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Base Hydrolysis of $[Co(tren)(NH_3)_2]^{3+}$, *s*-$[Co(Me(tren))(NH_3)_2]^{3+}$, and *anti-p*-$[Co(Me(tren))(NH_3)_2]^{3+}$ and the Determination of Ion-Pairing and Acidity Constants

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Deviations from the rate law $k_{obsd} = k_{OH}[OH^-]$ for base hydrolysis of cobalt(III) acido–amine complexes are very rare indeed with the linear relationship between k_{obsd} and $[OH^-]$ being followed up to at least 0.1–1.0 mol dm^{-3} OH^-.[1-3] This is generally regarded as a consequence of the amine protons being only weakly acidic, $K_a < K_w$, and in the one reported instance of curvature, that for *cis*-$[Co(en)_2Cl(NH_2Ph)]^{2+}$,[1,4] the enhanced acidity of coordinated aniline ($pK_a \sim 10$) was held responsible.[4] However, ion pairing with OH^- would also lead to curvature if K_{ip} were important, and the general question of ion pairing ($S_N1$ip mechanism) or conjugate base formation (S_N1cB) has not been adequately answered.[5] We have recently discovered three 3+ complexes, $[Co(tren)(NH_3)_2]^{3+}$, *s*-$[Co(Me(tren))(NH_3)_2]^{3+}$, and *anti-p*-$[Co(Me(tren))(NH_3)_2]^{3+}$ (tren = 2,2′,2″-triaminotriethylamine; Me(tren) = 2-methylamino-2′,2″-diaminotriethylamine),[14] which display the limiting rate law for base hydrolysis, and an analysis of the data allows both the degree of ion pairing and the acidity of the proton responsible for base hydrolysis to be determined. This has not been done previously, and it is also unusual to find coordinated ammonia lost in the base hydrolysis reaction.

Experimental Section

^1H NMR spectra were recorded on Varian T-60 or HA-100 instruments or on a Jeol Model PMX-60 at 32 °C. Proton exchange rates of the complexes in D_2O were measured by using sodium deuterioxide with chloroacetic acid-d_1 or acetic acid-d_1 as buffers. Measurements of pD and pH were made on a Radiometer 22 pH meter previously standardized with solutions of sodium tetraborate (1.00×10^{-2} mol dm^{-3}, pH 9.185, 25.0 °C) and potassium hydrogen phthalate (5.00×10^{-2} mol dm^{-3}, pH 4.008, 25.0 °C). Base hydrolysis rates were measured by using a D-110 Durrum stopped-flow spectrophotometer equipped with a Biomation Model 805 waveform recorder and on a Gilford 2400 instrument. First-order rate constants were evaluated from plots of log (peak height) against time for H exchange in D_2O and from plots of log $(A_\infty - A_t)$ against time for base hydrolysis.

Materials. Acetic acid-d_1 was prepared by the reaction of acetic anhydride with D_2O, and chloroacetic acid-d_1 was prepared by recrystallization (×3) of chloroacetic acid from D_2O. Other deuterated reagents were obtained from Sigma. All other reagents were of AnalaR quality.

$[Co(Me(tren))(NH_3)_2](ClO_4)_3$ (Isomers 1 and 2). $[Co(Me(tren))Cl_2](ClO_4)$ was added to excess liquid NH_3 and the resultant solution evaporated slowly to dryness in a dry atmosphere at room temperature. The resultant yellow-orange product which crystallized from dilute $HClO_4$ to which $NaClO_4$ had been added proved to be a mixture of the perchlorate salts of isomers **1** and **2**. The former was obtained by further recrystallization (×2) of the mixture from dilute $HClO_4$ with added $NaClO_4$ and was washed with cold ethanol–water (80:20) and then ethanol and dried. ^1H NMR (Me_2SO-d_6): δ 5.45 (br s, 1, N*H*CH$_3$), 4.90 (br s, 2, NH$_2$), 4.60 (br s, 2, NH$_2$), 3.8–2.6 (complex multiplet for the methylene protons and including resonances at δ 3.53 and 3.22 for the NH_3 protons, 18), 2.03 (d, *J* = 5.6 Hz, 3, NHC*H*$_3$). Anal. Calcd for $CoC_7H_{26}N_6Cl_3O_{12}$: C, 15.24; H, 4.75; N, 15.23. Found: C, 15.31; H, 4.71; N, 15.05.

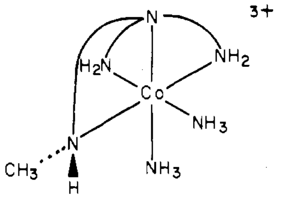
Isomer **2** was obtained from the crude reaction mixture by utilizing the large differential in the base hydrolysis rates of the two isomers. A sample of the mixture (4 g) in water (100 cm^3) was maintained at pH 9.5 and 25 °C for 8 min (pH stat control). The reaction mixture was quenched (pH 3, $HClO_4$), diluted with water (400 cm^3), and sorbed onto a column of Dowex 50W-X2 ion-exchange resin (H^+ form, 5 × 10 cm). The red 2+ product was removed by rapid elution with 1 mol dm^{-3} $NaClO_4$ 0.2 mol dm^{-3} in "Tris" buffer (pH 8.0) and the column was then immediately washed with water. The orange 3+ band was removed by gradient elution with HCl (0.5–6.0 mol dm^{-3}) and taken rapidly to dryness (rotary evaporator, 40 °C) and the product crystallized as the perchlorate salt as for isomer **1**. ^1H NMR (Me_2SO-d_6): δ 6.06 (br s, 1, N*H*CH$_3$), 5.26 (br s, 2, NH$_2$), 4.76 (br s, 1), 4.36 (br s, 1), 4.0–2.6 (complex multiplet for the methylene protons and including resonances at δ 3.83 and 3.53 for the NH_3 protons, 18), 2.16 (d, *J* = 5.6 Hz, 3, NHC*H*$_3$). The analytical sample was obtained as the more soluble iodide salt. Anal. Calcd for $CoC_7H_{26}N_6I_3$: C, 13.26; H, 4.13; N, 13.25; I, 60.05. Found: C, 13.52; H, 4.31; N, 13.55; I, 59.84. For the NMR experiments **2** was converted to the chloride salt by passage of a solution of the perchlorate salt through Dowex 1-X8 anion-exchange resin (Cl^- form, 200 mesh) and isolated as a hygroscopic solid on the rotary evaporator.

$[Co(tren)(NH_3)_2](ClO_4)_3$. Treatment of $[Co(tren)Cl_2](ClO_4)$ with liquid ammonia as for the corresponding Me(tren) complex yielded $[Co(tren)(NH_3)_2]^{3+}$ which was similarly isolated as the perchlorate salt. Anal. Calcd for $CoC_6H_{24}N_6Cl_3O_{12}$: C, 13.39; H, 4.46; N, 15.63. Found: C, 13.50; H, 4.66; N, 15.82.

$[Co(tren)(NH_3)_2](ClO_4)_3$ Base Hydrolysis Product. $[Co(tren)(NH_3)_2](ClO_4)_3$ (0.5 g) in NaOH (0.1 mol dm^{-3}, 50 cm^3) was allowed to stand for 30 min at room temperature before the solution was sorbed on Dowex 50W-X2 (H^+ form, 2 × 20 cm^3). Elution with HCl (1.5 mol dm^{-3}) showed only a single orange-red band moving as a 3+ ion. Annation of the eluted aqua product (3 mol dm^{-3} HCl, 40 °C), a reaction proceeding with 100% stereochemical retention,[13] gave red *p*-$[Co(tren)(NH_3)Cl]^{2+}$ exclusively with no detectable formation (ion-exchange chromatography) of the purple *t* isomer. The annated product was crystallized twice as the chloride perchlorate salt from dilute HCl with added $NaClO_4$. Anal. Calcd for $CoC_6H_{21}N_5Cl_3O_4$: C, 18.36; H, 5.39; N, 17.84. Found: C, 18.16; H, 5.23; N, 17.53.

Results

Base hydrolysis of *anti-p*-$[Co(Me(tren))(NH_3)_2]^{3+}$ (**1**),



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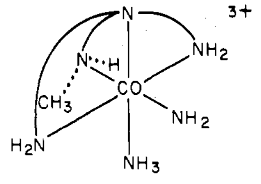

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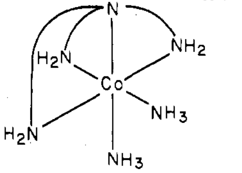

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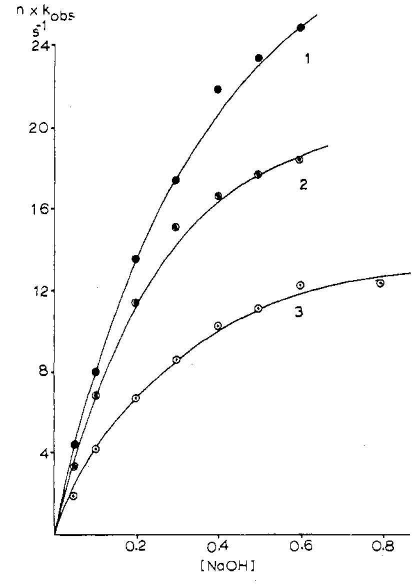
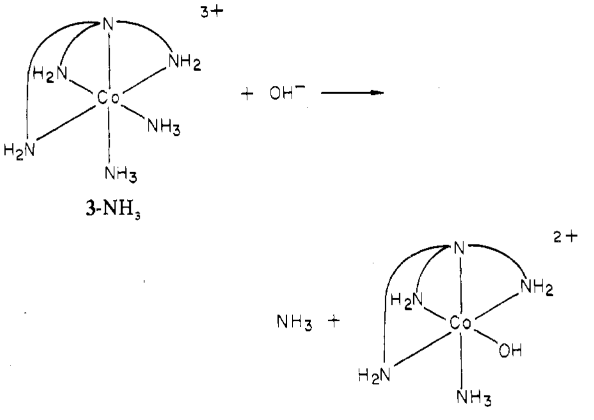


Figure 1. Hydrolysis rates of **1** ($n = 1$), **2** ($n = 50$), and **3** ($n = 1000$) as a function of [OH⁻]; λ 530 nm and [Co] = 5×10^{-3} mol dm^{-3}.

s-$[Co(Me(tren))(NH_3)_2]^{3+}$ (**2**), and $[Co(tren)(NH_3)_2]^{3+}$ (**3**) was followed spectrophotometrically over the NaOH range 0.05–0.8 mol dm^{-3}, μ = 1.0 $NaClO_4$, 25.0 °C. Clean, first-order kinetics were followed in each case ($>4t_{1/2}$) and the first-order rate constants, Figure 1, fit the rate law

$$k_{\rm obsd} = kK[{\rm OH^-}]/(1 + K[{\rm OH^-}]) \qquad (1)$$

with k (s^{-1}) and K (mol^{-1} dm^3) values of 43 and 2.3 (**1**), 0.65 and 2.4 (**2**), and 1.8×10^{-2} and 3.0 (**3**). Clearly all three complexes approach limiting rates at about the same NaOH concentration (~1.0 mol dm^{-3}), but the k values differ appreciably. Hydrolysis involves replacing the "in-plane" NH_3 group by OH^- in each case (eq 2 for **3**), but for the Me(tren) complexes a mixture of *anti-p*, *syn-p*, and *s* isomers results.[6,14] These only differ in the stereochemistry of the methyl group in relation to OH^-; a complete characterization of the various isomers will be reported separately.[7]



3-NH$_3$

(2)

3-OH

Proton exchange of the various amine centers was followed by ^1H NMR spectroscopy in D_2O buffers by the collapse of the NH_2 and $NHCH_3$ proton signals, and for the latter (**1**, **2**) by collapse of the methyl doublet to a singlet. Double irradiation experiments established that the lowest field amine signal (cf. Experimental Section) was associated with the $NHCH_3$ group in **1** and **2**. The second-order rate constants (k_{-H}) are listed in Table I, and Figure 2 demonstrates that for **1** and **3** the fastest exchanging protons follow a first order in [OD⁻] behavior. The same result was obtained for **2** from more limited data and for all three complexes for the slower exchanging protons. The rate law

$$k_{\rm obsd} = k_{-\rm H}[{\rm OD^-}] \qquad (3)$$

therefore holds quite generally. It is clear that for **1** and **2** the fastest exchanging proton is that of the $NHCH_3$ center; the NH_3 groups did not show any exchange in the time for complete exchange of the $-NH_2$ and $-NHCH_3$ protons.

Table I. Second-Order Rate Constants for H Exchange ($k_{-\rm H}$, mol^{-1} dm^3 s^{-1}) in D_2O[a] and H_2O,[b] $\mu \simeq 1.0$

amine group	complex 1	complex 2	complex 3
$-NHCH_3$	2.0×10^8 (D_2O) 1.8×10^9 (H_2O)	2×10^7 (D_2O) 1.8×10^8 (H_2O)	
$-NH_2$	2.0×10^8 (D_2O)	~7×10^5 (D_2O)	2.6×10^7 (D_2O)
$-NH_2$	~1.0×10^8 (D_2O)		
$-NH_3$	$<10^6$ (D_2O)	$<10^6$ (D_2O)	$<10^6$ (D_2O)

[a] Data in D_2O; [OD⁻] calculated by using pD = pH (measured) + 0.4 (Glascoe, P. K.; Long, F. A. *J. Phys. Chem.* **1960**, *64*, 188); $pK_{D_2O} = 14.88$ and $\gamma = 0.67$ ($\mu \simeq 1$). [b] Data in H_2O, $pK_{H_2O} = 13.77$ ($\mu = 1.0$).

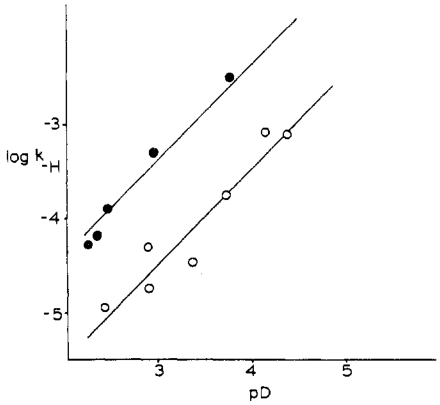


Figure 2. Exchange rates of the fastest exchanging proton (lowest field) of **1** (closed circles) and of **3** (open circles) in D_2O at 32 °C, μ ~ 1.0. The lines are drawn for a first order in [OD⁻] dependence.

H-exchange rates in H_2O for the $NHCH_3$ protons of **1** and **2** were obtained from line broadening experiments. Selected experimental data showing collapse of the methyl doublet to a singlet are given in Figure 3. Comparison with computer-generated curves showed a first order in [OH⁻] dependence and the second-order rate constants (Table I) were calculated by using the expression for intermediate exchange[8]

$$k_{-\rm H} = \sqrt{2}\pi J_{\rm NHCH_3}/[{\rm OH^-}] \qquad (4)$$

with $J_{\rm NHCH_3}$ = 5.6 Hz, and coalescence pHs of 5.90 (**1**) and 6.90 (**2**).

Discussion

The base hydrolysis data can be accommodated by the scheme

$$\text{Co}^{3+} + \text{OH}^- \overset{K_{\rm ip}}{\rightleftharpoons} \text{Co}^{3+},\text{OH}^- \overset{K_{-\rm H}}{\rightleftharpoons} \text{Co–H}^{2+} \xrightarrow{k_{\rm OH}} \text{products} \qquad (5)$$

in which Co^{3+} represents **1**, **2**, or **3**, Co^{3+},OH^- the corresponding ion pair with OH^-, and $Co–H^{2+}$ the conjugate base formed by dissociation of the proton responsible for hydrolysis. There is little doubt that $Co–H^{2+}$ is the immediate reactant leading to loss of the acido group and that an S_N1ip mechanism with Co^{3+},OH^- leading directly to the products does not operate. The main, and very persuading, argument in support of this is that K_{ip} values for ion pairing with other anions (e.g., Cl^-, Br^-, N_3^-, NO_3^-) are probably not very different from that for OH^-,[9,10] yet OH^- is extremely effective in catalyzing the

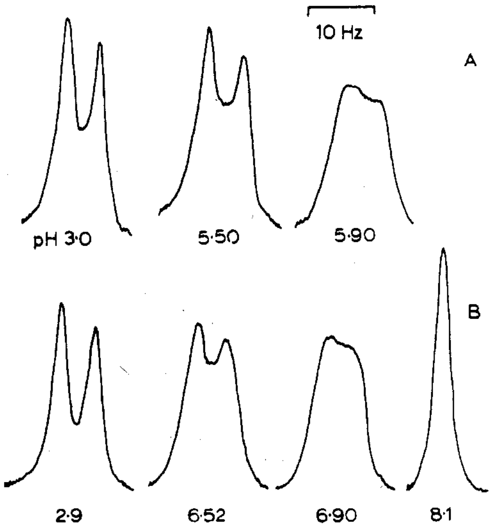


Figure 3. Changes in the methyl resonance of **1** (A) and **2** (B) as a function of pH in water at 32 °C and $\mu \sim 1.0$. Phosphate buffer (0.05–0.10 mol dm^{-3}) did not appreciably affect the line shapes. The observation of a singlet for the methyl resonance in **1** was prevented owing to rapid hydrolysis above pH 7.

reaction whereas Cl^-, Br^-, N_3^-, and NO_3^- are not. Also, base hydrolysis is not observed for 2+ or 3+ Co(III) complexes which do not have readily exchangeable NH protons. The above scheme leads to the expression

$$k_{\text{obsd}} = \frac{k_{\text{OH}}K_{\text{ip}}K_{\text{-H}}[\text{OH}^-]}{1 + K_{\text{ip}}[\text{OH}^-](1 + K_{\text{-H}})} \qquad (6)$$

and this simplifies to $k_{\text{obsd}} = k_{\text{OH}}K_{\text{ip}}K_{\text{-H}}[\text{OH}^-]/(1 + K_{\text{ip}}K_{\text{-H}}[\text{OH}^-]) = k_{\text{OH}}K_a[\text{OH}^-]/(K_w + K_a[\text{OH}^-])$ if OH^- is sufficiently basic to completely remove the proton (i.e., $K_{\text{-H}} \gg 1$; $K_{\text{ip}}K_{\text{-H}} = K_a/K_w$) and to $k_{\text{obsd}} = k_{\text{OH}}K_{\text{ip}}K_{\text{-H}}[\text{OH}^-]/(1 + K_{\text{ip}}[\text{OH}^-])$ if the ion pair predominates. The central issue is which one of these two processes governs the curvature shown in Figure 1.

The answer comes from an evaluation of K_a for **1**–**3**. This can be done by using the $k_{\text{-H}}$ data for H exchange (Table I) and an Eigen plot recently developed for H transfer to substituted amine centers including metal complexes.[11] Such a plot is given in Figure 4. It can be seen that for the more acidic amines with $pK_b > 2.5$ ($=pK_w - pK_a$) deprotonation by OH^- is diffusion controlled with an average rate constant ($k_{\text{-H}}$) of $10^{10.35}$ mol^{-1} dm^3 s^{-1}. For the two basic metal–amine systems on the left-hand side of the figure, reprotonation of the conjugate base occurs at the constant rate of $10^{9.1}$ s^{-1}, and these data together with those for the acetamidium and *N*-methylguanidinium ions define a good correlation between $k_{\text{-H}}$ and K_a in the region of interest. This correlation gives K_a/K_w values of 1.2, 0.1, and 0.2 for **1**, **2**, and **3**, respectively, and comparison with the experimental K values (2.3, 2.4, 3.0) shows that only for **1** is there reasonable agreement. This suggests that only for this complex is the amine proton sufficiently acidic to be completely abstracted by OH^-, when k (43 s^{-1}) represents the first-order rate for loss of NH_3 from the conjugate base ($k = k_{\text{OH}}$). For **2** and **3** the amine protons are not sufficiently acidic, and an equilibrium between the ion pair Co^{3+},OH^- and $Co\text{-}H^{2+}$ obtains. Here the experimental first-order limiting rates ($k = 0.65$ s^{-1} (**2**), 1.8×10^{-2} s^{-1} (**3**)) relate to $k_{\text{OH}}K_{\text{-H}}$ in the above scheme.

The reasonable agreement between K and K_a/K_w for **1**, the most acidic complex, supports the view that the most acidic $NHCH_3$ proton is responsible for hydrolysis; certainly K_a/K_w values larger than K do not occur for any of the complexes. However, a less acidic proton could still account for the facts even for **1**, but in this case the curvature in Figure 1 would also result from ion-pair formation with OH^-.

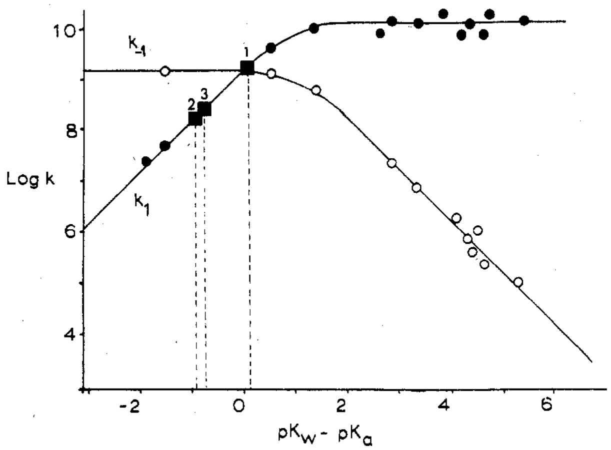


Figure 4. Logarithms of rate constants for deprotonation of substituted ammonium ions and metal–amine complexes k_1 (solid circles) and the reverse reprotonation k_{-1} (open circles) vs. logarithm of amine acidity. Data taken from ref 11 except for extreme left-hand circle which is for $[Co(en)_3]^{3+}$; $k_{\text{-H}}(D_2O) = 2.4 \times 10^6$ mol^{-1} dm^3 s^{-1} (Palmer, J. W.; Basolo, F. *J. Inorg. Nucl. Chem.* **1960**, *15*, 279) giving $k_{\text{-H}}(H_2O) \sim 2 \times 10^7$ mol^{-1} dm^3 s^{-1} by using the same solvent isotope factor as found for the $NHCH_3$ protons of this study; $pK_a = 14.9$ at $\mu = 0$ (Goodall, D. M.; Hardy, M. J. *J. Chem. Soc., Chem. Commun.* **1975**, 919) giving $pK_a \simeq 15.9$ at $\mu = 1.0$. The solid squares are $k_{\text{-H}}(H_2O)$ values for complexes **1**, **2**, and **3** giving $K_a/K_w = 1.2$ (**1**), 0.1 (**2**), and 0.2 (**3**).

These results pinpoint the difficulty in interpreting experimental data, especially spectral changes and ^1H NMR data,[12] in terms of K_a or K_{ip} values for weakly acidic complex ions.[5] For most Co(III) systems $K_a < K_w$, and the Co^{3+},OH^- ion pair will always predominate irrespective of the OH^- concentration. In such cases it is essential to have an experimental method which measures the concentration of the very small amount of conjugate base present in order to evaluate the unimolecular rate, k_{OH}.[15]

Registry No. $[Co(tren)(NH_3)_2](ClO_4)_3$, 69961-06-4; *anti-p*-$[Co(Me(tren))(NH_3)_2](ClO_4)_3$, 70004-71-6; *s*-$[Co(Me(tren))(NH_3)_2](ClO_4)_3$, 70006-01-8; $[Co(tren)(NH_3)Cl]Cl(ClO_4)$, 54713-96-1; $[Co(tren)Cl_2](ClO_4)$, 33393-50-9; $[Co(Me(tren))Cl_2](ClO_4)$, 69991-09-9; $[Co(Me(tren))(NH_3)_2]I_3$, 70004-72-7.

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(14) The nomenclature employed here is a logical extension of that used for the $[Co(tren)(NH_3)X]^{2+}$ ions;[13] viz., *p*, *s*, and *t* denote primary, secondary, and tertiary N centers, respectively, trans to the in-plane ammine group (group being substituted), and *anti* and *syn* denote the relationship of the methyl substituent to this ammine.

(15) After the completion of the present work ion-pair formation between $Ru(NH_3)_6^{3+}$ and OH^- ($K_{\text{ip}} = 5.4 \pm 0.8$ M^{-1} at 25 °C, $\mu = 0.1$ M) and the hydrolysis of $Ru(NH_3)_5(NH_2)^{2+}$ ($K_{\text{-H}} = 1.8 \pm 0.2$) have been reported: Waysbort, D.; Navon, G. *Inorg. Chem.*, **1979**, *18*, 9.