Table IV

Amt of CO, ml	Carbonyl bands, cm^{-1}	Amt of CO, ml	Carbonyl bands, cm^{-1}
0.5	1910	2.0	1990, 1930
1.0	1910	3.0	1990, 1930

2. Preparation of $Co(CO)Br[(EtO)_3P]_3$. A solution of 2.2 g (3.5 mmol) of $CBr[(EtO)_3P]_3$ in 4 ml of hexane was placed in a serum bottle and CO was added from a 20-ml reservoir (total pressure drop 75 psi). The resulting solution was then cooled to −35 °C for several days. The dark red crystals were collected, washed with hexane, and vacuum-dried, giving 0.9 g (1.4 mmol, 39% yield); mp 35 °C (evacuated capillary). There was a single carbonyl at 1925 cm^{-1} (Nujol) and a benzene solution was essentially diamagnetic as judged by the Evans technique.[4]

Anal. Calcd for $C_{19}H_{45}O_{10}P_3CoBr$: C, 34.30; H, 6.82. Found: C, 34.11; H, 6.66.

3. Preparation of $Co(CO)_2Br[(EtO)_3P]_2$. A solution of 1.84 g (2.9 mmol) of $CoBr[(EtO)_3P]_3$ in 10 ml of hexane was placed in a pressure bottle and CO was added until the pressure remained at 30 psig. The mixture was cooled to −35 °C under CO pressure for several days. The yellow crystals were collected, washed with hexane, and vacuum-dried, giving 1.30 g (2.5 mmol, 85% yield); mp 70 °C (evacuated capillary). A benzene solution was essentially diamagnetic by the Evans method.[4] There were two IR carbonyl bands (Nujol): a strong one at 1932 and a much weaker one at 1990 cm^{-1}.

Anal. Calcd for $C_{14}H_{30}O_8P_2CoBr$: C, 31.89; H, 5.74. Found: C, 31.98; H, 5.65.

Registry No. $CoH[(PhO)_3P]_4$, 24651-64-7; $[(PhO)_3P]_4Co_2[P(OPh)_2]_2$, 61024-91-7; $CoBr[(PhO)_3P]_3$, 61026-10-6; $[Co(CO)_3(PhO)_3P]_2$, 21118-36-5; $Co(CO)Br[(PhO)_3P]_3$, 61026-11-7; $Co(CO)_2Br[(PhO)_3P]_2$, 14653-41-9; $Co(CO)_2Cl[(EtO)_3P]_2$, 61026-12-8; $Co(CO)Cl[(EtO)_3P]_3$, 61026-13-9; $CoCl[(EtO)_3P]_3$, 15488-43-4; $Co(CO)Br[(EtO)_3P]_3$, 61025-73-8; $Co(CO)_2Br[(EtO)_3P]_2$, 61025-83-0; CO, 630-08-0; ^{31}P, 7723-14-0.

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Preparation, Structure, and Interconversion Kinetics of Mono- and Binuclear Aquo(nitrilotriacetato)cobaltate(III) Complexes

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Our attempts to synthesize the previously reported complex ion $K[Co(NTA)(OH)(H_2O)]\cdot nH_2O$ in the pure solid form failed, the procedure used inevitably leading to samples of the di-μ-hydroxo species, $K_2[Co_2(NTA)_2(OH)_2]$. The acid-catalyzed hydrolysis of this compound proceeds in two identifiable steps, each described by a rate equation of the form $k_{obsd} = k_2K_2[H^+]^2/(1 + K_2[H^+])$. The mechanistic implications of the rate data are discussed in relation to the considerable number of previous studies of μ-hydroxo-dicobalt(III) complex ions. It is concluded that a common multistep mechanism prevails, although the rate-determining characteristics of the mechanism vary considerably among the complexes considered.

Introduction

The first preparative study of the title complexes was carried out by Mori, Shibata, Kyuno, and Okubo,[1] who reported the existence of three different but related species. Two of these were stated to be mononuclear α and β geometric isomers of composition $K[Co(NTA)(OH)(OH_2)]$ (where NTA ≡ $[N(CH_2COO)_3]^{3-}$ ≡ nitrilotriacetate ion) and were postulated to differ only in the location of the aquo proton (see Figure 1). The third species proposed was the binuclear di-μ-hydroxo complex $K_2[Co_2(NTA)_2(OH)_2]$, also shown in Figure 1. The aquo–hydroxo isomerism is possible in the solid state but is probably questionable since facile proton transfer would be expected to render the suggested α and β forms indistinguishable. The structural proposals have also been questioned on the basis of NMR data[2] and conventional chemical evidence.[3] It now appears that Mori et al.'s α-$K[Co(NTA)(OH)(OH_2)]$ species is in fact binuclear[2] and is probably of the form already mentioned,[3] that their β-$K[Co(NTA)(OH)(OH_2)]$ does have the formula assigned but may be impure,[3] and that what they identified as a binuclear complex is in fact the species[3] $K[Co(HNTA)_2]\cdot 2H_2O$ (HNTA represents the monoprotonated triply coordinating form of NTA). While the last referenced work was in progress, we had become engaged in a similar type of preparative investigation since we wished to use the compound $Co(NTA)(OH_2)_2$ in an extension of our carbon dioxide uptake studies.[4] We found it rather easy to prepare aqueous solutions of the diaquo compound by decarboxylation of the carbonato congener $Co(NTA)CO_3^{2-}$, as reported in our kinetic study of the latter process.[5] However, our attempts to prepare pure solid samples of complexes of the formula $K[Co(NTA)(OH)(H_2O)]\cdot nH_2O$ by the published procedures[1-3] failed, our purified product inevitably turning out to be $K_2[Co(NTA)_2(OH)_2]$. Our kinetic studies of the acid-catalyzed hydrolysis of this di-μ-hydroxo species confirm some of the findings of Thacker and Higginson[3] which have been sufficiently extended to enable further clarification of the chemistry of this interesting system, as well as of related μ-hydroxo-cobalt(III) species.

Experimental Section

Materials. Nitrilotriacetic acid was obtained from Eastman Kodak Co. and used without further purification. All other chemicals were of reagent grade. Concentrated nitric acid was diluted to double the volume and then bubbled with nitrogen for about 2 h to remove dissolved oxides of nitrogen. The concentration of the acid was determined by titration with standard base and it was stored in the dark in a Pyrex container. The preparation of $K[Co(NTA)(OH)(OH_2)]$ was attempted according to the procedure of Mori et al.[1] and also by a slightly modified method in which the order of mixing of the reagents was reversed. A blue finely divided solid was obtained in both cases and was recrystallized from water at 55–60 °C. These products have identical spectra in aqueous solution (see Figure 2). After three more recrystallizations from water, deep purple platelets were obtained. These were washed five times with absolute ethanol

Table I. Rate of Hydrolysis of $[Co_2(NTA)_2(OH)_2]^{2-}$ ($T = 25$ °C; $I = 2.0$ M ($NaNO_3$))

Run no.	$10^2[H^+]$, M	10^2k_{obsd}, s^{-1}	Run no.	$10^2[H^+]$, M	10^2k_{obsd}, s^{-1}	Run no.	$10^2[H^+]$, M	10^2k_{obsd}, s^{-1}
1	0.172	0.21	11	0.819	3.67	21[c]	16.4	2.04
2	0.431	1.09	12	1.11	6.66	22[a,c]	16.4	3.92
3[a]	0.431	3.55	13	1.64	11.6	23	22.3	383
4[a]	0.431	3.54	14	2.01	17.9	24[e]	22.3	150
5	0.517	1.55	15	3.01	33.0	25	59.5	1010
6[b]	0.802	4.40	16	4.01	47.5	26[c]	59.5	8.92
7[b,c]	0.802	0.017	17	5.57	75.3	27	93.5	1480
8[b,c]	0.802	0.016	18[e]	5.57	29.6	28	144	2247
9[d]	0.812	4.98	19	11.1	178	29[c]	144	22.6
10[d]	0.812	5.17	20[e]	11.1	67.6	30	195	2950

[a] D_2O solvent. [b] $I = 1.0$ M ($NaClO_4$). [c] Rate constant for the second reaction. [d] $I = 2.0$ M ($NaClO_4$). [e] At 15 °C.

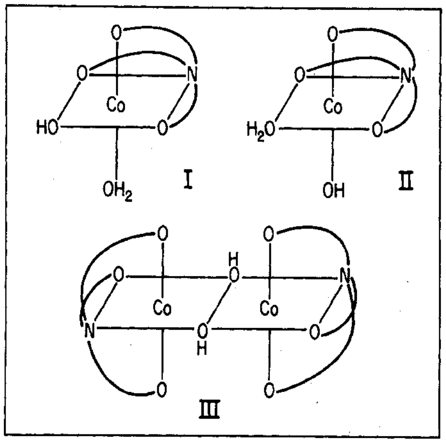


Figure 1. Proposed geometry of various aquo(nitrilotriacetato)cobaltate(III) complex ions: I and II, α and β mononuclear complexes, respectively; III, di-μ-hydroxo complex.

and three times with anhydrous ether to yield a lilac powder. Anal.[6] Calcd for $K_2[Co_2(NTA)_2(OH)_2]$: C, 23.77; H, 2.33; N, 4.62. Found: C, 23.58; H, 2.48; N, 4.64.

When titrated rapidly with dilute acid and back-titrated with base, aqueous solutions of the complex showed no evidence of basic or acidic properties, behaving much like a simple neutral salt. This behavior is analogous to that of other di-μ-hydroxo complexes,[7] particularly that of the anionic species, Durrant's salt.[8] However, when the complex is allowed to stand at room temperature in moderately acidic solution for 20–30 min, a spectral change occurs (see Figure 2) and the product solution exhibits the conventional weak dibasic acid properties identified previously[3] for $Co(NTA)_2(H_2O)_2$ (at 25 °C, $I = 1.00$ M ($NaClO_4$), $pK_1 = 6.71 \pm 0.01$ and $pK_2 \approx 10$). Finally, the osmotic pressure of a solution of our lilac powder containing 4.84 mg/ml of water is 0.50 atm.[9] This value is very close to the theoretical prediction[10] for a typical A_2B electrolyte assuming the formulation we have suggested above (fw 606.3) and accepting the normal value of about 0.75 for the mean activity coefficient at this concentration. It is not, however, as satisfactorily compatible with the other possible structural representations of the complex.

Kinetic Measurements. For the reactions at the lower acidities (slower rates) the data were obtained by means of a Cary Model 118 spectrophotometer using a manual rapid-mixing device. This same instrument was employed to record the complete spectra shown in Figure 2. At the higher acidities (faster reaction rates) an automated stopped-flow assembly as previously described[11] was utilized. Most of our runs were carried out at 350 nm where the absorbances of the significant species show considerable differences.[12] A few runs were made at the same wavelength as in the earlier study,[3] 340 nm, which yielded rate constants identical with those of replicate runs at 350 nm. Temperature control of the reaction solutions was maintained to within ±0.1 °C by means of a circulating water bath system. The ionic strength was constant at 2.0 M utilizing $NaNO_3$.

In a typical experiment, a few milligrams of complex is dissolved in a small amount of water (about 0.5 ml). A portion of this solution (usually 100 μl) is added to a large excess (3 ml) of the appropriate $HNO_3/NaNO_3$ solution and the decomposition of the complex is monitored spectrally as explained above. For the experiments in D_2O, the complex is dissolved in 99.7% heavy water[13] and added to $DNO_3/NaNO_3$ solution. The latter is prepared by adding a 250-fold excess of D_2O to a small volume of concentrated HNO_3 in a volumetric flask in which has already been placed the necessary amount of solid $NaNO_3$. The desired concentration of H^+ or D^+ in any given experiment is achieved by dilution of stock solutions. The pseudo-first-order rate constants for runs made on the Cary Model 118 instrument are deduced from conventional semilogarithmic plots of the derived absorbance vs. time data. For the stopped-flow runs, the rate constants and their standard deviations are provided directly by means of the programmed computation.

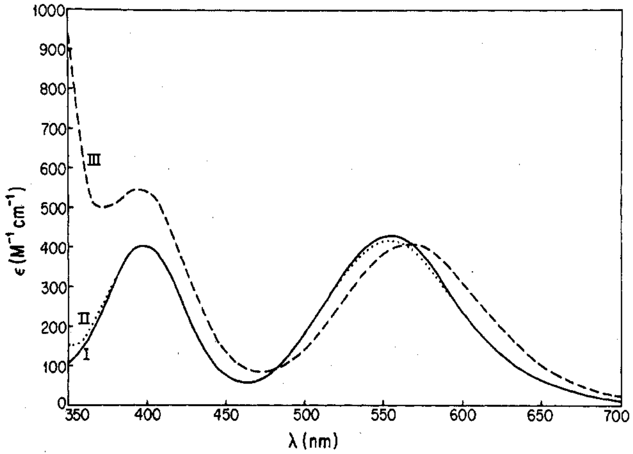


Figure 2. Spectra of various aquo(nitrilotriacetato)cobaltate(III) complex ions: I, diaquo mononuclear final product; II, intermediate μ-hydroxo complex; III, di-μ-hydroxo reactant.

Results and Discussion

Our preliminary rate data showed that the pure di-μ-hydroxo complex undergoes a rapid initial reaction followed by a much slower process (about 0.01 as fast under comparable conditions). Similar observations were made in the earlier kinetic study[3] but comprehensive data were obtained only for the slow reaction. We therefore concentrated our attention on the rapid process, obtaining data within the acid concentration range of 0.00172–1.955 M, as presented in Table I. A few runs were carried out on the slow reaction but these were found to be completely consistent with the Thacker and Higginson data[3,14] so no further study was made of this process except one run in heavy water solvent to be discussed later. Returning to the fast reaction data, inspection shows that simple second-order kinetics does not apply, contrary to the previous suggestion based on very limited data.[3] We have found the best fit to be attained by use of an equation of the form[15]

$$k_{obsd} = kK[H^+]^2/(1 + K[H^+]) \tag{1}$$

This can be cast into the inverted linear form

$$[H^+]/k_{obsd} = 1/k + 1/kK[H^+] \tag{2}$$

A linear regression analysis according to eq 2 of all of the runs in Table I except those footnoted[15] yields the values k = 17.5

Table II. Rate Constants for Acid-Catalyzed Cleavage of the First μ-OH Bond of Several μ-Hydroxy-dicobalt(III) Complex Ions at 25 °C

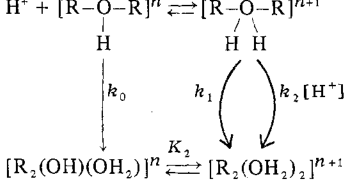
No.	Reactant	Form of rate law	$k_1K_1/M^{-1}\ s^{-1}$	Ref
1	$[(NH_3)_3Co(OH)_3Co(NH_3)_3]^{3+}$	$k_1K_1[H^+]/(1 + K_1[H^+])$	0.28	20
2	$[(NH_3)_4Co(OH)_2Co(NH_3)_4]^{4+}$	$k_1K_1[H^+]/(1 + K_1[H^+])$	1.2×10^{-3}	17
3	$[(NH_3)_3(H_2O)Co(OH)_2Co(NH_3)_3(H_2O)]^{4+}$	$k_1K_1[H^+]$	5×10^{-5} [a]	21
4	$[(en)_2Co(OH)_2Co(en)_2]^{4+}$	$(k_0 + k_1K_1[H^+])/(1 + K_1[H^+])$	1.8×10^{-2}	18
			1.4×10^{-2}	19
5	$[(NH_3)_3Co(NH_2)(OH)_2Co(NH_3)_3]^{3+}$	$k_1K_1[H^+]$	1.01	20
6	$[(NH_3)_4Co(NH_2)(OH)Co(NH_3)_4]^{4+}$	$k_0 + k_1K_1[H^+]$	8.2×10^{-5}	23
7	$[(NH_3)_5Co(OH)Co(NH_3)_5]^{5+}$	$k_0 + k_1K_1[H^+]$	5.4×10^{-3}	24
			6.2×10^{-3}	25
8	$[(en)_2(H_2O)Co(OH)Co(en)_2(H_2O)]^{5+}$	$(k_1K_1[H^+] + k_2K_1[H^+]^2)/(1 + K_1[H^+])$	5.9×10^{-2} (28)[b]	18
9	$[(C_2O_4)_2Co(OH)_2Co(C_2O_4)_2]^{4-}$	$k_1K_1[H^+]/(1 + K_1[H^+])$	4.1	22
10	$[(NTA)Co(OH)_2Co(NTA)]^{2-}$	$k_2K_1[H^+]^2/(1 + K_1[H^+])$	(750)[b,c]	This work
11	$[(NTA)(H_2O)Co(OH)Co(NTA)(H_2O)]^-$	$k_2K_1[H^+]^2/(1 + K_1[H^+])$	(12)[b,d]	3[e]

[a] Estimated at 25 °C from data at 20 °C using the temperature coefficient quoted for compound 6.[23] [b] k_2K_1 ($M^{-2}\ s^{-1}$). [c] $k_2 = 17.5\ M^{-1}\ s^{-1}$, $K_1 = 42.8\ M^{-1}$. [d] $k_2 = 0.131\ M^{-1}\ s^{-1}$, $K_1 = 91\ M^{-1}$. [e] See discussion in text.

± 1.1 $M^{-1}\ s^{-1}$ and $K = 42.8 \pm 2.7\ M^{-1}$. The three runs previously reported for this reaction[3] yielded k_{obsd} values of the same order of magnitude as ours though not in close agreement, but this is as expected since the earlier results were stated to be only approximate and were obtained in a different ionic medium.[16]

It was suggested by Thacker and Higginson[3] that the "rapid" and "slow" reactions described hydrolyses of two different isomeric forms of the di-μ-hydroxo complex ion, depending on whether it was prepared as the sodium salt directly or by double decomposition from the potassium salt. In our work we used only the potassium salt, which all of our tests show to be quite pure. Yet we observe both "rapid" and "slow" reactions with this material, and both processes appear to have kinetic properties essentially identical with those of the reactions observed in the previous study. We therefore conclude that the acid-catalyzed hydrolysis of the anion $[Co_2(NTA)_2(OH)_2]^{2-}$ takes place in two consecutive steps, one much more rapid than the other but both fitted by rate equations of the form of eq 1. This type of stepwise bridge fission of di-μ-hydroxo complex ions has been observed previously for the cationic species $[N_4Co(OH)_2CoN_4]^{4+}$ where N = NH_3[17] or $^1/_2$en.[18,19] In one of these studies, the existence of a short-lived intermediate was kinetically identified.[18] In the present study, the rate of formation of the intermediate is very much more rapid than that of its subsequent decomposition so that complete separation of the two processes becomes possible. A similar situation exists for the triply bridged species[20] $[(NH_3)_3Co(OH)_3Co(NH_3)_3]^{3+}$ and $[(NH_3)_3Co(NH_2,OH,OH)Co(NH_3)_3]^{3+}$ where the products of the first hydroxo bridge cleavages are relatively stable and readily identifiable. However, the di-μ-hydroxo product obtained from the cleavage of the tri-μ-hydroxo parent complex undergoes hydrolysis to the final product, $[Co(NH_3)_3(H_2O)_3]^{3+}$, with no observable evidence for a singly-bridged intermediate, presumably because of the rapid rate of hydrolysis of the latter.[21] The hydrolysis of the anionic di-μ-hydroxo complex $[Co_2(C_2O_4)_2(OH)_2]^{4-}$, which might be expected to show some similarities to the hydrolysis of the $[Co(NTA)_2(OH)_2]^{2-}$ species, is complicated by the internal redox reaction between oxalate and cobalt(III).[22]

The rate laws of the hydrolysis of μ-hydroxo-cobalt(III) complexes so far carried out sometimes involve an acid-independent term and invariably show an acid dependence for the reaction which varies from simple first-order to a combination of first- and second-order terms (see Table II). Several mechanisms have been proposed to account for such results, as summarized in the paper by El-Awady and Hugus[18] and further discussed by Sykes and his co-workers.[26] It turns out that one can readily develop alternatives for the acid catalysis which combine protonation of one of the hydroxo bridges with subsequent rate-determining bridge cleavage, and this latter process may or may not be acid catalyzed. A particularly simple and appealing mechanism is one involving the reactions of (3), in which R symbolizes the various types



(3)

of $Co^{III}L_5$ moieties and in some of which one or two of the L groups may also form part of a μ-bridge representative of a multiply bridged species.

Since, as is usual, the proton equilibration described by the association constant K_1 is very rapid, the rate expression corresponding to the given mechanism is

$$k_{obsd} = \frac{k_0 + k_1K_1[H^+] + k_2K_1[H^+]^2}{1 + K_1[H^+]} \tag{4}$$

It is seen that, with appropriate assumptions concerning the magnitude of the various constants, one can readily derive an expression corresponding to any one of those observed experimentally and summarized in Table II. Thus, in all cases except for reactants **4**, **6**, and **7**, the water-promoted reaction symbolized by k_0 is too slow to contribute. Further, if protonation is not very effective ($K_1[H^+] << 1$), and $k_1 >> k_2[H^+]$, simple first-order acid catalysis results, as is observed for reactants **3**, **5**, **6**, and **7**. All of these have multiple positive charges and three of them are multiply bridged. However, there seems to be no clear-cut mechanistic pattern, as all of the other reactants exhibit effective protonation of the μ-hydroxo bridge, whether positively or negatively charged and whether multiply bridged or not. There are, in fact, some unusual contrasts, such as between the two singly bridged species **7** and **8**, the latter being the only reactant for which both the k_1 and $k_2[H^+]$ paths are effective, as well as proton association. In the present study and that of Thacker and Higginson[3] (reactants **10** and **11** it appears that only the $k_2[H^+]$ path is involved, while for all of the others not yet mentioned specifically, the protonated intermediates decompose entirely by the k_1 path. This may be a consequence of the fact that both **10** and **11** are anionic species, but so is the highly charged reactant **9**, yet it shows only the k_1 path. In this it is very similar to reactants **2** and **4**, though these latter species have much smaller k_1K_1 values than does **9**, possibly attributable to greatly reduced K_1 values for the positively charged reactants **2** and **4**. The dominance of the $k_2[H^+]$ path for reactants **10** and **11** may also derive from their relatively high basicities, not only because of their negative charges but also because of the intrinsic basicities of the ligand acetato groups resulting from their inherent tendency (unlike the oxalato groups of **9**) to dechelate readily.[27,28]

It is also significant that a recent study[29] of the first μ-OH bridge cleavage of the heteronuclear di-μ complex ion $[(en)_2Cr(OH)_2Co(en)_2]^{4+}$ fits into the general scheme with the proviso that only the water-catalyzed process contributes. For this complex, k_0 has a value of $\sim 10^{-2}$ s^{-1} at 25 °C, very much more rapid than the corresponding value of $\sim 10^{-5}$ for reactants **4**[18,19] and **6**,[23] though closely comparable to that for the singly bridged species **7**, for which k_0 is found to have a value[30] of about 6×10^{-3} s^{-1}. A further study[31] involving the homonuclear di-μ chromium(III) complex ion $[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$ exhibits properties similar to its heteronuclear analogue, with a value for k_0 of 7×10^{-3} s^{-1} at 25 °C.

Finally, it should be noted that the limited deuterium solvent isotope effect data obtained in our study are completely consistent with the mechanistic suppositions. As shown in Table I, both the "slow" and "fast" reactions are more rapid in heavy water, the factor being about 2 for the former and 3.5 for the latter. While the proton-catalyzed step described by $k_2[H^+]$ might presumably be somewhat decelerated in D_2O solvent if direct proton transfer is the process involved, this effect is apparently overwhelmed by the positive effect accompanying the proton preequilibration. The predicted factor[32] for a protonated intermediate which is a moderately strong acid (see association constant values in Table II, footnoted *c* and *d*) is close to 3, in reasonable agreement with the observed experimental value of 3.5 for the "fast" reaction. For the second μ-OH bond fission (the "slow" reaction), the factor is somewhat smaller, possibly because there is an appreciable isotope effect in the opposite direction, associated with the direct proton transfer in the much slower rate-determining step governed by k_2.

Registry No. I, 61129-04-2; II, 61129-05-3; III, 56930-89-3.

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(6) (a) Instranal Laboratory, Inc., Rensselaer, N.Y. (b) When determined on the basis of $K[Co(NTA)OH(OH_2)]$, the calculated values are 22.43% C, 2.82% H, and 4.36% N. These are seen to be substantially different from the "found" values.

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(12) The extinction coefficients of the di-μ-hydroxo the intermediate (see discussion which follows) and the mononuclear diaquo species were respectively 942, 155, and 111 M^{-1} cm^{-1} at 350 nm.

(13) Diaprep, Inc., Milwaukee, Wis.

(14) Using the values of the derived constants and eq 2 from ref 3, we calculate values for k^s_{obsd} of 0.04, 2.0, 7.7, and 25.5 M^{-1} s^{-1} at acidities of 0.008, 0.164, 0.595, and 1.955 M, to be compared with our experimental values of 0.02, 2.0, 8.9, and 22.6 (run no. 7 or 8, 21, 26, and 29).

(15) (a) This is mathematically identical with eq 2 of ref 3 mentioned in footnote 14 but is in a form more suited to our later analysis of the mechanism. (b) Changing the supporting electrolyte from $NaNO_3$ to $NaClO_4$ does slightly accelerate the reaction (cf. run 9 or 10 with 11) but reduction of the ionic strength from 2.0 to 1.0 has little effect (cf. run 6 with 9 or 10). It is possible that use of $LiClO_4$ rather than $NaNO_3$ might have been preferable in an acid-dependency study such as this. However, our double-reciprocal plotting procedure favors the low-$[H^+]$ data, where substitution of Na^+ for H^+ is minimal.

(16) Thacker and Higginson's values[3] for k^r_{obsd} (25 °C, I = 1.0 M ($NaClO_4$)) are 0.35, 0.135, and 0.047 s^{-1} at acidities of 0.02, 0.008, and 0.003 M, respectively. Our calculated values according to eq 1 are 0.16, 0.035, and 0.006 s^{-1} at the same acidities but at I = 2.0 M ($NaNO_3$).

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(27) Evidence for this tendency is provided by the existence of the stable complex ion $Co(HNTA)_2^-$.[3]

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Thiolato and Selenido Complexes of Rhodium(III)

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Three routes for the synthesis of dithiolato- and diselenido[difluoro-3,3′-(trimethylenedinitrilo)bis(2-pentanone oximato)borate]rhodium(III) complexes, $(RE)_2[C_2(DO)(DOBF_2)]Rh^{III}$ (E = S, Se), have been demonstrated. These are (1) $[C_2(DO)(DOBF_2)]Rh^I$ + REER, (2) $[C_2(DO)(DOBF_2)]Rh^I$ + 2REH, and (3) $Cl_2[C_2(DO)(DOBF_2)]Rh^{III}$ + 2RE$^-$. These reactions have been expanded to include germanium-bearing sulfur and selenium substituents. The synthesis and physical properties of two hydrosulfidorhodium complexes, $(HS)_2[C_2(DO)(DOBF_2)]Rh^{III}$ and $(SH)(H)[C_2(DO)(DOBF_2)]Rh^{III}$, are also discussed.

Introduction

We are presently engaged in the synthesis and characterization of compounds comprised of heavy elements covalently bound in a linear array. Our synthetic approach to this problem has centered about the oxidative addition[1,2] of disulfides and diselenides to a square-planar, macrocyclic rhodium(I) complex. The desired one-dimensional character of the heavy-atom backbone is ensured by the rigorous geometric demands of the rigidly planar, tetradentate ligand.

The development of one-dimensional materials has been the subject of considerable interest during the past decade. Activity has recently intensified due to the demonstration of highly anisotropic electrical conduction in some of these materials.[3] We expect compounds of the type described herein