COMMUNICATION

Quantifying the orbital contribution in the “Spodium Bond” *via* Natural Orbital for Chemical Valence-Charge Displacement analysis

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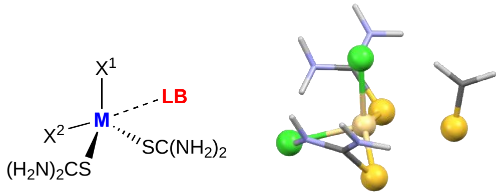
The term “spodium bond” (SpB) has been recently proposed for the non-coordinative interaction between a polarised group 12 metal and a mild Lewis base. In most of the systems showing short metal-donor distances, however, SpB coexists with other weak interactions, including hydrogen and halogen bonding. Here we show their mutual importance can be probed by dissecting the orbital component of the interaction through the Natural Orbital for Chemical Valence-Charge Displacement analysis. NOCV-CD gives us straightforward snapshots of relative energies and electrons involved, either for model and “real” adducts, allowing us to demonstrate the lack of a direct correlation between a favourable metal-base distance and the presence of an orbital contribution for the SpB.

σ-hole bonding,[1] i.e. the attractive interaction between a polarised main group atom and a Lewis base or anion, is gaining considerable importance within the family of non-covalent interactions. It arises from an anisotropic charge distribution around the polarised atom, which creates a region of positive electrostatic potential (σ-hole) attracting electron-rich moieties. The most notable example is the halogen bond (XB),[2] which is increasingly establishing as a versatile tool in crystal engineering, catalysis and photoluminescence.[3] More recently, the family σ-hole interactions has been expanding throughout the periodic table to chalcogen (ChB),[4] pnictogen (PB)[5] and tetrel bond (TB).[6] Along with the latter, π-hole interactions demonstrated to be worth of attention. [7]

The latest addition to this group is the metal bond,[8] which entails systems where a σ-hole is localised on a transition metal having a completely filled d shell. An interesting case is that of group 12 metals, for which the capability of forming the so-called “spodium bond” (SpB) has been proposed.[9] In a very recent contribution,[10] Frontera *et al.* analysed a series of bis(thiourea-S)MX$_2$ complexes (M = Zn, Cd, Hg; X = Cl, Br, I) and revealed that σ-holes located along the bisector of the S–M–S bond can establish weak, non-coordinative interactions with Lewis bases such as CO, CH$_3$CN or CH$_2$O. This theoretical finding correlates, apparently, with the existence of a number of structures of group 12 compounds showing intermolecular M···donor distances shorter than the sum of the corresponding van der Waals radii in the solid-state.

However, both experimental and model adducts generally show the concomitant presence of a series of weak interactions, including hydrogen (HB) and chalcogen bonds (ChB), as evidenced by the quantum theory of atoms in molecules (QTAIM).[10] Since they all contribute to the overall fragment interaction energy, it is important to disentangle these contributions in order to provide a precise assessment of the importance of SpB.



1: M = Cd, X^1 = X^2 = Cl, **2**: M = Cd, X^1 = X^2 = I,
3: M = Zn, X^1 = X^2 = Cl, **4**: M = Zn, X^1 = F, X^2 = Cl,
5: M = Hg, X^1 = X^2 = Cl, LB = CH$_2$S, CH$_2$O, CO, CH$_3$CN

Scheme 1. Numbering of the complexes studied and optimized structure of **1CH$_2$S**.

In this work, we take advantage of the Natural Orbital for Chemical Valence[11]-Charge Displacement[12] (NOCV-CD) analysis to evaluate the orbital contribution of the SpB. Our specific aim is to assess how the SpB orbital energy is modulated by the structure of the adduct and what is the role played by other intermolecular interactions in determining the energy of association. As the electrostatic and dispersion components are not interaction-specific, the decomposition of the orbital contributions is crucial for an efficient disentanglement of concomitant weak interactions.[13]

Here, we analysed the interaction of model complexes **1**-**5** (Scheme 1) with different Lewis bases (CH$_2$S, CH$_2$O, CO and CH$_3$CN), taking inspiration from the results by Frontera *et al.* Then, we applied such analysis to selected cases of crystallographically characterised adducts to evaluate if and when short M···donor distances measured at the solid state correspond to net SpB charge transfer or arise from other intermolecular forces where SpB plays a minor role.

NOCV-CD and EDA[14] calculations were performed at the M06-D3/TZVP/ZORA level[8] (see ESI for computational details and Table S1 for complete EDA results). Starting with **1CH$_2$S**, we observed that the total interaction energy (E$_{\mathrm{int}}$) between **1** and

CH_2S amounts to -10.5 kcal/mol and it is composed by a steric energy (E_{st} = Pauli repulsive term + electrostatic term) of 2.2 kcal/mol, a dispersion energy of -0.9 kcal/mol and a considerable orbital contribution (E_{orb}) of -11.8 kcal/mol. Decomposing E_{st} revealed that the electrostatic contribution is still dominant, as usually observed for all σ-hole bonding type interactions. E_{orb} shows to be quite stable with respect to the functional (see ESI).

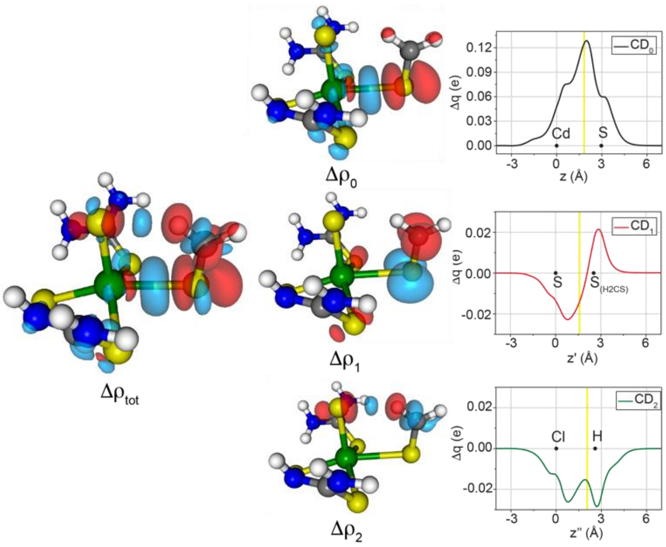


Figure 1. Isodensity surface plots (isodensity value 1 me a.u.$^{-3}$ except for $\Delta\rho_1$, 0.7 me a.u.$^{-3}$) for the deformation maps relative to $\Delta\rho_{tot}$ and $\Delta\rho_k$ (k = 0, 1 and 2) of the [**1**]···[CH_2S] interaction. The charge flux is red → blue. Aside each $\Delta\rho_k$ map, the corresponding Charge Displacement function is shown. Black dots indicate the position on the axis of the atomic nuclei. A yellow vertical band indicates the boundary between the fragments.

The total electronic deformation map ($\Delta\rho_{tot}$) shows the overlap of two major contributions: a Cl···H hydrogen bond and a Cd···S Spodium Bond (Figure 1). Treating $\Delta\rho_{tot}$ with the NOCV method successfully leads to the decomposition of such interactions. $\Delta\rho_0$ exclusively describes the SpB (depletion regions around the sulfur, accumulation along the internuclear axis) and the polarization of the cadmium fragment (accumulation regions around the other ligands). The energy associated to this contribution (E_0) is -7.2 kcal/mol.

The second component, $\Delta\rho_1$, shows instead a strong C→S polarization (depletion/ accumulation regions) around the double bond of CH_2S, together with small depletion regions around the two S atoms of **1**. The accumulation regions around the sulfur of H_2CS have a pointed shape indicating a small but noticeable S_{CH2S}→S_{urea} inter-fragment charge transfer. This is associated with an energy E_1 of -0.9 kcal/mol. Finally, $\Delta\rho_2$ is related exclusively to the Cl···H HB, with the same pattern seen before and an energy (E_2) of -1.7 kcal/mol (Figure 1). The QTAIM analysis reported in literature[10] confirms the SpB and the HB but it does not detect the weak charge transfer between the coordinated sulfur and that of CH_2S.

$\Delta\rho_k$ can be separately integrated to have quantitative information about the electron density involved in each single contribution (Δq, in millielectrons, me). Each interaction has been integrated along its axis (Cd-S for $\Delta\rho_0$, the bisector of the SSS angle for $\Delta\rho_1$ and Cl-H for $\Delta\rho_2$) to give 3 separate CD functions.[15] CD_0 is found to be positive at any position, suggesting that the Cd←S charge transfer overcomes any polarization effect. The value of Δq at the isoboundary, CT_0 (CT_{SpB}) is 125 me. CD_1 has a different behaviour as it is negative at first (charge transfer from **1** to CH_2S) and then it changes sign because of the double bond polarization. At the isoboundary position, CT_1 (CT_{ChB}) is equal to -11 me. The latter is the sum of the projections of each single S → S CT on the chosen axis. Considering that the SSS angle is 86.7°, each S → S charge transfer can be estimated as -7.6 me.[16] The CD relative to the HB is negative, as the direction of the flux is Cl→H, but there is no change of sign, as also the polarization is toward the same direction. CT_2 (CT_{HB}) is -18 me.

Summarizing, the total orbital energy in **1CH₂S** is then made of SpB (61%), HB (14%) and S-S CT (8%), suggesting that SpB plays an important role in interaction between the fragments. The remaining part of E_{orb}, around 17%, is fragmented in many polarization contributions, generally with k > 4 and negligible E_k values (< 0.5 kcal/mol each).

For the other Cd model systems, EDA data show that E_{orb} varies significantly as a function of the Lewis base and this is reflected also in its composition in the NOCV analysis. For example, replacing CH_2S with CO in **1** lowers the total interaction energy by over 6 kcal/mol (E_{int} = -4.4 kcal/mol), with an E_{orb} of only -2.8 kcal/mol. This clearly corresponds to the lack of HB but, more importantly, to a much weaker SpB contribution (Table 1). Obviously, the two things are not mutually independent, as the presence of an interaction can make the others stronger.[15] The other donors investigated in combination with **1** fall in between these two extremes, in the order E_{SpB} CH_2S > CH_2O > CH_3CN > CO, with a clear correlation between E_{int}, E_{orb} and E_{SpB}.

Interestingly enough, when chlorides are replaced by iodides in the CO adduct (**2CO**), a small I→CO contribution emerges, similar to what happens with coordinated triple bonds (see Figure S4, ESI).[17,18] This contribution is larger, in energy, than SpB and S-S CT (Table 1).

In the case of stronger Lewis bases, coordinative bond takes place, as in **1NH₃**, where a small yet noticeable back-donation contribution can be noted (see ESI).

The nature of the metal also plays an important role in tuning these interactions. Passing from Cd to Zn, the orbital contribution of the SpB becomes almost negligible in the whole series, both in terms of energy (around -0.2 kcal/mol) and electrons involved (1-9 me), reasonably owing to the lower polarizability of Zn. Anyway, if the chloride *trans* to the LB is swapped with a fluoride, the SpB returns to be relevant for E_{orb} (-1.9 kcal/mol and 31 me for **4H₂CO**).

Hg complexes have an intermediate behaviour between that of Cd and Zn ones. For example, **5CH₂S** shows an E_{SpB} of -2.8 kcal/mol, corresponding to a charge transfer of 54 me, 71 me lower than that of **1CH₂S**. This fits with the findings by Frontera *et al.*, which showed that van der Waals-corrected Cd···LB distances are generally shorter than Hg···LB ones and electrostatic potentials are more positive on Cd than on Hg.[10] This is likely due to the combination of the smaller atomic radius of Hg and the steric congestion around the metal, which do not allow an efficient approach by the LB. This is even more evident for the other donors in the series, where the SpB has a similar or lower energy than HB contributions.

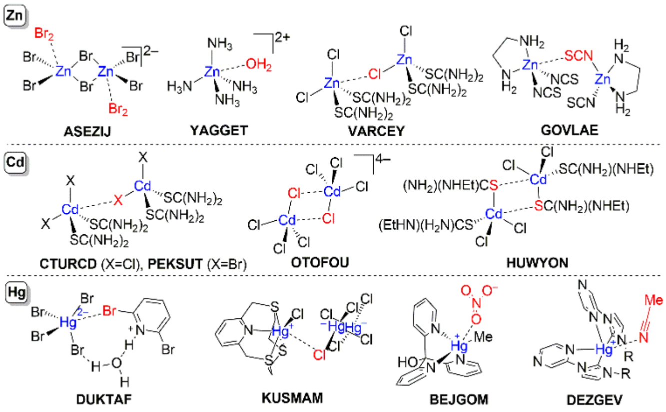
Table 1. Orbital energies (in kcal/mol) and CT values (in me) relative to the different bond components for the adducts between complexes **1**-**5** and CH_3CN, CO, CH_2O, CH_2S.

Adduct	E_{orb}	E_{SpB} (CT_{SpB})	E_{HB} (CT_{HB})	E_{ChB} (CT_{ChB})
1CH_3CN	-6.2	-2.5 (42)	-1.4 (-17)	-0.3 (5)
1CO	-2.8	-0.7 (15)	-	-0.3 (-2)
1CH_2O	-8.2	-4.5 (65)	-1.5 (-17)	-0.5 (1)
1CH_2S	-11.8	-7.2 (125)	-1.7 (-18)	-0.9 (-11)
2CO	-2.4	-0.6 (18)	-1.0 (-16)[a]	-0.5 (-6)
3CH_3CN	-3.8	-0.2 (1)	-1.5 (-31)	-0.6 (8)
3CO	-1.5	-0.3 (9)	-	-0.7 (-3)
3CH_2O	-3.0	-	-1.2 (-27)	-0.7 (11)
3CH_2S	-3.6	-	-1.2 (-12)	-0.3 (-1)
4CH_2O	-4.5	-1.9 (31)	-1.2 (-14)	-
5CH_3CN	-4.8	-1.2 (18)	-1.8 (-24)	-0.2 (5)
5CO	-2.1	-0.5 (16)	-0.1 (-2)[a]	-0.2 (-3)
5CH_2O	-4.6	-1.9 (27)	-1.4 (-15)	-0.2 (1)
5CH_2S	-6.1	-2.8 (54)	-1.7 (-19)	-0.4 (-3)

[a] Halogen → CO transfer

From our analysis, it clearly appears that the relative extent of the SpB orbital contribution strongly depends on the system investigated. Also, while generally larger SpB contributions lead to shorter M···LB distances, there is no linear correlation between donor-acceptor distance and interaction energy in none of the compound series. For this reason, it is of interest to extend NOCV-CD to experimentally characterised group 12 complexes showing short, but not coordinative X-M···LB arrangements. This allows to probe whether they arise from a net SpB charge transfer and what is the role of the other intermolecular interactions in determining such arrangements.

By analysing the database of structures with reduced M···LB distances compatible with SpB,[10] we have selected exemplificative adducts for each metal containing different ligands, charges and donor types (Scheme 2). We deliberately chose fragments with a large span of interactions energies, ranging from very positive (OTOFOU) to very negative (DUKTAF) values of E_{int}, to check how the latter impacts on E_{orb} and its decomposition into contributions.



Scheme 2. Experimentally characterised structures selected for NOCV-CD analysis with their respective CCDC code; dashed lines represent putative SpB interactions.

Our EDA results (see Table S1 for full detail) show clearly that all the structures have a favourable orbital contribution to E_{int} (E_{orb} <0), even when the two fragments would repel each other when taken out of the crystal lattice, such as in OTOFOU. The decomposition of E_{orb} for such structures by NOCV (Table 2) offers interesting details about the impact of the different intermolecular interactions.

There are cases in which no SpB charge transfer could be identified, such as in ASEZIJ where the short Zn···Br_2 interaction is mainly due to halogen bonding with the bromide bound to the metal. In HUWYON, the proximity of sulfur to Cd is related to the establishment of hydrogen bonding between the chlorides and the -NHEt moiety of the thiourea. In DUKTAF, the most important contributions to E_{orb} are instead coming from Br···H_2O HB and Br···Br XB.

In the other cases, detectable charge transfer from the LB to the metal is observed, compatible with SpB. This revealed to be true for all the metals. For example, in the dimer extracted from YAGGET, the oxygen of water prefers to establish a SpB with Zn rather than a HB with the ammonia protons (Figure 2). In GOVLAE, despite the stronger HB contribution between the NCS moiety and one NH of the ligand, a small SpB charge transfer is observed.

The Cd dimers PEKSUT and CTURCD gave similar results to their respective model system **1**, showing a mild SpB contribution of -2.7 and -2.3 kcal/mol, respectively, in both cases convoluted with a weak ChB. By substituting cadmium with zinc (VARCEY), the SpB disappears and only the ChB is visible.

An interesting case is that of BEJGOM, where an oxygen atom of the NO_3^- anion undergoes both HB with a C–H of the ligand and charge transfer to the cationic Hg center. As the Hg-O distance is 5.0 Å, this is compatible with SpB (a coordinated nitrate would be expected at a distance of about 2.6-3.0 Å[19]).

In summary, we have shown here that the NOCV-CD analysis allows the disentanglement of the complex network of weak interactions that drives the non-coordinative attraction between group 12 complexes and Lewis bases.

By assessing the orbital contribution to the interaction energy, we could characterise each component separately and observe that a net LB→M charge transfer, compatible with the establishment of the so-called Spodium Bond (SpB), can occur. The extent of such contribution is strongly affected by the metal, ligands and bases involved and generally, when the same ligand set is investigated, it seems to be more important for Cd complexes than for Hg and Zn.

Table 2. Orbital energies (in kcal/mol) and CT values (in me) relative to the different bond components for experimental solid-state dimers from CCDC.

Adduct	E_{orb}	E_{SpB} (CT_{SpB})	E_{HB} (CT_{HB})	E_{ChB} (CT_{ChB})	E_{XB} (CT_{XB})
			M = Zn		
ASEZIJ-a	-6.1	-	-	-	-4.5 (-77)
ASEZIJ-b	-14.8	-	-	-	-12.9 (-136)
YAGGET	-3.2	-1.8 (25)	-	-	-
VARCEY	-3.8	-	-1.3 (24)	-	-
GOVLAE	-6.6	-1.1 (a)	-2.4 (-45)	-	-
			M = Cd		
PEKSUT	-6.5	-2.7 (56)[b]	-	-1.1 (1)	-
CTURCD	-6.1	-2.3 (46)[b]	-	-	-
OTOFOU	-14.1	-3.1 (c)	-	-	-
HUWYON	-10.4	-	-2.5 (c) -1.6 (c)	-	-
			M = Hg		
DUKTAF	-19.7	-	-3.2 (-52)	-	-5.7 (-64)
KUSMAM	-23.5	-5.4 (-79) -2.4 (4)	-	-3.7 (-45)	-
BEJGOM	-14.2	-5.2 (58)	-1.3 (-33)	-	-
DEZGEV	-6.2	-2.8 (33)	-	-	-

a: mixed wth E_{HB}, see Supporting Information; b: mixed with ChB, see Supporting Information c: integration unfeasible due to the symmetry of the adduct.

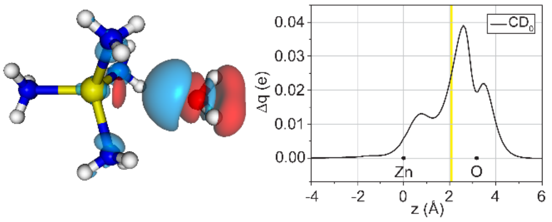


Figure 2. (left) Isodensity surface plots (isodensity value 0.5 me a.u.$^{-3}$) for the deformation maps relative to $\Delta\rho_0$ of the **YAGGET** adduct. The charge flux is red → blue. (right) The corresponding Charge Displacement function is shown. Black dots indicate the position on the axis of the atomic nuclei. A yellow vertical band indicates the boundary between the fragments.

The application of this method to "real-life" structures revealed that there is no direct correlation between short M⋯LB distances and LB→M charge transfer, as other intermolecular forces such as hydrogen, chalcogen or halogen bond can intervene in determining the structural features of that particular molecular network. Therefore, while it can be used as a screening parameter while looking for potential SpB interactions, a M⋯LB distance shorter than the sum of the van der Waals radii does not guarantee that a net SpB will be present, so each structure needs to be evaluated individually. NOCV-CD, at this point, can be used to quickly visualise whether the bond has an orbital contribution or not.

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Conflicts of interest

There are no conflicts to declare.

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