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The Stability, Structure and Reactivity of the Outer Sphere Complex formed between the Hexakis (d^4-Methanol) Cobalt(II) Ion and Pyridine in d^4-Methanol

JACK R. VRIESENGA

Department of Chemistry, Syracuse University, Syracuse, N.Y. 13210, U.S.A.

and GEORGE H. FAIRCHILD

Department of Chemistry, State University of New York, College at Oswego, Oswego, N.Y. 13126, U.S.A.

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Abstract

Proton NMR spin–lattice (T_l) relaxation times and chemical shifts were used to characterize the outer sphere complex formed between the hexakis (d^4-methanol) cobalt(II) ion and pyridine in d^4-methanol. Analysis of the bulk α-hydrogen T_l data of pyridine resulted in an outer sphere complex stability constant (K_{os}) which varied from 0.51 ± 0.16 M^{-1} at −60.0 °C to 0.62 ± 0.17 M^{-1} at −40.0 °C. The extrapolated K_{os} value at 25.0 °C (1.0 M^{-1}) is almost an order of magnitude larger than predicted by theory. The combination of T_l and shift data suggested a preferred orientation of pyridine in the outer sphere of the $[Co(CD_3OD)_6]^{2+}$ ion. Further quantitative structural information was obtained by the application of the Solomon-Bloembergen relationship to the system studied. Pyridine dissociation rate constant data were combined with solvent exchange and equilibrium data to obtain values for the interchange probability or statistical factor (f) which ranged from $(7.0 \pm 3.7) \times 10^{-3}$ at −60.0 °C to $(9.5 \pm 4.7) \times 10^{-3}$ at −40.0 °C. These values are more than two orders of magnitude smaller than normally assumed and represent the first direct measurement of an ion-neutral outer sphere complex's reactivity. Implications regarding the relationship between outer sphere complex stability and reactivity are discussed.

Introduction

An overwhelming body of evidence indicates that outer sphere complexes are precursors to substitution reactions of transition metal complexes [1–10]. These precursors can strongly influence the reactivity and stereochemical course of the reaction [1, 11].

Ion pairs have been the most widely studied type of outer sphere complex. Ion pair formation constants have been measured using a number of techniques [12–19], and include electronic spectroscopy [20–22], kinetic studies [20, 22–26], and NMR techniques [27–29]. Equations for calculating ion pair formation constants have been derived from statistical considerations [30, 31] and diffusion theory [32–34]. Reasonable agreement has been found between theory and experiment at low ionic strengths [35, 36]. Further characterization of ion pairs include structural [37–39] and reactivity [40–44] studies. The latter studies often involve the measurement of a statistical factor or interchange probability factor [43–45].

In contrast to ion pairs, relatively little is known about outer sphere interactions between metal ions and neutral ligands. To date, there have been no direct experimental determinations of ion–neutral outer sphere complex stability constants, K_{os}. A number of 'kinetically determined' ion–neutral K_{os} values have been reported [6, 9, 46]; however, this approach requires an assumed and untested value for the interchange probability factor, f. Many ion–neutral K_{os} values have been reported based on the Eigen-Fuoss equation [9, 12, 47]; however, this method for approximating ion–neutral K_{os} values has been criticized on several grounds [9, 36, 48, 49]. Furthermore, except for the pioneering work of Eaton [5, 50–52] very little is known about ion–neutral outer sphere complex structure. Finally, at present, there have been no direct, experimental determinations of f for an ion–neutral species.

We have developed and applied an NMR method for measuring the stability, structure, and reactivity of ion–neutral outer sphere complexes. The method has been applied to characterize the ion–neutral outer sphere complex $[Co(CD_3OD)_6...py]^{2+}$. The results provided some interesting and possibly important insights into the factors controlling outer sphere complex stability and the relationship between outer sphere complex stability and reactivity.

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Experimental

Reagents

Anhydrous cobalt(II) trifluoromethanesulfonate, $Co(CF_3SO_3)_2$, was synthesized by reacting an excess of cobalt(II) carbonate, $CoCO_3$, with a methanol solution containing trifluoromethanesulfonic acid, CF_3SO_3H (Aldrich). Filtration of the unreacted $CoCO_3$ and subsequent evaporation yielded the desired salt. The crude product was recrystallized twice in acetonitrile prior to use.

Reagent grade pyridine, 2-methyl-2-propanol and Aldrich gold label d^4-methanol (99.5%D) were dried by passing the liquid through columns containing meshed, activated 3 Å molecular sieves (Linde) under an inert atmosphere.

NMR Samples

All NMR samples were prepared from separate stock solutions of $Co(CF_3SO_3)_2$, pyridine, and 2-methyl-2-propanol in d^4-methanol using standard inert atmosphere syringe techniques. Each sample was degassed and sealed in vacuo.

NMR Measurements

All NMR spectra were recorded on a Varian CFT-20 spectrometer in the proton mode. The solvent deuterium resonance was used as a lock signal. Spin–lattice relaxation times (T_l) were determined using standard inversion-recovery techniques [53]. Chemical shifts were measured relative to the methyl resonance of 2-methyl-2-propanol.

Results

Outer Sphere Complex Stability

The outer sphere equilibrium and associated outer sphere stability constant, K_{os}, for the ion-neutral outer sphere complex $[Co(CD_3OD)_6...py]^{2+}$ (py = pyridine) are defined as

$$\underset{\mathbf{1}}{[Co(CD_3OD)_6]^{2+}} + \underset{\mathbf{2}}{py} \overset{K_{os}}{\rightleftharpoons} \underset{\mathbf{3}}{[Co(CD_3OD)_6...py]^{2+}} \qquad (1)$$

$$K_{os} = [\mathbf{3}]/[\mathbf{1}][\mathbf{2}] \qquad (2)$$

Species **3** represents a pyridine molecule within the first solvation sphere of the $[Co(CD_3OD)_6]^{2+}$ ion, and is defined as the ion-neutral outer sphere complex. K_{os} was determined by studying the influence of the paramagnetic cobalt(II) ion on the NMR spin–lattice relaxation times, T_l, for the α, β, and γ-protons of pyridine [54, 55]. Due to the rapid exchange of pyridine between the non-outer sphere and outer sphere environments (**2** and **3**, respectively), each type of proton nucleus of pyridine appears as a single resonance. It follows that the observed spin–lattice relaxation time, $(T_l)_{obs}$, of each coalesced resonance is simply a weighted average of the T_l values for each environment ($T_l(2)$ and $T_l(3)$). The weighting factors are the mole fractions of pyridine in each environment (f_2 and f_3). The resulting expression is

$$(1/T_l)_{obs} = f_2/T_l(2) + f_3/T_l(3) \qquad (3)$$

The following quantities are defined:

$$\Delta(1/T_l)_{obs} = (1/T_l)_{obs} - (1/T_l(2)) \qquad (4)$$

$$\Delta(1/T_l(3)) = (1/T_l(3)) - (1/T_l(2)) \qquad (5)$$

Eqn. (3) then simplifies to

$$\Delta(1/T_l)_{obs} = f_3\Delta(1/T_l(3)) \qquad (6)$$

Under conditions of a large excess of cobalt(II) ion relative to pyridine ([**1**] >> [**3**]) the following expression can be derived:

$$f_3 = \frac{K_{os}[Co^{2+}]}{1 + K_{os}[Co^{2+}]} \qquad (7)$$

where $[Co^{2+}]$ represents the total concentration of $[Co(CD_3OD_6]^{2+}$ ([**1**] + [**3**]). Substitution of eqn. (7) into eqn. (6) results in the equation

$$\Delta(T_l)_{obs} = \frac{\Delta T_l(3)}{K_{os}[Co^{2+}]} + \Delta T_l(3) \qquad (8)$$

where

$$\Delta(T_l)_{obs} = \{\Delta(1/T_l)_{obs}\}^{-1} \qquad (9)$$

and

$$\Delta T_l(3) = \{\Delta(1/T_l(3))\}^{-1} \qquad (10)$$

The concentration of $[Co(CD_3OD)_6]^{2+}$ was computed from the total cobalt(II) concentration minus the concentration of bound pyridine species such as $[Co(CD_3OD)_5py]^{2+}$. The concentrations of the bound pyridine species were calculated from the corresponding equilibrium constant data [55, 56]. The T_l measurements were made at low temperatures (–40.0 °C to –60.0 °C) to ensure that pyridine exchange between the bound and bulk environments had a negligible effect on the bulk $(T_l)_{obs}$ values. Under these conditions, eqn. (8) can be used to determine K_{os}.

$(T_l)_{obs}$ data for the bulk α-H of pyridine were collected at –40.0°, –44.0°, –52.0°, and –60.0 °C; Table I contains the –44.0 °C data. $T_l(2)$ values for the bulk α-H of pyridine were determined for each sample as described previously [54]. The resulting $\Delta(T_l)_{obs}$ values are plotted in accordance with eqn. (8) (Fig. 1). Table II summarizes the K_{os} and $T_l(3)$ values obtained at various temperatures. Based on the semi-logarithmic plot of K_{os} versus $1/T$ (Fig. 2), the resulting thermodynamic parameters describing the temperature dependence of K_{os} were calculated to be ΔH = 1.0 kcal/mol and ΔS = 3.4 eu.

TABLE I. $(T_l)_{obs}$ of the Bulk α-H of Pyridine as a Function of $[Co(CD_3OD)_6]^{2+}$ Concentration at −44.0 °C[a, b].

$[Co^{2+}]$, (M)	$(T_l)_{obs}$, (msec)	$T_l(2)$, (msec)	$\Delta(T_l)_{obs}$, (msec)
0.265 ± 0.002	51.0 ± 1.1	130 ± 11	84.0 ± 7.1
0.362 ± 0.002	40.8 ± 0.4	113 ± 8	64.1 ± 3.3
0.530 ± 0.002	31.2 ± 0.6	86.4 ± 5.3	49.0 ± 3.1
0.596 ± 0.002	28.9 ± 0.3	84.7 ± 5.3	43.8 ± 1.9
0.679 ± 0.002	26.4 ± 0.6	80.6 ± 5.2	39.2 ± 2.3

[a] $[py]_{total}$ = 0.0480–0.0496 M. [b] Corresponding data at other temperatures are reported in Ref. 55.

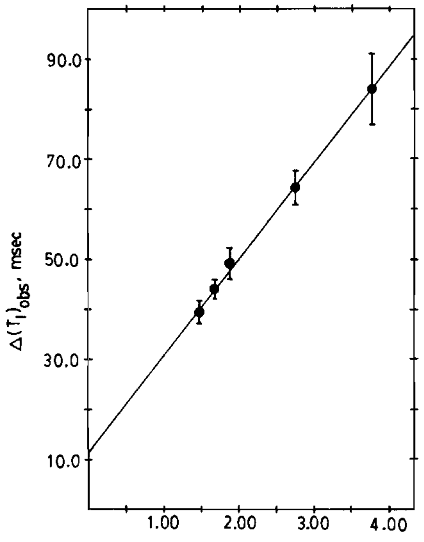

Fig. 1. Plot of $\Delta(T_l)_{obs}$ versus $1/[Co^{2+}]$; bulk α-H of pyridine; temp. = −44.0 °C.

TABLE II. Results of the Analysis of the Bulk α-H of Pyridine T_l Data: K_{os} and $T_l(3)$ Values.

Temp. (°C)	K_{os}, (M^{-1})	$T_l(3)$, (msec)
−40.0	0.62 ± 0.17	12 ± 3
−44.0	0.60 ± 0.16	11 ± 2
−52.0	0.54 ± 0.17	9.5 ± 2.7
−60.0	0.51 ± 0.16	8.7 ± 2.6

Outer Sphere Complex Structure

The $T_l(3)$ values of the α-proton are directly related to the average reciprocal sixth power distance of separation between the α-proton and the cobalt(II) ion, $\langle r^{-6}\rangle$. This relationship is expressed by the well-known Solomon-Bloembergen equation [57, 58]:

$$1/T_l = \frac{2S(S+1)\gamma_I^2 g^2 \beta^2}{15\langle r^6\rangle}\left[3\tau_c + \frac{7\tau_c}{1+\omega_s^2\tau_c^2}\right] = \frac{Q}{\langle r^6\rangle} \qquad (11)$$

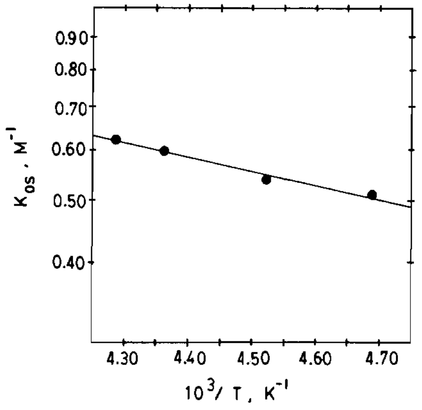

Fig. 2. Temperature dependence of K_{os}.

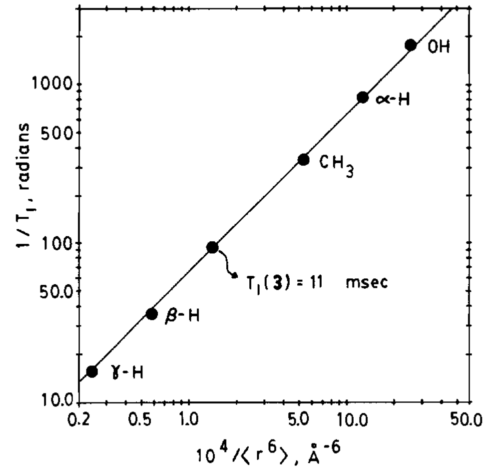

Fig. 3. Plot of log $(1/T_l)$ versus log $1/\langle r^6\rangle$ for the proton nuclei of methanol and pyridine bound to cobalt(II); temp. = −44.0 °C.

The value of the constant Q was determined for the system studied by assembling a set of T_l values for the protons of ligands coordinated to the cobalt(II) ion. The values of $\langle r^{-6}\rangle$ were computed from known structural data, taking into account rotational averaging when necessary [55]. A logarithmic plot of $1/T_l$ versus $\langle r^{-6}\rangle$ at −44.0 °C is shown (Fig. 3). The resulting linear relationship has a theoretically predicted slope of one. The excellent linearity over three orders of magnitude of T_l values supports the point dipole approximation implicit in the Solomon-Bloembergen equation. Based on this relationship, the average distance of separation between the cobalt(II) ion and the α-proton in the outer sphere complex was determined to be 4.4 ± 0.2 Å.

Further qualitative structural information was obtained from a comparison of the relative T_l values for the various proton nuclei of bulk pyridine. If the pyridine molecule in the outer sphere complex has its C_2 axis lying coincident with the C_3 axis of $[Co(CD_3OD)_6]^{2+}$ with a Co^{2+}–N distance of 3.7 Å, then the ratios $(T_l)_{obs}{}^{\beta}/(T_l)_{obs}{}^{\alpha} = 3.7$ and $(T_l)_{obs}{}^{\gamma}/(T_l)_{obs}{}^{\alpha} = 4.4$ are predicted. At the lowest cobalt(II) concentration (0.3054 M) where there was no overlap of the β and γ-proton resonances, and long range effects on proton T_l values are at a minimum, the $(T_l)_{obs}{}^{\beta}/(T_l)_{obs}{}^{\alpha}$ and $(T_l)_{obs}{}^{\gamma}/(T_l)_{obs}{}^{\alpha}$ ratios were found to be 3.5 and 3.9, respectively. This indicates that pyridine is highly oriented in the outer sphere complex. Any significant rotation of the pyridine molecule about axes perpendicular to its C_2 axis will cause the ratio of T_l's to quickly approach unity. An idealized picture of the outer sphere complex can be proposed (Fig. 4). Clearly, a more correct picture would account for variations in the distance of approach between the pyridine molecule and the $[Co(CD_3OD)_6]^{2+}$ ion. However, the fact remains that the pyridine molecule maintains a high degree of orientation within the outer sphere complex.

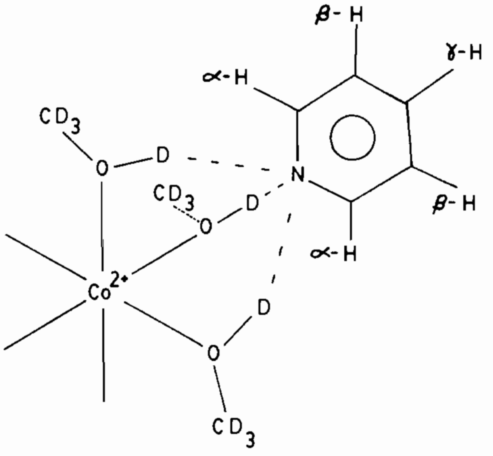

Fig. 4. Proposed structure of the $[Co(CD_3OD)_6...py]^{2+}$ outer sphere complex.

The paramagnetic chemical shifts, $\Delta\nu_{obs}$, also support the preferred orientation of pyridine in the outer sphere complex. The paramagnetic shift for a particular resonance in the presence of cobalt(II) ion is defined as follows:

$$\Delta\nu_{obs} = \nu_{obs} - \nu_o \qquad (12)$$

where ν_{obs} is the observed resonance frequency and ν_o is the corresponding resonance frequency in the absence of cobalt(II) ion. The order of shifts was found to be $\Delta\nu_{obs}(\alpha) > \Delta\nu_{obs}(\beta) > \Delta\nu_{obs}(\gamma)$. It is interesting to note that the values of the shift ratios $\Delta\nu_{obs}(\alpha)/\Delta\nu_{obs}(\beta)$ and $\Delta\nu_{obs}(\alpha)/\Delta\nu_{obs}(\gamma)$ were very close to that predicted from the proposed structure, assuming that $\Delta\nu_{obs}$ is dominated by a dipolar mechanism in which the principal magnetic axis is induced along the C_3 axis of the $[Co(CD_3OD)_6]^{2+}$ ion and along which the pyridine molecule approaches. We feel that such an agreement is probably somewhat fortuitous, because $\Delta\nu_{obs}$ is most likely a composite of both Fermi and dipolar shifts.

Outer Sphere Complex Reactivity

The reactivity of the outer sphere complex $[Co(CD_3OD)_6...py]^{2+}$ is related to the rate for the following interchange process:

$$\underset{\mathbf{3}}{[Co(CD_3OD)_6...py]^{2+}} \xrightarrow{k_i} \underset{\mathbf{4}}{[Co(CD_3OD)_5py]^{2+}} + \underset{\mathbf{5}}{CD_3OD} \qquad (13)$$

For a hexasolvated metal ion, the interchange rate constant k_i can be expressed as [44, 46].

$$k_i = f6k_{ex} \qquad (14)$$

where k_{ex} is the solvent exchange rate constant per solvent molecule, and f is the interchange probability factor. The latter quantity represents the probability that the pyridine molecule in species **3** will enter the inner sphere of the cobalt(II) ion per cobalt(II)-methanol dissociation event.

The value of f was obtained from the net substitution process

$$\underset{\mathbf{1}}{[Co(CD_3OD)_6]^{2+}} + \underset{\mathbf{2}}{py} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{\mathbf{4}}{[Co(CD_3OD)_5py]^{2+}} + \underset{\mathbf{5}}{CD_3OD} \qquad (15)$$

The equilibrium constant for the process can be written as

$$K_l = k_f/k_r = K_{os}k_i/k_r = K_{os}f6k_{ex}/k_r \qquad (16)$$

where k_r is the pyridine dissociation rate constant for the $[Co(CD_3OD)_5py]^{2+}$ ion; the other terms have been previously defined. Rearrangement of eqn. (16) yields

$$f = K_lk_r/K_{os}6k_{ex} \qquad (17)$$

Values for K_l, k_r, and k_{ex} were determined from previous temperature dependence studies [55, 56, 59]. These data and the resulting values for f are sum-

TABLE III. Equilibrium and Rate Constant Data for the System Studied, and the Resulting Interchange Probability Factor Values.

Temp., (°C)	K_l, (M^{-1})	$10^3 k_r$, (sec^{-1})	k_{ex}, (sec^{-1})	$10^3 f$[a]
−40.0	20.8 ± 1.6	38.8 ± 1.6	22.8 ± 2.3	9.5 ± 4.7
−44.0	22.1 ± 1.7	19.8 ± 0.8	13.6 ± 1.4	8.9 ± 4.4
−52.0	25.3 ± 2.0	4.78 ± 0.19	4.55 ± 0.46	8.2 ± 4.4
−60.0	29.1 ± 2.3	1.04 ± 0.04	1.41 ± 0.14	7.0 ± 3.7

[a]Calculated using eqn. (17); see Table II for K_{os} values.

TABLE IV. Summary of Some 'Apparent' Ion–Neutral K_{os} Values at 25 °C.

Reaction[a]	Solvent	k_f, (M^{-1} sec^{-1})	k_{ex}, (sec^{-1})	K_{os}'[b] (M^{-1})	Ref.
$Co^{2+} + NH_3$	H_2O	1.1×10^5	1.2×10^6	0.092	6
Co^{2+} + imid[c]	H_2O	1.3×10^5	1.2×10^6	0.11	6
Co^{2+} + phen[d]	H_2O	3.2×10^5	1.2×10^6	0.27	6
Co^{2+} + py	CH_3CN	1.16×10^5	3.2×10^5	0.36	6
Co^{2+} + bipy[e]	CH_3OH	1.92×10^3	1.8×10^4	0.11	f
Co^{2+} + py	CD_3OD	1.66×10^3[g]	1.5×10^4	0.11	this work

[a]Reaction involves hexasolvated metal ion. [b]$K_{os}' = k_f/k_{ex}$. [c]imid = imidazole. [d]phen = 1,10-phenanthroline. [e]bipy = 2,2′-bipyridine. [f]Ref. 60. [g]Calculated using $k_f = K_l K_r$.

marized in Table III. The important result here is that f is much less than one; that is, the $[Co(CD_3OD)_6 \ldots py]^{2+}$ species undergoes many methanol dissociations per interchange event.

Discussion

The K_{os} values obtained for the ion–neutral species $[Co(CD_3OD)_6 \ldots py]^{2+}$ (Table II) are larger than the predicted value of 0.1 M^{-1} estimated by the Eigen-Fuoss equation. In fact, based on the ΔH and ΔS values determined in this study, the value of K_{os} at 25 °C is predicted to be approximately 1.0 M^{-1}, almost an order of magnitude larger than normally assumed. These results clearly point to the inadequacy of using the Eigen-Fuoss equation for this system [47]. The large K_{os} values obtained for this ion–neutral outer sphere complex suggest that hydrogen bonding is a major stabilizing force. The proposed structure of the $[Co(CD_3OD)_6 \ldots py]^{2+}$ outer sphere complex (Fig. 4) with its short cobalt(II)–nitrogen distance is consistent with the existence of hydrogen bonding between pyridine and the bound methanols in the face of the $[Co(CD_3OD)_6]^{2+}$ ion. Apparently the hydrogen bond alternates randomly among the three facial methanols at any instant, depending on the methanols' rotational conformation.

The concept of preferred orientation in outer sphere complexes involving neutral ligands was first introduced by Eaton [5, 50–52]. The results obtained here support many of the conclusions of these previous studies. It is assumed that molecular rotations and tumbling cause variations in the outer sphere complex structure. However, on the average, the data strongly suggest a highly oriented structural arrangement for this species.

The interchange probability factor reported here represents the first direct measurement of this quantity for an ion–neutral outer sphere complex. The values obtained for f (Table III) are more than two orders of magnitude smaller than the often assumed value of unity [44]. The results of this study suggest, but not necessarily prove, that an inverse relationship exists between outer sphere complex stability and reactivity. Other factors such as steric hindrance, choice of solvent, and temperature certainly must also affect the value of f to varying degrees. However, as a first approximation, the greater the stability of the outer sphere complex, that is, the larger K_{os}, the less likely interchange will occur upon solvent dissociation, as reflected by the small value of f. This idea is supported by the data in Table IV which summarizes a series of 'kinetically determined' ion–neutral outer sphere complex stability constants for the hexasolvated cobalt(II) ion in various solvents. These 'apparent' K_{os} values, K_{os}', were determined by dividing the rate constant for the overall substitution process, k_f, by the solvent exchange rate constant, k_{ex}. However, according to the Eigen-Wilkins mechanism [45, 46], this calculation results in the composite quantity $\{fK_{os}\}$, where K_{os} is the actual outer sphere complex stability constant. It is of interest to note that the 'apparent' outer sphere complex stability constant for the $[Co(CD_3OD)_6...py]^{2+}$ species determined from the results of this study (Table IV) is in good agreement with other K_{os}' values. However, the actual K_{os} value for this species is approximately an order of magnitude larger than this 'apparent' K_{os} value. In view of the wide variety of ligands and solvents studied, it is conceivable that the actual K_{os} values for these systems vary considerably, but this variation is masked by the apparent inverse relationship between K_{os} and f. The application of the method outlined here to characterize other ion–neutral outer sphere complexes is being pursued.

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