 7.09 (dd, J = 8.2, 1.5 Hz), 7.22 (d, J = 8.2 Hz), 7.47–7.52 (m, 2H), 7.60 (s, 1H). ^{13}C NMR: δ_{C} = 20.0, 20.0, 22.8, 79.8, 85.6, 126.1, 127.2, 127.9, 129.0, 129.7, 129.8, 131.4, 135.9, 137.4, 138.7, 139.4, 141.6, 161.3, 167.8, 185.7. Elemental Analysis (%): calc'd. (found) for $\text{C}_{22}\text{H}_{21}\text{Cl}_2\text{NO}_3$: C 61.19 (61.24); H 5.25 (5.46); N 3.24 (3.32). A sample of **1-ii** (2.01 g, 4.80 mmol) was dissolved in MeOH (50 mL) with KOH (4.53 g, 80.5 mmol). The target product was collected as a light pink coloured solid (0.62 g; 49%). Mp.: 143–145°C. TLC (45% EtOAc / *n*-hexanes: v/v): R_f = 0.28. ^1H NMR: δ_{H} = 1.41 (s, 6H, 1), 2.39 (s, 3H, 14), 4.13 (s, 2H, 3), 5.50 (s, 1H, 6), 7.33 (d, J = 8.3 Hz, 1H, 9), 7.59 (dd, J = 8.3, 1.8 Hz, 1H, 13), 7.71 (d, J = 1.8 Hz, 1H, 12), 9.93 (s, 1H, 4) ^{13}C NMR: δ_{C} = 20.2, 27.1, 58.6, 73.9, 79.0, 125.6, 128.8, 129.4, 135.7, 136.7, 138.5, 169.6, 186.4. MS-EI (m/z): calc'd (found): $[\text{M}]^+$ = 265.7 (265.8). Elemental Analysis (%) calc'd. (found) for $\text{C}_{14}\text{H}_{16}\text{ClNO}_2$: C 63.28 (63.17); H 6.07 (5.97); N 5.27 (5.19).

(Z)-1-(4-chloro-3-methylphenyl)-2-(4',4'-dimethyloxazolin-2'-yl)eth-1-en-1-ol (**1jj**)

In an identical manner to **1cc**, the intermediate amide was **Int-jj** was isolated as a yellow coloured powder (4.8 g; 86%). Mp.: 154–156°C. TLC (45% EtOAc / *n*-hexanes: v/v): R_f = 0.19. ^1H NMR: δ_{H} = 1.62 (s, 6H), 2.30 (s, 3H), 2.46 (s, 3H), 4.33 (s, 2H), 4.95 (s, 1H), 7.04 (d, J = 1.1 Hz, 1H), 7.09 (d, J = 7.9 Hz, 1H), 7.23 (dd, J = 8.0, 1.1 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.49 (dd, J = 7.8, 1.1 Hz, 1H), 7.70 (d, J = 1.1 Hz, 1H) ^{13}C NMR: δ_{C} = 20.1, 20.5, 22.8, 63.0, 79.8, 85.4, 125.5, 127.2, 127.8, 129.6, 130.7, 131.4, 133.5, 134.0, 135.2, 139.4, 139.6, 141.8, 161.4, 167.3, 185.1. Elemental Analysis (%): calc'd. (found) for $\text{C}_{22}\text{H}_{21}\text{Cl}_2\text{NO}_3$: C 61.19 (61.47); H 5.25 (5.34); N 3.24 (3.42). A sample of **Int-jj** (1.51 g; 3.60 mmol) was dissolved in MeOH (25 mL) containing KOH (2.20 g; 39.2 mmol) and isolated as for **1cc** as a pale yellow-coloured solid **1jj** (0.588 g; 69%). Mp.: 127–129°C. TLC (45% EtOAc / *n*-hexanes: v/v): R_f = 0.30. ^1H NMR: δ_{H} = 1.42 (s, 6H), 2.37 (s, 3H), 4.14 (s, 2H), 5.49 (s, 1H), 7.22 (d, J = 7.9 Hz, 1H), 7.61 (dd, J = 7.9, 1.7 Hz, 1H), 7.81 (d, J = 1.7 Hz, 1H), 9.79 (s, 1H) ^{13}C NMR: δ_{C} = 20.2, 27.2, 58.7, 73.9, 79.1, 125.1, 127.7, 130.8, 134.4, 138.6, 139.4, 169.8, 185.9. EI-MS (m/z): calc'd (found): $[\text{M} + \text{H}]^+$ = 265.7 (266.1). Elemental Analysis (%) calc'd. (found) for $\text{C}_{14}\text{H}_{16}\text{ClNO}_2$: C 63.28 (63.47); H 6.07 (5.97); N 5.27 (5.17).

(Z)-1-(3,4-dimethylphenyl)-2-(4',4'-dimethyloxazolin-2'-yl)eth-1-en-1-ol (**1kk**)

In an identical manner to **1cc**, the intermediate amide was **Int-kk** was isolated as a pale-yellow powder (1.1 g; 35 %). Mp.: 122–124°C. TLC (20% EtOAc / *n*-hexanes: v/v): R_f = 0.13. ^1H NMR: δ_{H} = 1.68 (s, 6H), 2.17 (s, 3H), 2.24 (s, 3H), 2.34 (s, 3H), 2.38 (s, 3H), 4.37 (s, 2H), 5.12 (s, 1H), 7.00–7.02 (m, 2H), 7.11 (dd, J = 1.5, 4.8 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.49–7.53 (m, 2H). ^{13}C NMR: δ_{C} = 19.7, 19.7, 19.8, 20.1, 22.8, 62.6, 79.7, 85.7, 124.9, 126.8, 128.5, 129.3, 130.1, 130.1, 132.4, 136.0, 137.4, 138.1, 140.3, 142.1, 161.2, 169.1, 186.8. Elemental Analysis (%) calc'd. (found) for $\text{C}_{24}\text{H}_{27}\text{NO}_3$: C 73.73 (73.93); H 7.33 (7.33); N 3.58 (3.61). A sample (0.843g; 2.23 mmol) of this material (**Int-kk**) was added to a solution of KOH (2.15 g; 38.3 mmol) in MeOH (25 mL). The target product (**1kk**) was collected as a pale yellow solid (0.300 g; 56%). Mp.: 149–151°C. TLC (35% EtOAc / Hexane: v/v): R_f = 0.18. ^1H NMR: δ_{H} = 1.42 (s, 6H), 2.28 (d, J = 5.8 Hz, 6H), 4.12 (s, 2H), 5.56 (s, 1H), 7.14 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.64 (s, 1H), 9.91 (s, 1H). ^{13}C NMR: δ_{C} = 19.8, 19.9, 27.1, 58.5, 73.8, 73.9, 124.4, 128.1, 129.4, 136.2, 137.6, 139.5, 169.5,

187.7. EI-MS (m/z): calc'd (found): $[\text{M} + \text{H}]^+$ = 245.3 (246.4). Elemental Analysis (%) calc'd. (found) for $\text{C}_{15}\text{H}_{19}\text{NO}_2 \cdot 0.25(\text{H}_2\text{O})$: C 72.12 (71.99); H 7.87 (7.64); N 5.61 (5.39).

(Z)-1-(naphthalen-1'-yl)-2-(4',4'-dimethyloxazolin-2'-yl)-eth-1-en-1-ol (**1ll**)

In an identical manner to **1cc**, the intermediate amide was **Int-ll** was isolated as a pale yellow coloured solid (12.6 g, 76%) but not further purified or characterised but carried forward. A sample of crude (10.2 g; 24.1 mmol) **Int-ll** was added to a solution of KOH (4.52 g; 80.7 mmol) in MeOH (55 mL). The target product (**1ll**) was collected as per **1cc** as a white coloured solid (1.5 g; 23%) following purification via flash column chromatography with a solvent mixture containing 1:1 (v/v) ethyl acetate / hexanes. Mp.: 129–132°C. TLC (50% EtOAc / *n*-Hexanes: v/v): R_f = 0.29. ^1H NMR: δ_{H} = 1.46 (s, 6H), 4.14 (s, 2H), 5.36 (s, 1H), 7.43–7.57 (m, 3H), 7.63 (d, J = 7.0 Hz) 7.85 (d, J = 7.7 Hz, 2H), 8.48 (d, J = 8.20, 1H) 9.93 (s, 1H) ^{13}C NMR: δ_{C} = 27.2, 58.6, 78.8, 79.0, 124.9, 125.1, 125.8, 126.3, 126.3, 128.1, 129.5, 130.3, 133.8, 140.6, 169.1, 191.6. MS-EI (m/z): calc'd (found): $[\text{M}]^+$ = 258.1 (258.0). Elemental Analysis (%) calc'd. (found) for $\text{C}_{17}\text{H}_{17}\text{NO}_2$: C 76.38 (76.29); H 6.41 (6.35); N 5.24 (5.11).

Synthesis of M(II) complexes derived from **1a** – **1c**

Cobalt

Co(**1a** – H)₂ (Complex **2a**) and Co(**1a** – H)₃ (Complex **4a**)

A sample of **1a** (0.764 g; 4.04 mmol) was dissolved in MeOH (15 mL) and o the solution was added $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.598 g; 2.51 mmol) and the mixture stirred for 1 h. The resulting tan coloured precipitates were collected via vacuum filtration which were then recrystallized from 1:1 mixture of RT Et₂O / CHCl₃ to reveal bright orange coloured needles (0.35 g; 39%). Mp.: 240°C (decomp.) IR (cm⁻¹): 2968, 2903, 1591, 1569, 1527, 1486, 1418, 1354, 1261, 1192, 1108, 989, 945, 865, 746, 696, 668. UV-Vis (9.19 × 10⁻⁵ M): $\lambda_{\text{max}1}$ = 527 nm (ϵ = 58.0 Lmol⁻¹cm⁻¹), $\lambda_{\text{max}2}$ = 311 nm (ϵ = 1.63 × 10⁴ Lmol⁻¹cm⁻¹), $\lambda_{\text{max}3}$ = 282 nm (ϵ = 1.52 × 10⁴ Lmol⁻¹cm⁻¹), $\lambda_{\text{max}4}$ = 236 nm (ϵ = 1.82 × 10⁴ Lmol⁻¹cm⁻¹). MS-EI (m/z): found (calc'd) $[\text{M}]^+$ = 436.1 (436.8). Elemental Analysis (%) calc'd. (found) for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4\text{Co}$: C 60.70 (60.49); H 4.63 (4.70); N 6.43 (6.49).

Complex **2a** (0.034 g) was dissolved neat in DCM and, upon standing for several days, the gradual formation of a new material (**4a**) was noted. The pure complex was obtained as a blackish-green coloured solid (0.034 g; 49%). No other materials could be isolated from the mixture. Mp.: 235°C (decomp.). IR (cm⁻¹): 2921, 2108, 1612, 1526, 1478, 1454, 1420, 1353, 1317, 1266, 186, 1109, 1066, 990, 948, 871, 791, 736, 695. UV-Vis (5.77 × 10⁻⁶ M): $\lambda_{\text{max}1}$ = 556 nm (ϵ = 556 Lmol⁻¹cm⁻¹), $\lambda_{\text{max}2}$ = 441 nm (ϵ = 1.31 × 10³ Lmol⁻¹cm⁻¹), $\lambda_{\text{max}3}$ = 347 nm (ϵ = 2.28 × 10⁴ Lmol⁻¹cm⁻¹), $\lambda_{\text{max}4}$ = 268 nm (ϵ = 8.99 × 10⁴ Lmol⁻¹cm⁻¹), $\lambda_{\text{max}5}$ = 262 nm (ϵ = 9.72 × 10⁴ Lmol⁻¹cm⁻¹), $\lambda_{\text{max}6}$ = 258 nm (ϵ = 9.37 × 10⁴ Lmol⁻¹cm⁻¹), $\lambda_{\text{max}7}$ = 245 nm (ϵ = 8.71 × 10⁴ Lmol⁻¹cm⁻¹). Elemental Analysis (%) calc'd. (found) for $\text{C}_{33}\text{H}_{30}\text{N}_3\text{O}_6\text{Co}$: C 60.41 (61.05); H 4.96 (4.69); N 6.31 (5.99).

Co(**1b** – H)₂ (Complex **2b**) and Co(**1a** – H)₃ (Complex **4b**)

In a similar manner to **2a** above, the complex was made with **1b** (0.630 g; 2.87 mmol), EtOH (20 mL), NEt₃ (0.60 mL; 4.3 mmol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.412 g; 1.42 mmol). The resulting tan coloured materials were then recrystallized from a 1:1 mixture of warm DCM and diffusing with RT Et₂O. The pure complex was obtained as a bright red solid (0.595 g; 85%). Mp.: 251 °C (decomp.). IR (cm⁻¹): 2960, 1587, 1566, 1531, 1498, 1396, 1358, 1321, 1301, 1245, 1194, 1170, 1113, 1056, 1028, 992, 948, 869, 838, 770,

672. UV-Vis (1.94×10^{-5} M): $\lambda_{\max 1} = 547$ nm ($\epsilon = 73.0$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 2} = 317$ nm ($\epsilon = 4.04 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 3} = 263$ nm ($\epsilon = 2.32 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 4} = 242$ nm ($\epsilon = 2.06 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). MS-EI (m/z) found (calc'd) $[M+H]^+ = 495.4$ (496.2). Elemental Analysis (%) calc'd. (found) for C₂₄H₂₄N₂O₆Co: C 49.18 (49.12); H 4.37 (4.80); N 4.50 (5.17).

Complex **2b** (0.040 g) was dissolved neat in DCM which led to the formation of **4b** after standing in open air for several days. The pure complex was obtained as a blackish-green coloured solid (0.050 g: 86% conversion). No other materials could be isolated from the mixture. Mp.: >230 °C (decomp.). IR (cm $^{-1}$): 2923, 1599, 1529, 1495, 1437, 1358, 1319, 1299, 1244, 1167, 1111, 1071, 126, 992, 950, 876, 837, 756, 723. UV-Vis (5.61×10^{-6} M): $\lambda_{\max 1} = 553$ nm ($\epsilon = 683$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 2} = 429$ nm ($\epsilon = 1.34 \times 10^3$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 3} = 343$ nm ($\epsilon = 2.06 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 4} = 276$ nm ($\epsilon = 6.38 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 5} = 269$ nm ($\epsilon = 7.43 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 6} = 265$ nm ($\epsilon = 7.15 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 7} = 244$ nm ($\epsilon = 4.46 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). Elemental Analysis (%) calc'd. (found) for C₃₆H₃₆N₃O₉Co: C 59.47 (59.84); H 5.20 (5.54); N 5.78 (5.04).

Co(**1c** – H)₂ (Complex **2c**)

This compound was made with **1c** (0.042 g: 0.16 mmol), EtOH (5 mL), NEt₃ (0.1 mL: 72 mmol) and Co(NO₃)₂·6H₂O (0.023 g: 0.079 mmol). The resulting tan coloured material was recrystallized from a 1:1 mixture of warm CHCl₃ and diffusing with RT Et₂O. The pure complex was obtained as a bright red coloured solid (0.036 g: 79%). Mp.: 220 °C (decomp.). IR (cm $^{-1}$): 1592, 1529, 1462, 1437, 1359, 1280, 1240, 1194, 1134, 1107, 1058, 1025, 995, 949, 899, 801, 761, 677. UV-Vis (7.00×10^{-5} M): $\lambda_{\max 1} = 524$ nm ($\epsilon = 94.0$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 2} = 321$ nm ($\epsilon = 2.11 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 3} = 296$ nm ($\epsilon = 1.51 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 4} = 243$ nm ($\epsilon = 1.91 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). Elemental Analysis (%) calc'd. (found) for C₂₂H₁₆Cl₄N₂O₄Co: C 43.90 (44.43); H 2.75 (2.78); N 4.55 (4.66).

Copper

Cu(**1a** – H)₂ (Complex **3a**)

A sample of **1a** (0.755 g, 3.99 mmol) was dissolved in MeOH (15 mL) and CuBr₂ (0.560 g, 2.51 mmol) was then added. Stirring was continued for 4 h and then pastel green coloured precipitates were collected *via* vacuum filtration (0.59 g: 70%). Mp.: >260 °C (decomp.). IR (cm $^{-1}$): 2890, 1605, 1578, 1540, 1487, 1454, 1414, 1360, 1328, 1263, 1200, 1110, 1063, 995, 951, 750, 689, 655. UV-Vis (1.36×10^{-4} M): $\lambda_{\max 1} = 320$ nm ($\epsilon = 7.17 \times 10^3$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 2} = 285$ nm ($\epsilon = 8.58 \times 10^3$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 3} = 233$ nm ($\epsilon = 8.45 \times 10^3$ Lmol $^{-1}$ cm $^{-1}$). Elemental Analysis (%) calc'd. (found) for C₂₂H₂₀N₂O₄Cu: C 60.06 (59.89); H 4.58 (4.76); N 6.37 (6.36).

Synthesis of M(II) complexes derived from **1aa** – **1ll**

Cobalt

Co(**1aa** – H)₂ (Complex **2aa**)

A round-bottom flask was charged with **1aa** (1.01 g: 4.64 mmol), NEt₃ (3.00 mL: 21.5 mmol), and EtOH (10 mL). After the yellow-coloured solids were completely dissolved, Co(NO₃)₂·6H₂O (0.671 g: 2.31 mmol) was added to the solution as an EtOH solvate (5 mL). Upon addition of the two, the solution turned colour from yellow to a bright red. The solution was stirred at RT for 2 h. Thereafter, red coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH to give **2aa** (0.927 g: 81%). Mp.: 198–201 °C. $\mu_{\text{eff}} = 4.45$ B.M. (see ESI). IR (cm $^{-1}$): 2986, 2889, 1740, 1589, 1570, 1520, 1485, 1471, 1407, 1353, 1304, 1172, 1103, 994, 952, 860, 840, 754, 695, 653. UV-Vis (5.70×10^{-5} M): $\lambda_{\max 1} = 534$ nm ($\epsilon =$

60.0 Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 2} = 314$ nm ($\epsilon = 2.39 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 3} = 232$ nm ($\epsilon = 2.14 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). MS-EI (m/z): found (calc'd) $[M + H]^+ = 492.3$ (491.5). Elemental Analysis (%) calc'd. (found) for C₂₆H₂₈N₂O₄Co: C 63.54 (63.49); H 5.74 (5.72); N 5.70 (5.43).

Co(**1bb** – H)₂ (Complex **2bb**)

In a similar manner to **2aa** (above), **2bb** was produced using **1bb** (0.103 g: 0.42 mmol), EtOH (20 mL), NEt₃ (0.10 mL: 0.72 mmol) and Co(NO₃)₂·6H₂O (0.058 g, 0.20 mmol). Red coloured precipitates were collected were recrystallized in a mixture of 1:1 DCM / MeOH to give **2bb** (0.118 g: 99%). Mp.: 243–245 °C. IR (cm $^{-1}$): 2969, 2882, 1610, 1584, 1560, 1524, 1498, 1396, 1355, 1300, 1253, 1190, 1167, 1113, 1026, 999, 842, 769, 680. UV-Vis (1.27×10^{-4} M): $\lambda_{\max 1} = 540$ nm ($\epsilon = 30.0$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 2} = 316$ nm ($\epsilon = 1.14 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 3} = 263$ nm ($\epsilon = 7.32 \times 10^3$ Lmol $^{-1}$ cm $^{-1}$). Elemental Analysis (%) calc'd. (found) for C₂₈H₃₂N₂O₆Co: C 60.98 (60.90); H 5.85 (5.74); N 5.08 (5.10).

Co(**1cc** – H)₂ (Complex **2cc**)

In a similar manner to **2aa** (above), **2cc** was produced using **1cc** (0.533 g: 1.86 mmol), MeOH (25 mL) and Co(NO₃)₂·6H₂O (0.27 g: 0.92 mmol). Orange precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH to yield **2cc** (0.331 g: 56%). Mp.: 223–225 °C. IR (cm $^{-1}$): 2960, 1739, 1581, 1524, 1461, 1428, 1354, 1303, 1256, 1178, 1141, 1102, 1025, 878, 766, 670. UV-Vis (2.54×10^{-5} M): $\lambda_{\max 1} = 538$ nm ($\epsilon = 113$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 2} = 321$ nm ($\epsilon = 3.88 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 3} = 245$ nm ($\epsilon = 3.03 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). MS-EI (m/z): found (calc'd) $[M + H]^+ = 630.1$ (629.2). Elemental Analysis (%) calc'd. (found) for C₂₆H₂₄N₂O₄Cl₄Co: C 49.63 (49.48); H 3.84 (3.90); N 4.45 (4.40).

Co(**1dd** – H)₂ (Complex **2dd**)

In a similar manner to **2aa** (above), **2dd** was made with **1dd** (0.120 g: 0.458 mmol), EtOH (20 mL), NEt₃ (1.0 mL: 7.2 mmol) and Co(NO₃)₂·6H₂O (0.0670 g: 0.230 mmol). Orange precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH to yield **2dd** (0.097 g: 73%). Mp.: >240 °C (decomp.). IR (cm $^{-1}$): 2967, 1577, 1512, 1482, 1341, 1300, 1173, 1108, 1025, 992, 945, 862, 833, 777, 753, 703. UV-Vis (6.88×10^{-6} M): $\lambda_{\max 1} = 363$ nm ($\epsilon = 2.47 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 2} = 264$ nm ($\epsilon = 3.33 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). Elemental Analysis (%) calc'd. (found) for C₂₆H₂₆N₄O₈Co: C 51.02 (51.39); H 4.36 (4.28); N 8.98 (8.82).

Co(**1ee** – H)₂ (Complex **2ee**)

In a similar manner to **2aa** (above), this complex was made with **1ee** (0.119 g: 0.603 mmol), EtOH (20 mL), NEt₃ (0.20 mL: 1.4 mmol) and Co(NO₃)₂·6H₂O (0.0850 g: 0.292 mmol). Pink precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH to yield **2ee** (0.105 g, 79 %). Melting Point Range: >220 °C (decomp.) IR: (cm $^{-1}$) 2959, 1576, 1525, 1473, 1416, 1353, 1295, 1195, 1155, 1000, 948, 898, 803, 770, 729. UV-Vis (1.77×10^{-5} M): $\lambda_{\max 1} = 537$ nm ($\epsilon = 647$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 2} = 321$ nm ($\epsilon = 1.14 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\max 3} = 280$ nm ($\epsilon = 8.37 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). Elemental Analysis (%) calc'd. (found) for C₂₂H₃₆N₂O₄Co: C 58.53 (58.29); H 8.04 (8.07); N 6.21 (5.97).

Co(**1ff** – H)₂ (Complex **2ff**)

In a similar manner to **2aa** (above), this complex was made with **1ff** (0.503 g: 3.24 mmol), NEt₃ (1.00 mL: 0.726 g, 7.17 mmol), and EtOH (15 mL) and Co(NO₃)₂·6H₂O (0.435 g: 150 mmol). Bright pink precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH to yield **2ff** (0.300 g: 57%). Mp.: >210 °C (decomp.) IR (cm $^{-1}$): 2964, 1577, 1508,

1405, 1351, 1297, 1221, 1190, 1165, 1045, 991, 932, 760. UV-Vis (1.09×10^{-5} M): $\lambda_{\text{max}1} = 536$ nm ($\epsilon = 786$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}2} = 278$ nm ($\epsilon = 1.52 \times 10^5$ Lmol $^{-1}$ cm $^{-1}$). Elemental Analysis (%) calc'd. (found) for C₁₆H₂₄N₂O₄Co: C 52.32 (52.07); H 6.59 (6.37); N 7.63 (7.42).

Co(**1gg** – H)₂ (Complex **2gg**)

In a similar manner to **2aa** (above), **2gg** was made with **1gg** (0.500 g: 1.93 mmol), EtOH (5 mL), NEt₃ (1.00 mL: 7.17 mmol) and Co(NO₃)₂·6H₂O (0.268 g: 0.920 mmol). Bright pink coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH to yield **2gg** (0.500 g: 95%). Mp.: 184 °C (decomp.). IR (cm $^{-1}$): 2970, 2895, 1596, 1524, 1458, 1352, 1281, 1199, 1031, 1005, 960, 936, 828, 802, 758, 671. UV-Vis (2.10×10^{-4} M): $\lambda_{\text{max}1} = 536$ nm ($\epsilon = 72.0$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}2} = 489$ nm ($\epsilon = 51.0$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}3} = 285$ nm ($\epsilon = 1.56 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). Elemental Analysis (%) calc'd. (found) for C₁₆H₁₈Cl₆N₂O₄Co: C 33.48 (33.48); H 3.16 (3.13); N 4.88 (4.81).

Co(**1hh** – H)₂ (Complex **2hh**)

In a similar manner to **2aa** (above), **2hh** was made with **1hh** (0.502 g: 2.40 mmol), EtOH (10 mL) NEt₃ (1.00 mL: 7.17 mmol) and Co(NO₃)₂·6H₂O (0.317 g: 1.09 mmol). Bright pink coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH to yield **2hh** (0.478 g: 93%). Mp.: 220 °C (decomp.). IR (cm $^{-1}$): 2975, 1608, 1560, 1463, 1360, 1314, 1250, 1173, 1126, 1028, 992, 971, 872, 751, 749, 699. UV-Vis (1.94×10^{-5} M): $\lambda_{\text{max}1} = 534$ nm ($\epsilon = 389$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}2} = 273$ nm ($\epsilon = 7.38 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). Elemental Analysis (%) calc'd. (found) for C₁₆H₁₈F₆N₂O₄Co: C 40.44 (40.54); H 3.82 (3.77); N 5.89 (5.98).

Co(**1ii** – H)₂ (Complex **2ii**)

In a similar manner to **2aa** (above), this complex was made with **1ii** (0.425 g: 1.60 mmol), EtOH (25 mL) and Co(NO₃)₂·6H₂O (0.227 g: 0.779 mmol). Orange precipitates were collected and recrystallized in a mixture of 1:1 DCM / MeOH to give **2ii** (0.459 g, 61%). Mp.: 234–236 °C. IR (cm $^{-1}$): 2967, 2114, 1738, 1583, 1562, 1521, 1470, 1424, 1354, 1306, 1198, 1178, 1148, 1100, 1045, 1023, 993, 946, 877, 831, 802, 767, 690. UV-Vis (1.04×10^{-4} M): $\lambda_{\text{max}1} = 536$ nm ($\epsilon = 41.0$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}2} = 317$ nm ($\epsilon = 1.96 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}3} = 292$ nm ($\epsilon = 1.56 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}4} = 247$ nm ($\epsilon = 1.59 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). MS-EI (m/z): found (calc'd) [M]⁺ = 588.3 (588.3). Elemental Analysis (%) calc'd. (found) for C₂₈H₃₀Cl₂N₂O₄Co: C 57.16 (56.88); H 5.14 (5.22); N 4.76 (4.77).

Co(**1jj** – H)₂ (Complex **2jj**)

In a similar manner to **2aa** (above), **2jj** was produced with **1jj** (0.058 g: 0.22 mmol), EtOH (2 mL), NEt₃ (0.50 mL: 3.6 mmol) and Co(NO₃)₂·6H₂O (0.031 g: 0.11 mmol). Red coloured precipitates were collected and were then recrystallized in a mixture of 1:1 DCM / MeOH to give **2jj** (0.060 g: 94%). Mp.: 233–235 °C. IR (cm $^{-1}$): 2966, 1583, 1522, 1481, 1419, 1353, 1301, 1183, 1110, 1045, 1022, 995, 946, 890, 799, 767, 740, 731, 700. UV-Vis (6.80×10^{-5} M): $\lambda_{\text{max}1} = 533$ nm ($\epsilon = 32.0$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}2} = 317$ nm ($\epsilon = 1.36 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}3} = 237$ nm ($\epsilon = 1.07 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). MS-EI (m/z): found (calc'd) [M]⁺ = 588.2 (588.3). Elemental Analysis (%) calc'd. (found) for C₂₈H₃₀Cl₂N₂O₄Co: C 57.16 (56.89); H 5.14 (5.16); N 4.76 (4.80).

Co(**1kk** – H)₂ (Complex **2kk**)

In a similar manner to **2aa** (above), **2kk** was made with **1kk** (0.088 g: 0.34 mmol), EtOH (5 mL), NEt₃ (0.20 mL: 1.4 mmol) and Co(NO₃)₂·6H₂O (0.048 g: 0.17 mmol). Red coloured precipitates were collected and then

recrystallized in a mixture of 1:1 DCM / MeOH to give **2kk** (0.064 g: 71%). Mp.: 240 °C (decomp.). IR (cm $^{-1}$): 2965, 1584, 1561, 1522, 1487, 1457, 1354, 1308, 1241, 1185, 1092, 1023, 991, 807, 768. UV-Vis (4.39×10^{-5} M): $\lambda_{\text{max}1} = 542$ nm ($\epsilon = 66.0$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}2} = 315$ nm ($\epsilon = 2.96 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}3} = 257$ nm ($\epsilon = 1.78 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}4} = 248$ nm ($\epsilon = 1.90 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). MS-EI (m/z): found (calc'd) [M + H]⁺ = 548.3 (547.6). Elemental Analysis (%) calc'd. (found) for C₃₀H₃₆N₂O₄Co: C 63.71 (63.73); H 6.77 (6.57); N 4.95 (4.84).

Co(**1ll** – H)₂ (Complex **2ll**)

In a similar manner to **2aa** (above), **2ll** was made with **1ll** (0.237 g: 0.887 mmol), NEt₃ (1.25 mL: 8.97 mmol), EtOH (15 mL) and Co(NO₃)₂·6 H₂O (0.127 g: 0.436 mmol). Dark red coloured precipitates were collected which were then recrystallized in a mixture of 1:1 DCM / MeOH to give **2ll** (0.246 g: 95%). Mp.: 201–202 °C. IR (cm $^{-1}$): 3044, 2967, 2890, 1572, 1519, 1412, 1383, 1352, 1302, 1259, 1193, 1165, 1034, 989, 744, 666. UV-Vis (2.37×10^{-5} M): $\lambda_{\text{max}1} = 537$ nm ($\epsilon = 226$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}2} = 314$ nm ($\epsilon = 5.50 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}3} = 297$ nm ($\epsilon = 6.13 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}4} = 274$ nm ($\epsilon = 4.62 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). MS-EI (m/z): found (calc'd) [M]⁺ = 592.3 (591.6). Elemental Analysis (%) calc'd. (found) for C₃₄H₃₂N₂O₄Co: C 69.03 (69.02); H 5.45 (5.44); N 4.74 (4.79).

Copper

Cu(**1bb** – H)₂ (Complex **3bb**)

A sample of **1bb** (0.10 g: 0.40 mmol) was dissolved in EtOH (15 mL) containing NEt₃ (0.1 mL: 0.7 mmol) with stirring. To this mixture was added Cu(NO₃)₂·2.5H₂O (0.045 g: 0.19 mmol) and the mixture stirred for 16 h. Dark green precipitates were collected which were then recrystallized in a mixture of 1:1 DCM / MeOH to give **3bb** (0.103 g: 96%). Mp.: 203–205 °C IR (cm $^{-1}$): 2890, 1896, 1740, 1589, 1531, 1496, 1434, 1355, 1298, 1254, 1168, 1114, 1028, 999, 867, 836, 788, 766, 733, 701, 675. UV-Vis (7.91×10^{-5} M): $\lambda_{\text{max}1} = 455$ nm ($\epsilon = 478$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}2} = 325$ nm ($\epsilon = 1.33 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}3} = 299$ nm ($\epsilon = 1.32 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}4} = 252$ nm ($\epsilon = 8.03 \times 10^3$ Lmol $^{-1}$ cm $^{-1}$). MS-EI (m/z): found (calc'd) [M]⁺ = 556.3 (556.1). Elemental Analysis (%) calc'd. (found) for C₂₈H₃₂N₂O₆Cu: C 60.47 (60.66); H 5.80 (5.61); N 5.04 (5.08).

Cu(**1cc** – H)₂ (Complex **3cc**)

A round-bottom flask was charged with **1cc** (1.01 g: 3.49 mmol) and EtOH (10 mL). After the solids were completely dissolved, Cu(NO₃)₂·2.5H₂O (0.402 g: 1.75 mmol) was dissolved in EtOH (10 mL) and added to the solution. Upon addition of the two, the solution turned colour from yellow to a dark green. The solution was stirred at RT for 16 h. Following this time period, dark green precipitates were collected which were then recrystallized in a mixture of 1:1 DCM/MeOH to give **3cc** (0.628 g: 57%). Mp.: 208–210 °C. IR (cm $^{-1}$): 2964, 1750, 1593, 1527, 1458, 1353, 1304, 1179, 1139, 1101, 1027, 997, 943, 889, 823, 764, 727, 671. UV-Vis (1.89×10^{-5} M): $\lambda_{\text{max}1} = 434$ nm ($\epsilon = 1.62 \times 10^3$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}2} = 335$ nm ($\epsilon = 3.39 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}3} = 296$ nm ($\epsilon = 3.42 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$), $\lambda_{\text{max}4} = 246$ nm ($\epsilon = 4.21 \times 10^4$ Lmol $^{-1}$ cm $^{-1}$). MS-EI (m/z): found (calc'd) [M + H]⁺ = 634.1 (633.8). Elemental Analysis (%) calc'd. (found) for C₂₆H₂₄N₂O₄Cl₄Cu: C 49.27 (49.13); H 3.82 (3.63); N 4.42 (4.45).

Cu(**1dd** – H)₂ (Complex **3dd**)

In a similar manner to **3cc** (above), **3dd** was obtained from **1dd** (0.122 g: 0.465 mmol), EtOH (20 mL), NEt₃ (1.0 mL: 7.2 mmol) and Cu(NO₃)₂·2.5H₂O (0.0530 g: 0.228 mmol). Green coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH

(0.120 g; 90%). Mp.: 217–218 °C. IR (cm⁻¹): 1584, 1535, 1514, 1484, 1341, 1299, 1250, 1181, 1108, 1031, 998, 946, 861, 834, 779, 752, 750. UV-Vis (1.43 × 10⁻⁵ M): λ_{max1} = 717 nm (ε = 550 Lmol⁻¹cm⁻¹), λ_{max2} = 374 nm (ε = 1.78 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max3} = 306 nm (ε = 1.41 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max4} = 269 nm (ε = 3.11 × 10⁴ Lmol⁻¹cm⁻¹). Elemental Analysis (%) calc'd. (found) for C₂₆H₂₆N₄O₈Cu: C 53.29 (53.17); H 4.47 (4.45); N 9.56 (9.45).

Cu(**1ee** – H)₂ (Complex **3ee**)

In a similar manner to **3cc** (above), **3ee** was produced from **1ee** (0.128 g; 0.649 mmol), EtOH (20 mL), NEt₃ (0.20 mL: 1.4 mmol) and Cu(NO₃)₂·2.5H₂O (0.0740 g: 0.318 mmol). Green coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH (0.073 g; 50%). Mp.: 203–204 °C. IR (cm⁻¹): 2958, 1590, 1527, 1474, 1415, 1349, 1297, 1249, 1197, 1153, 1036, 1003, 945, 890, 848, 803, 788, 729. UV-Vis (2.10 × 10⁻⁵ M): λ_{max1} = 411 nm (ε = 1.11 × 10³ Lmol⁻¹cm⁻¹), λ_{max2} = 309 nm (ε = 8.15 × 10³ Lmol⁻¹cm⁻¹), λ_{max3} = 275 nm (ε = 2.38 × 10⁴ Lmol⁻¹cm⁻¹). Elemental Analysis (%) calc'd. (found) for C₂₂H₃₆N₂O₄Cu: C 57.94 (58.17); H 7.96 (7.85); N 6.14 (5.92).

Cu(**1ff** – H)₂ (Complex **3ff**)

In a similar manner to **3cc** (above), this complex was made with **1ff** (0.399 g; 2.57 mmol), EtOH (5 mL), NEt₃ (0.50 mL: 3.6 mmol) and Cu(NO₃)₂·2.5H₂O (0.297 g: 1.28 mmol). Green coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH (0.303 g; 64%). Mp.: 128.5–130 °C. IR (cm⁻¹): 2959, 1592, 1535, 1457, 1413, 1350, 1296, 1174, 1047, 1015, 993, 952, 844, 774, 741. UV-Vis (5.38 × 10⁻⁵ M): λ_{max1} = 656 nm (ε = 58.7 Lmol⁻¹cm⁻¹), λ_{max2} = 421 nm (ε = 6.85 × 10² Lmol⁻¹cm⁻¹), λ_{max3} = 299 nm (ε = 8.54 × 10³ Lmol⁻¹cm⁻¹), λ_{max4} = 269 nm (ε = 1.46 × 10⁴ Lmol⁻¹cm⁻¹). Elemental Analysis (%) calc'd. (found) for C₁₆H₂₄N₂O₄Cu: C 51.67 (51.41); H 6.50 (6.77); N 7.53 (7.57).

Cu(**1gg** – H)₂ (Complex **3gg**)

In a similar manner to **3cc** (above), this complex was made with **1gg** (0.216 g; 0.836 mmol), EtOH (5 mL), NEt₃ (0.5 mL: 3.6 mmol) and Cu(NO₃)₂·2.5H₂O (0.101 g: 0.434 mmol). Green coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH (0.150 g; 62%). Mp.: 161–163 °C. IR (cm⁻¹): 2956, 1606, 1541, 1438, 1353, 1287, 1206, 1040, 1008, 956, 938, 825, 801, 754, 673. UV-Vis (7.26 × 10⁻⁵ M): λ_{max1} = 694 nm (ε = 68.8 Lmol⁻¹cm⁻¹), λ_{max2} = 425 nm (ε = 6.46 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max3} = 302 nm (ε = 1.85 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max4} = 280 nm (ε = 1.98 × 10⁴ Lmol⁻¹cm⁻¹). Elemental Analysis (%) calc'd. (found) for C₁₆H₁₈N₂O₄Cl₆Cu: C 33.22 (33.40); H 3.14 (3.07); N 4.84 (4.91).

Cu(**1hh** – H)₂ (Complex **3hh**)

In a similar manner to **3cc** (above), complex **3hh** was made with **1hh** (0.211 g; 1.01 mmol), EtOH (5 mL), NEt₃ (0.5 mL: 3.6 mmol) and Cu(NO₃)₂·2.5H₂O (0.120 g: 0.516 mmol). Green coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH (98 mg, 40 % yield). Mp.: 124–125 °C. IR (cm⁻¹): 3111, 2973, 1621, 1573, 1360, 1320, 1256, 1120, 1035, 999, 969, 872, 841, 791, 746, 701. UV-Vis (1.04 × 10⁻⁴ M): λ_{max1} = 667 nm (ε = 70.6 Lmol⁻¹cm⁻¹), λ_{max2} = 402 nm (ε = 7.20 × 10² Lmol⁻¹cm⁻¹), λ_{max3} = 291 nm (ε = 1.63 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max4} = 266 nm (ε = 1.62 × 10⁴ Lmol⁻¹cm⁻¹). Elemental Analysis (%) calc'd. (found) for C₁₆H₁₈N₂O₄F₆Cu: C 40.05 (40.10); H 3.78 (3.81); N 5.84 (5.84).

Cu(**1ii** – H)₂ (Complex **3ii**)

In a similar manner to **3cc** (above), compound **3ii** was produced from **1ii** (0.450 g; 1.69 mmol), EtOH (10 mL) and Cu(NO₃)₂·2.5H₂O (0.196 g: 0.839

mmol). Dark green coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH (0.380 g; 76%). Mp.: >210 °C (decomp.). IR (cm⁻¹): 2959, 2113, 1750, 1593, 1563, 1529, 1466, 1352, 1307, 1198, 1102, 1031, 1002, 946, 878, 826, 807, 766, 731, 677. UV-Vis (4.72 × 10⁻⁵ M): λ_{max1} = 436 nm (ε = 788 Lmol⁻¹cm⁻¹), λ_{max2} = 330 nm (ε = 1.81 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max3} = 299 nm (ε = 1.88 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max4} = 247 nm (ε = 1.79 × 10⁴ Lmol⁻¹cm⁻¹). MS-EI (*m/z*) found (calc'd) for [M]⁺: 594.3 (593.1). Elemental Analysis (%) calc'd. (found) for C₂₈H₃₀Cl₂N₂O₄Cu: C 56.71 (56.89); H 5.10 (5.01); N 4.72 (4.75).

Cu(**1jj** – H)₂ (Complex **3jj**)

In a similar manner to **3cc** (above), complex **3jj** was made with **1jj** (0.111 g; 0.418 mmol), EtOH (20 mL) and Cu(NO₃)₂·2.5H₂O (0.086 g: 0.372 mmol). Green coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH (0.118 g; 95%). Mp.: 207–209 °C. IR (cm⁻¹): 2963, 1589, 1529, 1483, 1457, 1355, 1305, 1179, 1114, 1030, 997, 942, 894, 799, 765, 708. UV-Vis (2.83 × 10⁻⁵ M): λ_{max1} = 445 nm (ε = 815 Lmol⁻¹cm⁻¹), λ_{max2} = 330 nm (ε = 2.13 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max3} = 301 nm (ε = 2.16 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max4} = 244 nm (ε = 1.99 × 10⁴ Lmol⁻¹cm⁻¹). MS-EI (*m/z*): found (calc'd) [M]⁺ = 594.1 (593.1). Elemental Analysis (%) calc'd. (found) for C₂₈H₃₀Cl₂N₂O₄Cu: C 56.71 (56.94); H 5.10 (5.16); N 4.72 (4.80).

Cu(**1kk** – H)₂ (Complex **3kk**)

In a similar manner to **3cc** (above), compound **3kk** was made with **1kk** (0.149 g; 0.607 mmol), EtOH (10 mL), NEt₃ (1.00 mL: 7.17 mmol) and Cu(NO₃)₂·2.5H₂O (0.069 g: 0.30 mmol). Green coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH (150 mg, 91%). Mp.: 218–220 °C. IR (cm⁻¹): 2961, 1740, 1590, 1561, 1526, 1488, 1457, 1352, 1308, 1191, 1129, 1095, 131, 992, 944, 881, 811, 764, 731, 700. UV-Vis (1.45 × 10⁻⁵ M): λ_{max1} = 443 nm (ε = 1.72 × 10³ Lmol⁻¹cm⁻¹), λ_{max2} = 325 nm (ε = 4.04 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max3} = 293 nm (ε = 5.18 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max4} = 250 nm (ε = 3.74 × 10⁴ Lmol⁻¹cm⁻¹). MS-EI (*m/z*): found (calc'd) [M]⁺ = 552.3 (552.2). Elemental Analysis (%) calc'd. (found) for C₃₀H₃₆N₂O₄Cu: C 65.26 (64.99); H 6.57 (6.50); N 5.07 (5.07).

Cu(**1ll** – H)₂ (Complex **3ll**)

In a similar manner to **3cc** (above), this complex was made with **1ll** (0.299 g; 1.12 mmol), EtOH (15 mL), NEt₃ (0.20 mL: 1.4 mmol) and Cu(NO₃)₂·2.5H₂O (0.128 g: 0.55 mmol). Green coloured precipitates were collected which were recrystallized in a mixture of 1:1 DCM / MeOH (0.300 g; 91%). Mp.: 171–173 °C. IR (cm⁻¹): 3041, 2955, 2112, 1916, 1581, 1548, 1457, 1420, 1390, 1352, 1308, 1260, 1199, 1174, 1062, 1040, 1000, 935, 880, 771, 714, 669. UV-Vis (2.01 × 10⁻⁵ M): λ_{max1} = 425 nm (ε = 1.21 × 10³ Lmol⁻¹cm⁻¹), λ_{max2} = 293 nm (ε = 3.21 × 10⁴ Lmol⁻¹cm⁻¹), λ_{max3} = 247 nm (ε = 3.33 × 10⁴ Lmol⁻¹cm⁻¹). MS-EI (*m/z*): found (calc'd) [M]⁺ = 596.3 (596.2). Elemental Analysis (%) calc'd. (found) for C₃₄H₃₂N₂O₄Cu: C 68.50 (68.47); H 5.41 (5.34); N 4.70 (4.78).

Acknowledgments

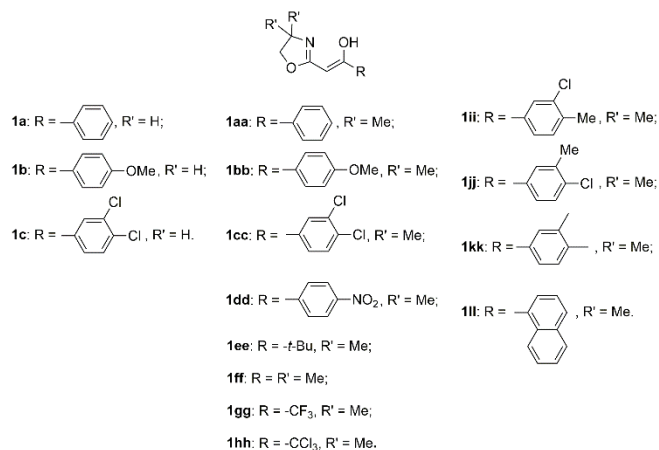
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Keywords: coordination chemistry • cobalt • copper • oxazoline
• enolate • polymerisation

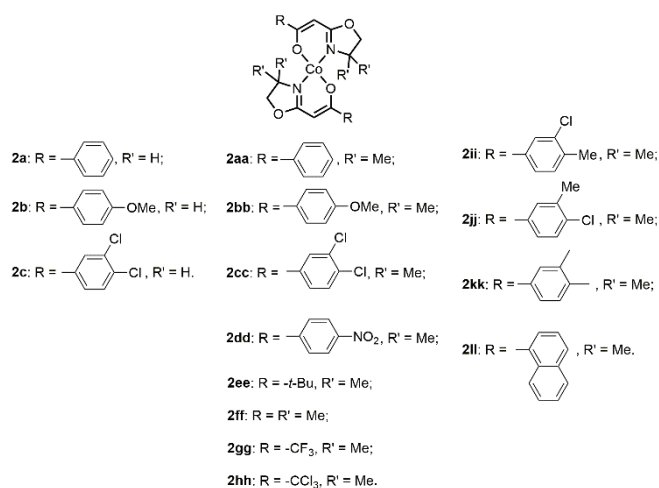
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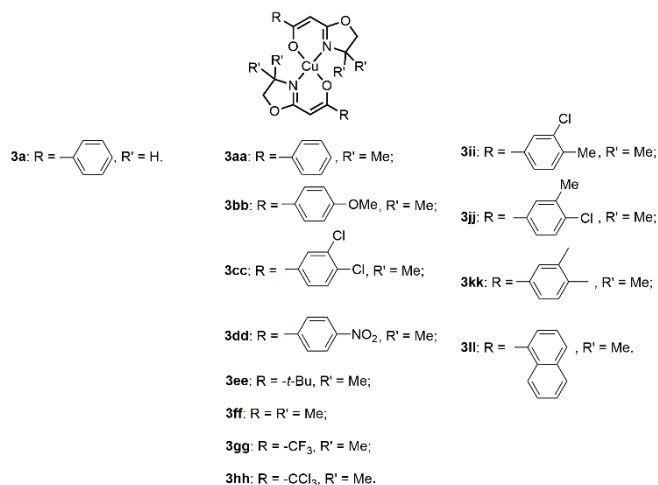
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- [142] For the sake of convenience and clarity, we have chosen to name the free ligand materials using the *enol* tautomer as the base structure.
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Scheme 1. Numbering schemes for the ligands investigated herein; enol isomer shown.



Scheme 2. Numbering scheme for the Cobalt complexes studied herein.



Scheme 4. Numbering scheme for the Copper complexes studied herein.

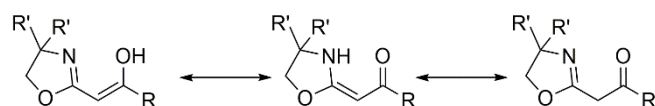


Figure 1. Three possible tautomers for *Tohda's Ligands* (enol: left; enamine: centre and keto: right).

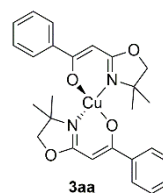


Figure 2. Schematic representation of complex **3aa**, which features a high degree of distortion from SQP geometry around the Cu centre.

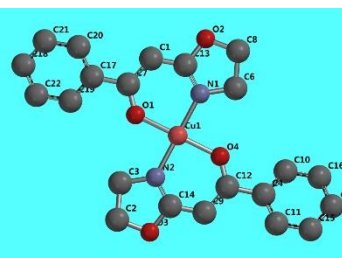
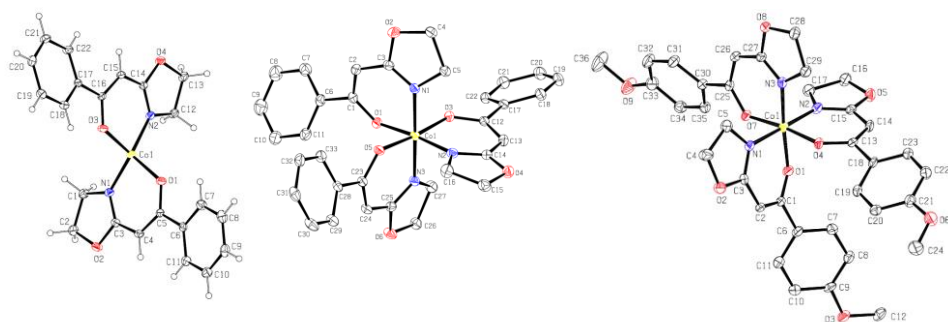
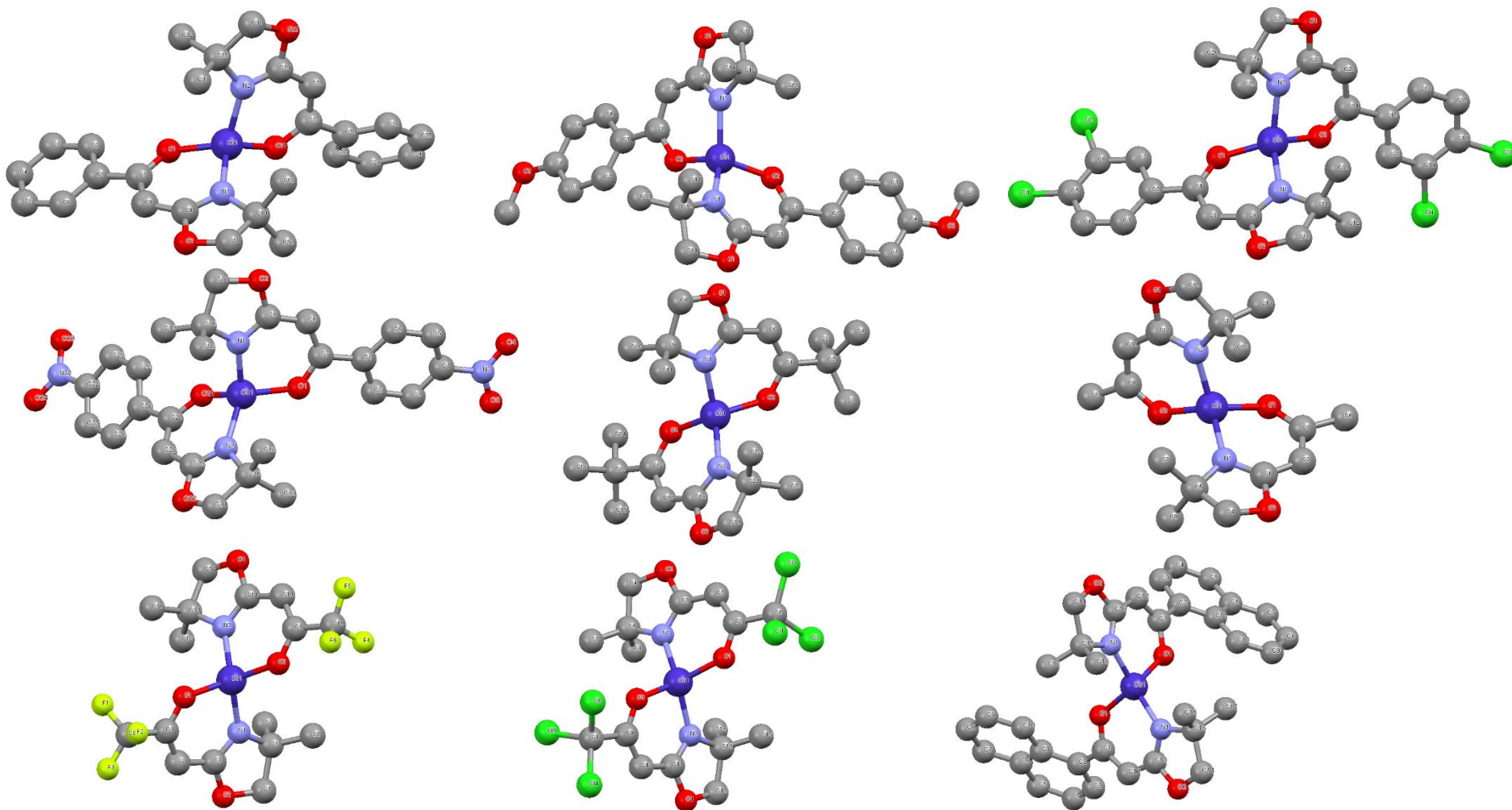


Figure 3. Calculated (DFT: M11-L / 6-311+G(2df, 2p) level of theory) gas phase structure of one possible ground state conformer of **3a**; H-atoms have been omitted for clarity.



Scheme 3. ORTEP representations of unit cell molecules of **2a** (left), **4a** (middle) and **4b** (right).

Scheme 4. MERCURY© representations of a single unit cell molecule of complexes **2aa** – **2cc** (top: left to right), **2dd** – **2ff** (middle: left to right), **2gg** – **2hh** (bottom: left and centre) and **2ii** (bottom: right); atoms at 30% probability levels; H atoms omitted for clarity (grey spheres: C; purple spheres: Co; red spheres: O; blue spheres: N; green spheres: Cl; yellow spheres: F).



Scheme 5. ORTEP representations of a single unit cell molecule of complexes **3cc** (top: left), **3dd** (top: centre), **3ee** (top: right), **3ff** (bottom: left), **3gg** (bottom: centre) and **3ll** (bottom: right); atoms at 30% probability levels; H atoms omitted for clarity in some cases.

