On the Use of Aqueous Metal-Aqua pK_a Values as a Descriptor of Lewis Acidity

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Supporting Information Placeholder

ABSTRACT: The behavior of Lewis acidic metal ions in multimetallic systems has become a subject of intense interest in recent years. Parametrizing the behavior of these ions in non-aqueous conditions, commonly used in the field, is challenging due to the lack of direct measures of the Lewis acidity of metal ions in polar organic solvents. Here, we report the use of triphenylphosphine oxide (TPPO) as a ^{31}P nuclear magnetic resonance (NMR) probe to quantify the Lewis acidity of a library of metal triflate salts using the Gutmann-Beckett method. A plot of the pK_a values of the corresponding metal-aqua species, $[\mathbf{M}(H_2O)_m]^{n+}$, measured in H_2O, vs. the ^{31}P NMR shifts of TPPO in the presence of these metals in deuterated acetonitrile (d_3-MeCN) and deuterated dichloromethane (CD_2Cl_2) displays a tightly co-linear relationship, suggesting similar behavior for these ions in water, d_3-MeCN, and CD_2Cl_2. This collinearity reinforces the utility of the common approach of using the aqueous pK_a values as a descriptor of Lewis acidity, regardless of the solvent used in the immediate experiments, and provides an insight into the usefulness of this descriptor in wide-ranging applications. Titration studies in d_3-MeCN suggest 1:1 binding of TPPO with monovalent ions, greater than 1:1 binding with divalent ions, and formation of multiple species with the highly Lewis acidic trivalent ions. Together, these data suggest that both aqueous pK_a values and other single-measurement descriptors, while useful, provide only a snapshot of the influence of Lewis acidity on multimetallic chemical systems.

1. INTRODUCTION

Promotion of small-molecule activation processes by Lewis acids has emerged as an effective strategy for achieving otherwise difficult transformations. For example, the rate of CO_2 reduction by reduced metal complexes can be profoundly accelerated by incorporation of Lewis acids that promote C–O bond cleavage.[1] Similarly, the strong U–O bonds of the uranyl ion (UO_2^{2+}) can often only be activated through concerted action of both Lewis acids and strong chemical reductants.[2,3] As the interactions between redox-active metals and the Lewis acid play a crucial role in determining reaction outcomes, significant effort remains devoted to development of ligand frameworks designed to bring Lewis acids into close proximity of metal centers, substrates, or reactive moieties of interest.[4,5,6,7]

Inspired by the presence of an essential Ca^{2+} ion in the Oxygen-Evolving Complex (OEC) of Photosystem II,[8,9] numerous research groups have turned to redox-inactive metal ions as a useful class of Lewis acids for modulating redox reactivity.[10,11] Common metal ions used for these purposes span a significant range of sizes/coordination numbers, and are often chosen from among mono-, di-, and tri-valent ions such as K^+, Na^+, Ca^{2+}, Y^{3+}, and Lu^{3+}. Strongly Lewis acidic trivalent cations such as Sc^{3+} attract especially significant attention, as the effects they promote are

typically more pronounced than those engendered by weaker acids.[12,13,14,15] Indeed, understanding the relative effect(s) of Lewis acids is of particular interest from the standpoint of tunability and rational catalyst design.

Quantification of Lewis acidities remains an area of significant work despite efforts spanning decades.[16] Perhaps the most common Lewis acidity scale is based upon the pK_a value(s) of bound water ligands in metal-aqua complexes of the corresponding Lewis acidic ions. These values were compiled nearly 40 years ago in Perrin's highly cited volume,[17] and although some ions are associated with only a few measurements, pK_a values are available for most mono-, di-, and tri-valent ions, giving this scale significant power. It has been successfully deployed in many studies in recent years, including those aimed at understanding modulation of reduction potentials in important bioinorganic model compounds and diverse redox-active species.[18,19]

Most studies of Lewis acidic ion-modulated chemistry are carried out in acetonitrile (MeCN), dichloromethane (CH_2Cl_2), and other polar organic solvents; consequently, the pK_a-based Lewis acidity descriptor measured in water is often used to parametrize behavior in these other solvents, a situation of significant concern since solvent effects are known to strongly influence the outcomes of chemical reactivity. In our view, the abundance of Lewis acid effects that can be successfully interpreted with this scale is surprising. Fukuzumi and co-workers have attempted to bridge the gap, however, by developing an alternative scale based upon parameters derived from Lewis acid-modulated electron paramagnetic resonance spectra collected on in situ-generated superoxide species.[20,21] However, this scale is less intuitive and requires specialized equipment for further development, likely impeding its wider adoption.

On the other hand, we were surprised to find that the Gutmann-Beckett method, in which Lewis acidity is interrogated by ^{31}P nuclear magnetic resonance (NMR) spectroscopy with a suitable phosphorus-containing probe molecule, typically a phosphine oxide, has not been employed for systematic quantification of the Lewis acidity of redox-inactive metal ions.[22,23] As this method has been found to be effective for alkaline earth metal complexes and some transition metal compounds,[24,25] we anticipated that studies of the wider family of redox-inactive metal ions by this method might enable direct comparisons with the common aqueous pKa scale as well as provide insights for new studies of Lewis acid-modulated chemistry.

Here, we report the first uniform measurements of the Lewis acidities of mono-, di-, and tri-valent redox-inactive metals (in the form of their triflate salts) with a modified form of the Gutmann-Beckett method. The chemical shift ($\delta^{31}P$) values of triphenylphosphine oxide (TPPO, our chosen probe molecule) in the presence of various ions display clear

trends in both d_3-MeCN and CD_2Cl_2, confirming the usefulness of this method in assaying the Lewis acidity of these metal ions. Titration studies reveal that TPPO binds to monovalent ions (Li^+, Na^+, K^+, Rb^+, and Cs^+) with 1:1 stoichiometry, whereas it can bind multiple divalent ions (Ba^{2+}, Sr^{2+}, and Ca^{2+}) cooperatively as shown by Hill analysis. Together with related findings for the trivalent ions, these studies highlight that association constants and concentration-dependent speciation should be considered carefully in studies of Lewis acid-modulated chemistry.

2. RESULTS

In order to carry out this study, we selected the triflate (OTf^-) salts of common monovalent (Li^+, Na^+, K^+, Rb^+, Cs^+), divalent (Ba^{2+}, Sr^{2+}, Ca^{2+}, Zn^{2+}) and trivalent (La^{3+}, Y^{3+}, Lu^{3+}, Sc^{3+}) redox-inactive metals. These salts are attractive in that most are commercially available, all are soluble in common polar organic solvents (MeCN, CH_2Cl_2), and they all feature the weakly coordinating triflate counterion that should not interfere with binding of other ligands (like phosphine oxides) to the metal centers under our conditions. In the case of the commercially available LiOTf, NaOTf, KOTf, $Ba(OTf)_2$, $Ca(OTf)_2$, $Zn(OTf)_2$, $La(OTf)_3$, $Y(OTf)_3$, $Lu(OTf)_3$, and $Sc(OTf)_3$, we confirmed the purity of the salts after extensive drying (180°C, 24 h; see Experimental Section and Supporting Information) by ^{1}H and ^{19}F NMR spectroscopy, encountering no unusual features. RbOTf, CsOTf, and $Sr(OTf)_2$, which are not commercially available, were prepared by addition of triflic acid (HOTf) to aqueous suspensions of Rb_2CO_3, Cs_2CO_3, and $SrCO_3$ followed by extraction with MeCN. Characterization by NMR and powder X-ray diffraction (XRD) analysis (see Experimental Section and Supporting Information) confirmed clean generation of the desired salts, which were also dried thoroughly before use.

In Gutmann's pioneering work,[22] triethylphosphine oxide (TEPO) was used as a Lewis base to determine the Lewis acidity of weakly coordinating solvents by observing changes in the ^{31}P chemical shift value ($\delta^{31}P$) when dissolved in the various solvents of interest. Beckett later extended this method, using TEPO to study the Lewis acidity of boron-based Lewis acids.[23] In our work, we selected the more commonly available triphenylphosphine oxide (TPPO) as a Lewis basic probe molecule; TPPO has the simultaneous advantages of high chemical stability and low cost (less than \$1 per gram) in comparison to TEPO (ca. \$70 per gram). Although the phenyl groups in TPPO are more sterically demanding than the ethyl groups in TEPO, our findings don't suggest any unusual steric influences in the studies reported here.

In order to provide a direct comparison of the Lewis acidities of each of the metal cations in this study, we prepared 1:1 mixtures of each corresponding metal salt and TPPO in both d_3-MeCN and CD_2Cl_2 and interrogated the samples by $^{31}P\{^1H\}$ NMR. In all cases, the $\delta^{31}P$ of TPPO was shifted downfield, indicating association between the Lewis acidic ions and the TPPO probe molecule. In d_3-MeCN, all of the samples (except Lu^{3+} and Sc^{3+}) revealed a single ^{31}P NMR resonance; very small $\Delta\delta^{31}P$ values were observed for the monovalent metal ions, while greater downfield shifts were measured for the di- and tri-valent metal ions (see Figure 1). In CD_2Cl_2, similar phenomena were observed, except the addition of Y^{3+} and Lu^{3+} resulted in the appearance of multiple resonances (see Supporting Information, Figures S7 and S8 for all spectra). Reasonable trends were observed in the data; for example, a fairly large $\Delta\delta^{31}P$ (12.5 ppm) was measured for $Zn(OTf)_2$ in d_3-MeCN in comparison with the value for $Ca(OTf)_2$ (7.0 ppm), consistent with the similar charge but smaller size of Zn^{2+}.[26,27,28]
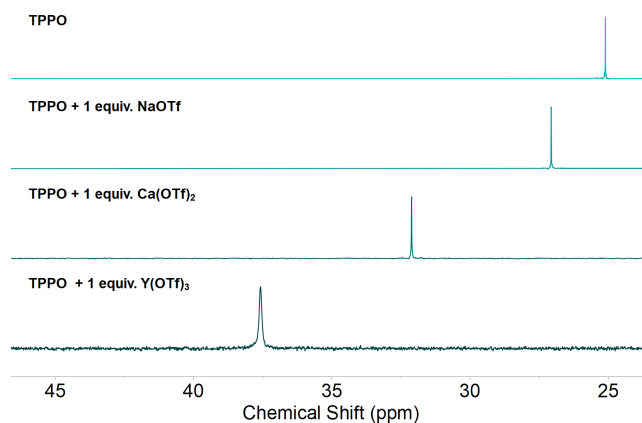
Figure 1. $^{31}P\{^1H\}$ NMR spectra of selected metal ions in the presence of 1 equiv. of TPPO showing the downfield shift with the increase in the Lewis acidity of the ions.

Plotting the tabulated $\Delta\delta^{31}P$ values (see Tables S2 and S3 in SI) for each Lewis acid in each solvent as a function of the pK_a values of the corresponding aqueous metal-aqua complexes[17] reveals clear and uniform trends in both cases (see Figure 2). In both solvent systems, the pK_a and $\Delta\delta^{31}P$ values are tightly co-linear, suggesting similar Lewis acid behavior of the ions in water, acetonitrile, and dichloromethane. The co-linearity of the data spans the full series of valencies studied here, indicating that the Gutmann-Beckett-like descriptor of $\Delta\delta^{31}P$ accommodates charge and ionic radius effects in a similar manner to that of the pK_a scale in water. This is perhaps not surprising, however, since deshielding of ^{31}P in TPPO by Lewis acids is not unlike the withdrawal of electron density from bound water molecules in metal-aqua complexes. Changes in Lewis acidity are, indeed, commonly invoked as a cause of metal redox-induced protonation/deprotonation events in systems that display proton-coupled electron transfer behavior.[29] Comparing the d_3-MeCN and CD_2Cl_2 solvent systems reveals greater scatter in the dichloromethane data, as judged by both goodness-of-fit (0.92 for CD_2Cl_2 versus 0.98 for d_3-MeCN) and error on the slope of the linear fit (10% and 5%, respectively); this may be due to the less coordinating nature of dichloromethane, which could make data collected in this solvent more sensitive to trace coordinating impurities (e.g., H_2O, Et_2O, tetrahydrofuran) that could be present under our otherwise air- and moisture-free conditions.
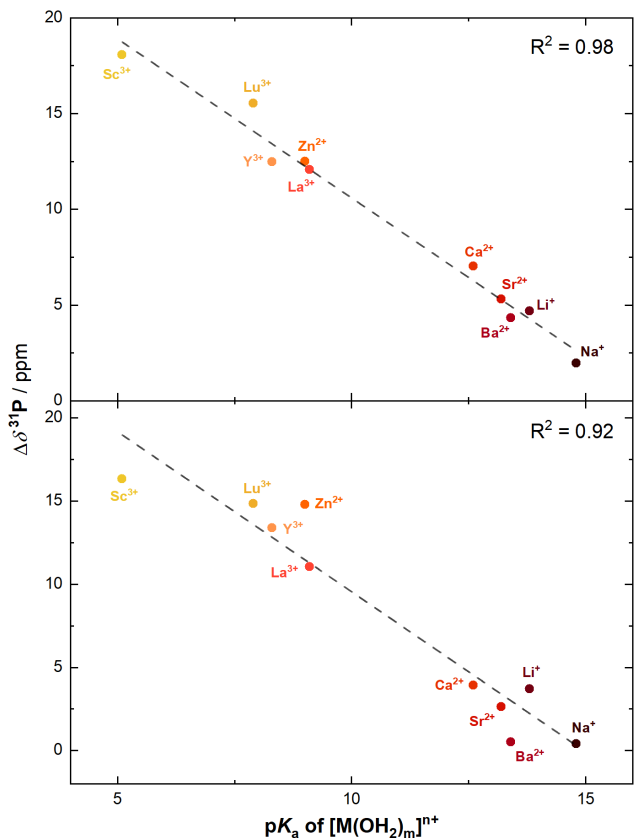
Figure 2. Relationship between the $\Delta\delta^{31}$P values for TPPO in the presence of various metal ions in d_3-MeCN (upper panel) and CD$_2$Cl$_2$ (lower panel) and the corresponding metal-aqua complex pK_a values. Metal-aqua pK_a values were taken from reference 17.

As mentioned above, a shortcoming of the aqueous metal-aqua pK_a values tabulated by Perrin[17] is the lack of data for certain challenging and/or uncommon ions. For example, no pK_a values are available for the less acidic Cs$^+$ and Rb$^+$ ions, and only a single imprecise value is available for K$^+$ (16.0-16.5), attesting to the experimental challenge of working at extreme pH values in water. However, with the relationships mapped in Figure 2, the pK_a values for Cs$^+$, Rb$^+$, and K$^+$ in water can be estimated by straightforward measurement of the δ^{31}P values for TPPO in the presence of 1 equivalent of the corresponding triflate salts. As expected, based on their increasing atomic radii, the estimated pK_a values determined in this way for K$^+$, Rb$^+$, and Cs$^+$ decrease across the series (16.03, 16.25, and 16.30; see Table 1). Notably, our value for K$^+$ is within error of a value (16.25) determined by ionization studies not included in Perrin's tabulation.[30] Estimations carried out with data collected in CD$_2$Cl$_2$ provide similar results within error (see Table S4 in SI).

Table 1. Data regarding select monovalent ions from this study.

M^{n+}	$\delta_{max}{}^{31}$P / ppm	$\Delta\delta_{max}{}^{31}$P / ppm	Estimated p$K_a{}^{\#}$
K$^+$	25.68	0.57	16.03 ± 0.96
Rb$^+$	25.34	0.20	16.25 ± 0.96
Cs$^+$	25.25	0.12	16.30 ± 0.97

$^{\#}$pK_a values for Cs$^+$, Rb$^+$, and K$^+$ in water were estimated by measuring δ^{31}P values for TPPO in the presence of 1 equivalent of the corresponding triflate salts.

With our modified form of the Gutmann-Beckett method in hand, more detailed studies are also possible, allowing movement beyond simple measurements on 1:1 solutions of metal triflate salts and TPPO. This is important, in part, due to the closeness of the estimated pK_a values for the monovalent ions given above. In particular, we imagined that titration studies of 1 equiv. of TPPO with increasing concentrations of individual metal salts could reveal association constants and speciation information of interest in interpreting Lewis acid-induced effects in diverse systems.[31] Thus, beginning with the triflate salts of the monovalent ions (Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$), we carried out titration studies (Figure 3) in d_3-MeCN wherein the δ^{31}P was measured for 1 equiv. of TPPO in the presence of increasing concentrations of the individual metal salts. As anticipated, the $\Delta\delta^{31}$P values shift as the concentration of metal salt is increased, initially undergoing greater changes but eventually levelling off at higher titrant ion equivalencies. Inspection of the raw ^{31}P NMR data (see Supporting Information, Figures S9-S13) also reveals that the more Lewis acidic ions (based on prior pK_a data) result in the largest absolute shifts in $\Delta\delta^{31}$P.
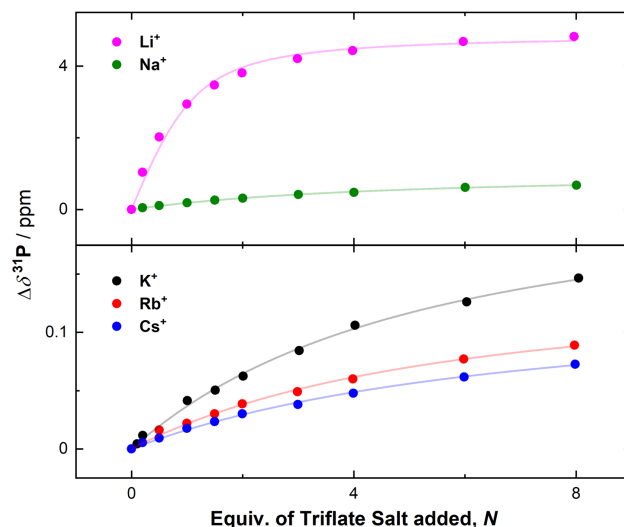
Figure 3. Titration studies showing 1:1 binding of monovalent metal ions and TPPO. Solvent: d_3-MeCN. $[\text{TPPO}]_0 = 3.59$ mM.

The titration data shown in Figure 3 strongly suggest that the monovalent ions in this study interact with TPPO in a 1:1 stoichiometry, even in the presence of large excesses (>5 equiv.) of the individual metal ions. This is borne out by fitting of the collected data to a 1:1 binding isotherm,[32] from which both the association constant (K_a) and maximum chemical shift ($\Delta\delta_{max}{}^{31}$P) can be extracted (see Table 2) using the following equation (Equation 1):

$$\frac{\Delta\delta}{\Delta\delta_{max}} = \frac{1}{2}\left(1 + N + \frac{1}{K_a[\text{H}_0]}\right) - \sqrt{\left(1 + N + \frac{1}{K_a[\text{H}_0]}\right)^2 + 4N}$$

In this expression, $\Delta\delta_{max}$ is the maximum achievable chemical shift difference; K_a is the association constant. N is the number of equivalents of the given metal ion per TPPO and is equal to the ratio of total concentration of metal ion and TPPO "host" species, $[\text{M}^{n+}]/[\text{H}_0]$. The K_a values quantify the tendency of each monovalent ion to associate with TPPO in d_3-MeCN, while the $\Delta\delta_{max}{}^{31}$P values describe the maximum possible deshielding of the ^{31}P center in TPPO, specifically at the condition where the metal ion of interest is maximally occupying its binding site on TPPO. From the data, an obvious trend emerges in the K_a values: the more strongly Lewis acidic ions associate more strongly with TPPO, as shown in the larger K_a values for the smaller ions (see Table 2 and

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Figure S25). The K_a value for Li$^+$ is the largest by far in this series, perhaps consistent with its quite large charge-to-radius ratio. Similarly, Li$^+$ serves to most strongly deshield the ^{31}P center in TPPO when it is maximally bound. Na$^+$ also induces a large $\Delta\delta_{max}{}^{31}P$ value, while the values for K$^+$, Rb$^+$, and Cs$^+$ are all similar. Thus, these more detailed findings measured in d_3-MeCN reinforce that the larger monovalent ions K$^+$, Rb$^+$, and Cs$^+$ all display similar properties in this solvent.

Table 2. Metal-aqua complex pK_a values and fitted parameters from 1:1 binding of TPPO to the monovalent metal ions in this study.

M^{n+}	pK_a of $[M(H_2O)_m]^{n+\#}$	r / Å for C.N. = 8[c]	K_a / M^{-1}	$\Delta\delta_{max}{}^{31}P$ / ppm
Li$^+$	13.8[a]	0.92	1009 ± 228[d]	4.89 ± 0.15[d]
Na$^+$	14.8[a]	1.18	72.6 ± 4.70	1.04 ± 0.03
K$^+$	16.03[b]	1.51	61.2 ± 6.0	0.23 ± 0.01
Rb$^+$	16.25[b]	1.61	55.4 ± 6.7	0.15 ± 0.01
Cs$^+$	16.30[b]	1.74	45.1 ± 4.4	0.13 ± 0.01

[a]Taken from reference 17. [b]pK_a values for Cs$^+$, Rb$^+$, and K$^+$ in water were estimated by measuring $\delta^{31}P$ values for TPPO in the presence of 1 equivalent of the corresponding triflate salts. [c]From reference 28. [d]Errors were calculated from the direct nonlinear fit of Equation 1, and are given as ±1σ.

A plot of $\log(\Delta\delta_{max}{}^{31}P)$ vs. pK_a for the data given in Table 2 reveals a tightly colinear relationship between these quantities (Figure 4). Thus, we conclude that both $\Delta\delta_{max}{}^{31}P$, measured for bound TPPO in d_3-MeCN, and pK_a values, measured for aqua ligands in water, similarly report on the ability of the monovalent ions to modulate the electron density on bound ligands. In the measurements of metal-aqua complex pK_a values, an implicit assumption underpinning the measurements is that the water molecule (aqua ligand) undergoing deprotonation/protonation at a given pH value is resident on the given metal ion. Stated another way, the water molecule which is serving as the probe of Lewis acidity must be closely associated with the metal complex and thus maximally able to readout the Lewis acidity of the metal center. Accordingly, the $\Delta\delta_{max}{}^{31}P$ values in Table 2 are especially tightly correlated with the aqueous pK_a values, since the $\Delta\delta_{max}{}^{31}P$ values represent a direct quantitation of the maximal deshielding effect that a single monovalent Lewis acid can induce on our TPPO probe molecule. In line with this picture, the error on the slope of the relationship in Figure 4 (3.6%) is significantly smaller than that for the $\Delta\delta^{31}P$ data (4.9%; at the arbitrary 1:1 ratio) shown in Figure 2a.
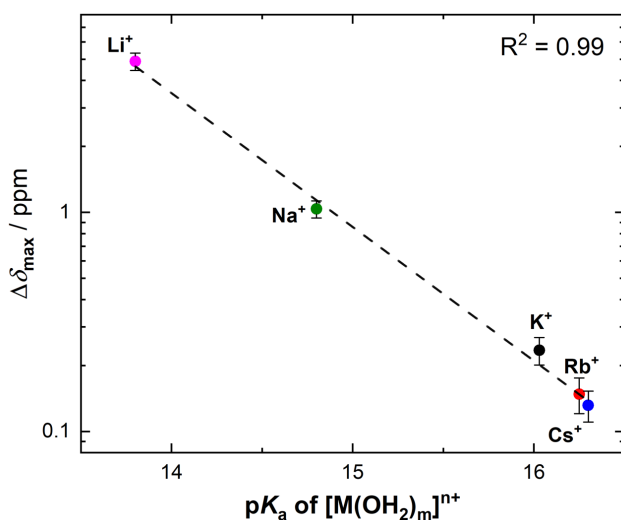
Figure 4. Plot of $\Delta\delta_{max}{}^{31}P$ for TPPO binding in d_3-MeCN to monovalent metal ions versus the corresponding aqueous metal-aqua pK_a values. Errors on individual $\Delta\delta_{max}{}^{31}P$ values were calculated from the direct nonlinear fit of Equation 1, and are given as ±3σ.

Titration studies were also extended to the cases of the divalent ions Ba^{2+}, Sr^{2+}, and Ca^{2+} (see Figure 5, upper panel). As we found with the monovalent ions, the $\Delta\delta^{31}P$ value for TPPO shifts as the concentration of the given divalent metal salt is increased (see Figures S14-S16 in SI for titration data). However, the large initial changes in $\Delta\delta^{31}P$ were all measured at low equivalencies; at or near 1:1 equivalence, the $\Delta\delta^{31}P$ value levels off near its apparent maximal value in the cases of all three divalent ions. This indicates that each of the ions tightly associates with TPPO. However, unlike the cases of the monovalent ions, fitting to a 1:1 binding isotherm[32] returns obviously poor results in each case, indicating that multiple binding events are involved in this chemistry and that 1:1 models for the behavior of these systems are inappropriate. Thus, we conclude that multiple divalent metal ions can interact with a single TPPO probe molecule in d_3-MeCN.

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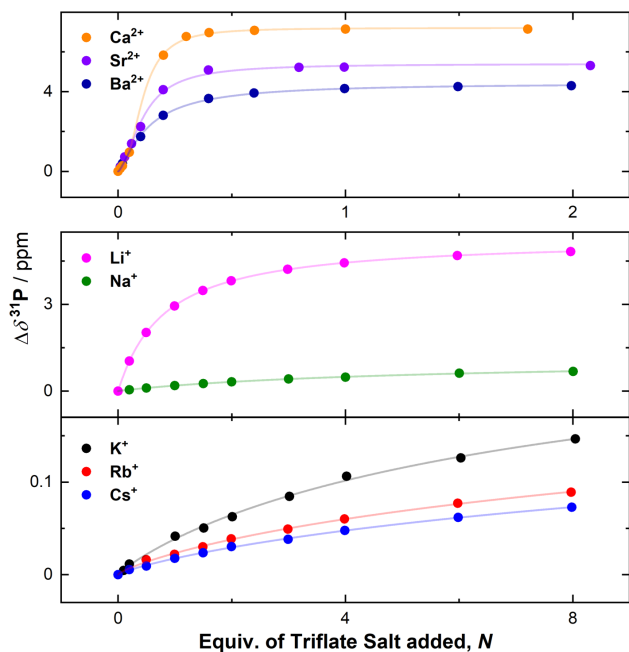
Figure 5. Titration data showing fit to the Hill-Langmuir equation given in the main text.

Significant work across several fields has been devoted to the problem of determining association constants for systems behaving with stoichiometries other than 1:1. From the perspective of supramolecular chemistry, the metal ion is the "guest" in our system and the TPPO is the "host"; TPPO can bind either one or two metal ions, and could serve as both a terminal ligand or bridging ligand between two metal centers. As structural work is limited on complexes of the redox-inactive metals with phosphine oxide ligands,[33] little prior work can guide interpretation of our results on the divalent metals. Thordarson,[32] Connors,[34] and others have considered the significant pitfalls in extracting equilibrium binding constants for even the 1:2 and 2:1 situations in host:guest chemistry; in these situations, contrasting with the relatively simple case of 1:1 binding, the needed binding isotherm equations are cubic and feature multiple unknown parameters that are challenging to extract.

On the other hand, the two regimes in our titration data for the divalent ions (with a nearly linear regime at low metal ion concentration and plateauing region at moderate to high concentrations) resemble behavior common in enzymology that can be described by the Hill-Langmuir Equation.[35,36,37] Indeed, we find that our titration data can be described by a form of the Hill-Langmuir equation; this enables quantitation of the influence of divalent metal ion concentration on the deshielding of the ^{31}P center in TPPO according to the following equation (Equation 2):

$$\Delta\delta = \frac{\Delta\delta'_{max}(N)^\alpha}{\left(K_{1/2}\right)^\alpha + (N)^\alpha}$$

In this equation, $\Delta\delta'_{max}$ is the maximum achievable chemical shift difference determined with this relationship, α is the Hill coefficient, and $K_{1/2}$ is the half-maximal concentration constant. N, as in Equation 1, is the number of equivalents of the given metal ion per TPPO at a given condition. Notably, Eq. 2 can be rearranged to give its linearized form known as the Hill equation (Equation 3) as follows:

$$\log\left[\frac{\Delta\delta}{\Delta\delta'_{max} - \Delta\delta}\right] = \alpha\log N - \alpha\log K_{1/2}$$

In both of these expressions, the Hill coefficient, α, provides a measure of the cooperativity of binding of the "guest" ion M to the TPPO "host," while $K_{1/2}$ provides a measure of the affinity between the metal ion and TPPO, by reporting the equivalents of M required to achieve half the value of $\Delta\delta'_{max}$ ^{31}P.

Our titration data obey the Hill-Langmuir Equation for both the challenging divalent ions, as well as for the monovalent ions (see Table 3). In the case of the monovalent ions, the $K_{1/2}$ values match the trend found for the K_a values from the nonlinear fitting to the 1:1 binding isotherm; the stronger Lewis acids with larger K_a values also have smaller $K_{1/2}$ values, meaning the half-maximum chemical shift difference is achieved at lower concentrations than in the case of weaker Lewis acids. Furthermore, the value of α is near unity for most of the monovalent ions (Li$^+$, Na$^+$, and K$^+$), consistent with strictly 1:1 binding that does not involve interaction of multiple ions with a single TPPO unit (see Figure S23 and Table 3).

On the other hand, the value of α is less than unity for Rb$^+$ and Cs$^+$, suggesting slightly negative cooperativity, perhaps due to binding of multiple of these large ions to TPPO at high metal ion concentrations (see Table 3). This may be reflective of the larger radii of these ions, which are known to give rise to a variety of structural effects in binding to ligands like crown ethers in supramolecular systems. The negative cooperativity measured here is consistent with these findings and suggests that the Lewis basicity of TPPO is diminished upon binding of a single Rb$^+$ or Cs$^+$ ion, resulting in a much smaller K_a value for the second binding event than the first.[38] However, as the values of α are only slightly less than unity, such binding of multiple ions does not play a major role in the chemistry under these conditions. We anticipate that TPPO can be reliably concluded on the basis of the direct fits to the Hill-Langmuir expression to interact with essentially only a single monovalent ion in these systems in d_3-MeCN.

**Table 3.** Fitted parameters from modeling of titration data with the Hill-Langmuir Equation.

M^{n+}	pK_a of $[M(H_2O)_m]^{n+}$	$\Delta\delta'_{max}$ ^{31}P / ppm [c]	$K_{1/2}$ / equiv. [c]	α [c]
Ca^{2+}	12.6[a]	7.20 ± 0.06	0.11 ± 0.01	2.42 ± 0.10
Sr^{2+}	13.2[a]	5.41 ± 0.11	0.11 ± 0.01	1.76 ± 0.15
Ba^{2+}	13.4[a]	4.45 ± 0.05	0.13 ± 0.01	1.31 ± 0.05
Li$^+$	13.8[a]	5.28 ± 0.01	0.79 ± 0.01	1.03 ± 0.01
Na$^+$	14.8[a]	1.18 ± 0.10	5.70 ± 1.07	0.96 ± 0.05
K$^+$	16.03[b]	0.30 ± 0.05	8.27 ± 3.19	0.90 ± 0.08
Rb$^+$	16.25[b]	0.26 ± 0.07	17.9 ± 10.2	0.81 ± 0.06
Cs$^+$	16.30[b]	0.23 ± 0.04	19.9 ± 7.4	0.83 ± 0.04

[a]From reference 17. [b]pK_a values for Cs$^+$, Rb$^+$, and K$^+$ in water were estimated by measuring δ ^{31}P values for TPPO in the presence of 1 equivalent of the corresponding triflate salts. [c]Errors were calculated from the direct nonlinear fit of Equation 2, and are given as ±1σ.

Conversely, the fitted parameters extracted for the cases of the divalent ions reveal significant positive cooperativity in their binding with TPPO (α values significantly larger than unity). Cooperativity of this type

implies a scenario in which the binding of one metal ion guest to the TPPO host facilitates or encourages the binding of a second metal ion guest. Considering this finding for binding of divalent metal ions to TPPO, we first mention that the few relevant results available from single-crystal X-ray diffraction (XRD) studies in the Cambridge Structural Database[39] reveal that phosphine oxides can serve as bridging ligands between redox-inactive metal ions like Na^{+} and Co^{2+}.[33,40] Thus, it is reasonable to imagine that multiple divalent metals could bind to a single TPPO unit. We anticipate that the positive cooperativity measured here is associated with formation of metal complexes bridged by TPPO ligands; for example, formation of a single μ2-TPPO bridge could promote binding of a second bridging μ2-TPPO. We prefer this viewpoint since it seems unlikely that binding of a single divalent ion to TPPO favors binding of a second divalent ion to the same TPPO unit; both steric congestion and the nascent diminished Lewis basicity of the TPPO unit would discourage such a situation. Indeed, such a scenario is implied by the behavior observed for Rb^{+} and Cs^{+}.

The quantified parameters described above are consistent with those that can be derived from plotting the measured data with the linearized form of the Hill-Langmuir expression to produce a so-called Hill Plot (Figure 6). The apparent linearity of the data for K^{+}, Na^{+}, and Li^{+} confirms the 1:1 binding stoichiometry and thus non-cooperative nature of the binding to TPPO. On the other hand, there are significant and obvious deviations from linearity in the data for the divalent ions, Ba^{2+} and Ca^{2+} in particular (see Figure S22 in SI for other Hill plots). Indeed, the S-shaped response for Ca^{2+} and Ba^{2+} is consistent with the positive cooperativity indicated by the α values that are greater than unity (see Figures S21-S23 in SI). Extrapolation of tangents from the extremes of the data in Figures 6 and S22 for the divalent ions can be used to estimate an interaction energy describing the difference in free energy change ($\Delta\Delta G$) associated with the first and last metal ion associations with TPPO in these systems displaying cooperative behavior that arises from the greater than 1:1 binding stoichiometry (see Figure S28 and Table S5 in SI).[38] The interaction energies for Ca^{2+}, Sr^{2+}, and Ba^{2+} are 3.13, 1.50, and 0.82 kcal/mol, respectively. Perhaps unsurprisingly, these values trend in accord with the Lewis acidity of these ions as judged by the aqueous pK_a values as well as their ionic radii (see Figures S26 and S27 in SI). This can be attributed to size-driven variations in their coordination environments, which promote formation of dimeric or multimeric units under these conditions to a greater extent with the smaller ions.
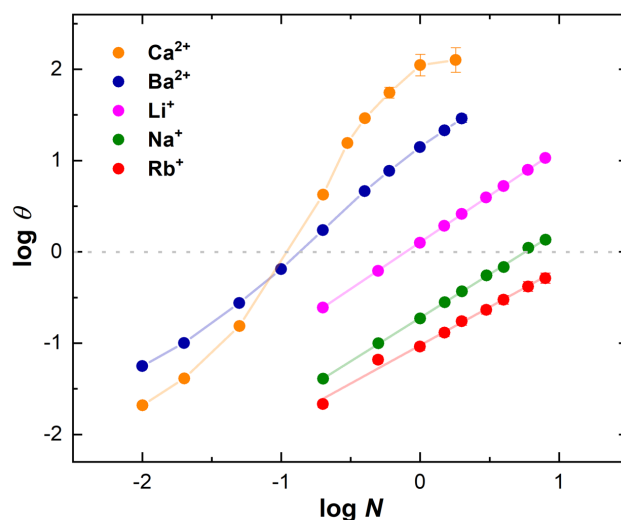
Figure 6. Hill plots for selected metal ions in this study. The y-axis is plotted from the relationship $\theta = [\Delta\delta/(\Delta\delta'_{max} - \Delta\delta)]$ representing normalization of the individual ^{31}P NMR shifts ($\Delta\delta$ values) for respective ions from their maximum shift ($\Delta\delta'_{max}$) determined from the direct nonlinear fit of the data to Equation 2. Errors on θ are plotted as ±0.3σ.

With these results in hand for titrations of the mono- and di-valent ions, we were excited to pursue similar work with trivalent ions. In particular, we have been interested in the trivalent ions since these highly Lewis acidic species can be reliably used to induce large changes in the chemistry of multimetallic systems.[7,14] However, we find that titration of TPPO with La^{3+}, Y[3+], Lu[3+], and Sc[3+] indicates complex speciation in all four cases, as evidenced by the observation of multiple species by ^{31}P{^{1}H} NMR (see Figures S17-S20 in SI). Moreover, the spectra do not uniformly or gradually shift, but rather display abrupt transitions, indicating formation and dissociation of multiple species that cannot be readily identified. Although unsatisfying for titration analysis, these results are consistent with the highly Lewis acidic nature of the trivalent ions, and their tendency to display higher coordination numbers that could promote the speciation behavior observed here. However, the maximum shifts in $\delta^{31}P$ are the greatest for the trivalent ions among all those in our study, confirming the usefulness of the behavior at 1:1 stoichiometry (Figure 2) as a descriptor of the Lewis acidity of these challenging ions.

3. DISCUSSION

We were inspired to carry out this study because of the widespread and successful utilization of metal-aqua pK_a values as a descriptor for Lewis acidity. In our own work, we have measured linear free-energy relationships for various properties of heterobimetallic complexes of Ni and UO$_2$[2+] with ranges of redox-inactive metal ions using this scale, despite making the measurements for our compounds in MeCN rather than H$_2$O.[7,14] The measurements and trends described in this work help to explain the usefulness of the metal-aqua pK_a descriptor, however, since we have found that the change in $\Delta\delta^{31}P$ for TPPO in the presence of various mono-, di-, and tri-valent metal ions in d_3-MeCN and CD$_2$Cl$_2$ is co-linear with the pK_a values of the corresponding metal-aqua complexes. The measurements of $\Delta\delta^{31}P$ represent a direct interrogation of the Lewis acidity of the metal ions themselves, as they induce deshielding of the ^{31}P center in TPPO when bound. As the $\Delta\delta^{31}P$ (d_3-MeCN or CD$_2$Cl$_2$) and pK_a (H$_2$O) values are tightly correlated, we plan to continue using the intuitive aqueous pK_a scale, even for work in polar organic solvents. In our ongoing work to interrogate changes in the chemical and

electrochemical properties of heterobimetallic complexes, we anticipate the pK_a-based descriptor will continue to be useful for both trend conceptualization and plotting of linear free-energy relationships.

On the other hand, this study also highlights that there is significant further work needed in order to better understand and quantify the chemistry of the di- and tri-valent metal ions. In particular, experimental work to reveal details of the speciation chemistry of these ions in both aqueous and organic media would be helpful to better understand the roles that the di- and tri-valent Lewis acids can take in modulating the chemistry of other species. In our titrations with TPPO with the strongly Lewis acidic trivalent ions, we directly observed the formation of various species by ^{31}P NMR under conditions where only TPPO, OTf$^-$, and d_3-MeCN were available as ligands. These conditions are not unlike those often used for modulation of molecular catalysts, in which exogenous Lewis acids are added to solutions containing reactive metal complexes that do not necessarily feature obvious binding sites for secondary metal ions. For example, the nature of interactions between Sc^{3+} and metal-oxo intermediates remains an area of vigorous investigation.[13,15] Consequently, we anticipate that significant opportunities lie in continued development of heterotopic ligand frameworks that can rationally direct binding of Lewis acids to redox-active metal complexes and catalysts. In such constructs, the speciation challenges of the trivalent ions may be overcome, unlocking their full potential to engender new, useful chemical reactivity modes.

4. CONCLUSIONS

We have used triphenylphosphine oxide (TPPO) as a ^{31}P NMR probe to quantify the Lewis acidity of redox-inactive metal ions in polar organic solvents, namely deuterated acetonitrile (d_3-MeCN) and deuterated dichloromethane (CD$_2$Cl$_2$). A plot of the pK_a values of the corresponding metal-aqua species, $[\mathbf{M}(H_2O)_m]^{n+}$, measured in H$_2$O, vs. the ^{31}P NMR shifts of TPPO in the presence of these metals reveals a tightly co-linear relationship, reinforcing the utility of the common approach of using the aqueous pK_a values as a descriptor of Lewis acidity, regardless of solvent. Our results show that concentration-dependent speciation and formation of multiple metal ion:ligand adducts are possible, especially for the more Lewis acidic di- and tri-valent metals. Taken together, these studies provide new insights into the behavior of the Lewis acidic metal cations in polar organic media and provide a new, uniform measure of Lewis acidity that may be useful in a variety of applications, especially the expanding field of small-molecule activation.

5. EXPERIMENTAL SECTION

5.1 General Considerations

All manipulations were carried out in dry N$_2$-filled gloveboxes (Vacuum Atmospheres Co., Hawthorne, CA) or under N$_2$ atmosphere using standard Schlenk techniques unless otherwise noted. All solvents were of commercial grade and dried over activated alumina using a PPT Glass Contour (Nashua, NH) solvent purification system prior to use, and were stored over molecular sieves. All chemicals were from major commercial suppliers and used as received or after extensive drying. CD$_3$CN and CD$_2$Cl$_2$ were purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA) and dried over 3 Å molecular sieves. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were collected on a 400 MHz Bruker spectrometer (Bruker, Billerica, MA, USA) and referenced to the residual protio-solvent signal[41] in the case of ^{1}H and ^{13}C. ^{31}P and ^{19}F NMR spectra were referenced and reported relative to H$_3$PO$_4$ and CCl$_3$F, respectively, as external standards following the recommended scale based on ratios of absolute frequencies (Ξ).[42,43] Chemical shifts (δ) are reported in units of ppm and coupling constants (J) are reported in Hz. All experiments were conducted at room temperature (298 K).

5.2 Synthesis and characterization

Synthesis of Sr(OTf)$_2$. SrOTf was synthesized by following a modified literature procedure.[44] A three-necked flask was loaded with strontium carbonate (SrCO$_3$, 2.59 g, 17.5 mmol) and CH$_3$CN, forming a suspension. Under an inert atmosphere of N$_2$, triflic acid (CF$_3$SO$_3$H, 5.0 g, 33 mmol) was added dropwise to the suspension. After the addition was complete, the reaction mixture was refluxed for 3-4 h. The resulting clear solution was filtered to remove unreacted SrCO$_3$ and the filtrate was evaporated and dried in vacuo at 180°C for 24 h to obtain a white solid, which was used without further purification. Yield: 99% (4.13 g).

Synthesis of RbOTf. RbOTf was synthesized by following a modified literature procedure.[45] A three-necked flask was loaded with rubidium carbonate (Rb$_2$CO$_3$, 4.05 g, 17.5 mmol) and water, forming a turbid solution. Under an inert atmosphere of N$_2$, triflic acid (CF$_3$SO$_3$H, 5.0 g, 33 mmol) was added dropwise to the solution. After the addition was complete, the reaction mixture was stirred at room temperature for one hour and then refluxed for four hours. Water was evaporated, and the resulting solid was extracted with CH$_3$CN to remove unreacted Rb$_2$CO$_3$. The filtrate was evaporated and dried in vacuo at 180°C for 24 h to obtain a white solid, which was used without further purification. Yield: 86% (6.72 g).

Synthesis of CsOTf. CsOTf was synthesized by following a modified literature procedure.[46] A three-necked flask was loaded with cesium carbonate (Cs$_2$CO$_3$, 5.71 g, 17.5 mmol) and water, forming a turbid solution. Under an inert atmosphere of N$_2$, triflic acid (CF$_3$SO$_3$H, 5.0 g, 33 mmol) was added dropwise to the solution. After the addition was complete, the reaction mixture was stirred at room temperature for 1 h and then refluxed for 4 h. Water was evaporated, and the resulting solid was extracted with CH$_3$CN to remove unreacted Cs$_2$CO$_3$. The filtrate was evaporated and dried in vacuo at 180°C for 24 h to obtain a white solid, which was used without further purification. Yield: 93% (8.70 g).

Spectroscopic characterization. The purities of these triflate salts were confirmed by ^{19}F NMR and powder X-ray diffraction (PXRD; see SI, Figures S1-S6).

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge on the ACS Publications website: NMR data and spectra; results from PXRD studies.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interests.

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Estimating the Lewis Acidity of Metal Ions with ^{31}P NMR