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Some Amine N-Oxide Complexes of Trivalent Cobalt

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Three new cobalt(III) coordination complexes with bidentate amine N-oxide ligands have been synthesized and characterized via elemental analyses, equivalent weight determination, molar conductance and magnetic susceptibility measurements, and infrared and electronic absorption spectroscopy. Two are ionic complexes with general formula $[CoL_3](ClO_4)_3$ *where L = 2,2'-bipyridine-N,N'-dioxide and 1,10-phenanthroline N-oxide. The third is a neutral* CoL'_3 *complex where L' = picolinate N-oxide. The compounds are six-coordinate, diamagnetic, and have electronic absorption spectra typical of the strong field* d^6 *configuration of trivalent cobalt. The perchlorate groups are not coordinated to cobalt(III) in the solid state or in solution.*

Introduction

A wide variety of amine N-oxides have been used as ligands to form coordination compounds. Three review articles have summarized the extensive research in this area [1–3], much of which centers around the use of substituted pyridine and quinoline N-oxides. Nearly 1100 amine N-oxide complexes have been reported, involving about 70 different metal ions. There is, however, a noticeable lack of complexes of trivalent cobalt. To our knowledge, only three such compounds have been reported. Two of these are neutral complexes involving the univalent anions derived from 2-carboxypyridine N-oxide or picolinic acid N-oxide [4] ($2\text{-}O_2CC_5H_4NO^-$, abbreviated as $PicO^-$) and 2-mercaptopyridine N-oxide or 1-hydroxy-2-pyridinethione [5] ($2\text{-}SC_5H_4NO^-$, abbreviated as $SPyO^-$). Both function as bidentate ligands, forming $Co(PicO)_3 \cdot H_2O$ and $Co(SPyO)_3 \cdot 2H_2O$. The third compound, $[Co(DMEO)_3](ClO_4)_3$, is an ionic cobalt(III) complex of the bidentate ligand N,N-dimethylethylenediamine N-oxide [6] ($(CH_3)_2N(O)CH_2CH_2NH_2$, abbreviated as DMEO).

There are several reasons for the lack of cobalt(III)-N-oxide complexes. First, most trivalent cobalt compounds are synthesized from aqueous solution by the *in situ* oxidation of cobalt(II). Any ligand which complexes with cobalt during the oxidation reaction must compete with water and counter ions for a position in the coordination sphere. The ligands must also be effective donors so that the trivalent oxidation state of cobalt is stabilized. Most N-oxides are weak donors and cannot effectively compete with water for coordination sites. In fact, the majority of N-oxide complexes that have been formed with the 70 or so metal ions have involved the *in situ* dehydration of a metal hydrate salt using solvents such as dimethoxypropane or triethylorthoformate in alcohol. Subsequent addition of ligand results in the precipitation of the complex. Second, there are very few simple cobalt(III) salts which are appropriate starting materials and most other known cobalt(III) complexes contain ligands which could not be easily replaced by the weaker N-oxides via substitution reactions. Finally, there is a lack of effective nonaqueous oxidation techniques for the conversion of cobalt(II) to cobalt(III).

In this study, $Co(OH)_3$ is used as a reactant and bidentate ligands are employed in order to increase the donor ability of the weak N-oxide bases. Two of the complexes reported here are ionic with 2,2'-bipyridine-N,N'-dioxide and 1,10-phenanthroline N-oxide (abbreviated as $BipyO_2$ and PhenO, respectively) as the ligands. The third is a neutral complex of picolinic acid N-oxide with different structural features than the one previously reported.

Results and Discussion

The three previously reported cobalt(III) N-oxide compounds were all synthesized using quite different approaches. Lever, *et al.* [4], synthesized $Co(PicO)_3 \cdot H_2O$ in 9% yield by chlorine oxidation of cobalt(II) acetate in the presence of HPicO with glacial acetic acid as solvent. Robinson [5, 7] prepared $Co(SPyO)_3 \cdot 2H_2O$ from $Na_3[Co(NO_2)_6]$ and NaSPyO in 50% methanol. Summers and Quagliano [6] synthesized $[Co(DMEO)_3](ClO_4)_3$ in aqueous solu-

TABLE I. Elemental Analyses and Physical Data.

Compound	%C		%H		%N		Equivalent wt. (g/equiv.)		Color	Decomposition point
	calc.	expr.	calc.	expr.	calc.	expr.	calc.	expr.		
$[Co(C_{10}H_8N_2O_2)_3](ClO_4)_3$	39.09	39.82	2.62	2.64	9.19	9.39	307.3	312.0	pale green	255–257 °C
$[Co(C_{12}H_8N_2O)_3](ClO_4)_3$	45.71	45.36	2.56	2.51	8.89	8.77	315.3	312.6	tan	220–223 °C
$Co(C_6H_4NO_3)_3$	45.68	45.15	2.56	2.38	8.88	8.72	–	–	dark green	230–231 °C

TABLE II. Conductance, Magnetic, and Spectral Data.

	$[Co(BipyO_2)_3](ClO_4)_3$	$[Co(PhenO)_3](ClO_4)_3$	$Co(PicO)_3$
Molar conductivity[a]			
Conc'n. in methanol	1.12×10^{-3} *M*	5.81×10^{-4} *M*	–
Λ_M cm^2 ohm^{-1} mol^{-1}	345	296	–
Magnetic susceptibility, μ_{eff} (25 °C), B.M.	0	0	0
Infrared spectral data (all values in cm^{-1})			
ν_{ClO} perchlorate	1083	1082	–
ν_{NO} complex (ligand)	1256 (1250) 1217 1196 sh	1209 (1212)	1270 (1279) 1245 (1250)
δ_{NO} complex (ligand)	852 (843)	842 (832)	870 (842)
Electronic spectral data			
Conc'n. (Solvent)	2.04×10^{-3} *M* (water)	2.00×10^{-3} *M* (water)	1.75×10^{-3} *M* (water)
λ_{max}, nm (ϵ, liter cm^{-1} mol^{-1})			
$^1A_{1g} \rightarrow {}^1T_{2g}$	466 (85)	–[b]	414 (239)
$^1A_{1g} \rightarrow {}^1T_{1g}$	671 (64)	–[b]	610 (159) 5.92×10^{-5} (methanol) 410 (360) 580 sh 638 (140)

[a] For this concentration range, 3:1 electrolytes are expected to have Λ_M values of about 330 cm^2 ohm^{-1} mol^{-1}. Ref. 8.

[b] Masked by charge transfer peak at 370 nm ($\epsilon = 3.1 \times 10^4$).

tion from $[Co(NH_3)_5Cl]Cl_2$ and DMEO in the presence of $NaClO_4$. The compounds reported here were synthesized using 'cobaltic hydroxide' (represented as $Co(OH)_3$ although technically a hydrated or hydroxy oxide). The reactions were as follows:

$$Co(OH)_3 + 3HPicO \rightarrow Co(PicO)_3 + 3H_2O$$

$$Co(OH)_3 + 3\,L + 3\,HClO_4 \rightarrow$$

$$[CoL_3](ClO_4)_3 + 3H_2O$$

$$L = BipyO_2, PhenO$$

Yields were low due to difficulties in purification. Analytical data which support the proposed formulas for the new compounds are given in Table I. Equivalent weight and conductance measurements (Tables I and II) confirm the existence of $[Co(BipyO_2)_3]^{3+}$ and $[Co(PhenO)_3]^{3+}$ cations in solution. The presence of non-coordinated perchlorate ions in the solid state is further confirmed by the presence of the broad single infrared absorption band (Table II) about 1080 cm^{-1} [9]. Shifts of infra-red bands in the N–O stretching and N–O bending regions (1280–1200 cm^{-1} and 870–840 cm^{-1}, respectively) support coordination of the N-oxide functional group.

As was the case with the three previously reported cobalt(III) compounds, the new compounds are all diamagnetic (Table II), indicating a strong field or low spin d^6 electron configuration for cobalt(III). The two spin-allowed d–d transitions expected for the strong field d^6 configuration ($^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$) are observed in the electronic absorption spectrum for all but the PhenO complex. In this case, the d–d transitions are apparently masked by a very strong charge transfer band at 370 nm with $\epsilon = 3.1 \times 10^4$ which extends well into the visible and near infrared regions. A similar phenomenon was observed in cobalt(II) and nickel(II) complexes of acridine N-oxide [10]. The ligand field parameter Dq was calculated for the $BipyO_2$ and $PicO^-$ complexes from the two spectral bands and give the following spectrochemical series for cobalt(III) N-oxide species: DMEO (1840 cm^{-1}) [6] > $PicO^-$ (1720 cm^{-1}) > $SPyO^-$ (1620 cm^{-1}) [5] > $BipyO_2$ (1560 cm^{-1}). As would be expected, DMEO, with both nitrogen and oxygen donor atoms, is the strongest ligand while $BipyO_2$, which forms a seven-membered chelate ring, is weakest.

Whereas the water molecules in $Co(SPyO)_3 \cdot 2H_2O$ were treated as hydrates [5], the $Co(PicO)_3 \cdot H_2O$ complex prepared by Lever, *et al.* [4] was reported as having an unusual structural feature. Only two $PicO^-$ ligands function as bidendate donors while the third $PicO^-$ was thought to be coordinated only through the carboxyl group with the water molecule occupying the sixth coordination position. Infrared data in the N–O stretching region were presented as evidence in support of this structure. Bands were observed at 1245, 1267, and 1277 cm^{-1} (shoulder), the latter being assigned to the non-coordinated N-oxide group. Several aspects of the data obtained in this study suggest the $Co(PicO)_3$ compound reported here is a true *tris* complex. First, the elemental analyses (Table I) more closely match the theoretical values for the anhydrous species (for comparison, calculated values for $Co(PicO)_3 \cdot H_2O$ are %C 44.00, %H 2.87, %N 8.56.) Second, the infrared spectrum of $Co(PicO)_3$ does not show a band in the 3500–3200 cm^{-1} region expected for coordinated water [9] nor the shoulder at 1277 cm^{-1} attributable to non-coordinated N-oxide. Third, Lever, *et al.* [4] report that $Co(PicO)_3 \cdot H_2O$ is soluble at least to the extent of 5×10^{-4} *M* in methanol while the compound reported here is about ten times less soluble (5.9×10^{-5} *M*) in absolute methanol. Possibly the solubility of $Co(PicO)_3 \cdot H_2O$ is enhanced by hydrogen bonding of the non-coordinated N-oxide group with the polar solvent. Finally, electronic spectral data for methanol solutions of $Co(PicO)_3 \cdot H_2O$ and $Co(PicO)_3$ are somewhat different in terms of λ_{max} and ϵ values, especially for the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition (for comparison, λ_{max} (ϵ) for $Co(PicO)_3 \cdot H_2O$ are 415 nm(302), 615 nm(214)) [4].

The data presented here support the synthesis of three new cobalt(III) amine N-oxide complexes. Although compounds of this metal ion seem to be somewhat rare in light of the abundance of known N-oxide coordination compounds, it is clear that trivalent cobalt can be stabilized even in aqueous solution with relatively strong bidentate N-oxide ligands.

Experimental

Syntheses

Starting Materials

Analytical reagent grade chemicals were used without further purification. *Picolinic acid N-oxide* was obtained commercially. *2,2'-Bipyridine-N,N'-dioxide* was prepared by the method of Simpson, *et al.* [11] *1,10-Phenanthroline N-oxide* was prepared by refluxing 5.0 g 1,10-phenanthroline monohydrate, 29 ml glacial acetic acid, and 6 ml of 30% hydrogen peroxide at 60–70 °C for 3 hours. After the first 1½ hours of heating, an additional 3½ ml of H_2O_2 were added. The solution was allowed to cool then poured slowly into a well stirred mixture of 250 ml diethyl ether and 250 ml acetone. The bright yellow precipitate which formed immediately was filtered and washed numerous times with 75 ml portions of diethyl ether. The crude product (m.p. 176–179 °C) was recrystallized from boiling 95% ethanol, yielding 1.2 g (24%) of pale yellow crystals with melting point 188–190 °C. Physical data are consistent with that reported by Corey, *et al.* [12]. *Cobaltic hydroxide* was prepared by treating an aqueous cobalt sulfate solution (3.0 g $CoSO_4 \cdot 7H_2O$ in 75 ml water) with 10 ml 6 *N* sodium hydroxide, followed by 2 ml of 30% hydrogen peroxide which was added dropwise with vigorous stirring. The mixture was allowed to stand for several hours before decantation and filtration. The black residue was washed well with water and never allowed to dry out completely.

Complexes

$[Co(BipyO_2)_3](ClO_4)_3$ was prepared as follows: An excess of freshly prepared and somewhat damp cobaltic hydroxide was added to 1.0 g of $BipyO_2$ in 30 ml of water. With constant stirring, 3 ml of 35% perchloric acid was added and the solution was heated gently for 30 minutes. The solution was filtered hot to remove any unreacted cobaltic hydroxide and allowed to cool, at which time the product precipitated. The product was filtered and washed with 95% ethanol and then diethyl ether. Yield was 0.84 g (51% of theoretical). *$[Co(PhenO)_3](ClO_4)_3$* was prepared as described above with substitution of 1.0 g of PhenO for $BipyO_2$, but required recrystallization. The crude product was dissolved in 20–25 ml of hot water. The volume was reduced to 15 ml and then the solution was placed in an ice bath. At first the solution became cloudy with an orange tint. When small tan-colored crystals began to form the solution was immediately filtered to remove the orange particles which were discarded. The filtrate was further reduced in volume to 10 ml by heating and again placed in an ice bath. The tan-colored product which precipitated was filtered, washed with 95% ethanol, and then diethyl ether. Yield was 0.12 g (7% of theoretical). *$Co(PicO)_3$* was prepared by refluxing 5.0 g of HPicO in 75 ml of water for 3 hours with an excess of freshly prepared and somewhat damp cobaltic hydroxide. The resulting green solution was allowed to cool and then filtered to remove any unreacted cobaltic hydroxide and/or HPicO. The filtrate was evaporated to dryness using a rotary evaporator, after which 100 ml acetone was

added to the residue. The residue was broken up and stirred vigorously with the acetone to dissolve any unreacted HPicO. After filtration, the product was treated similarly two more times with acetone. Finally the light green product was recrystallized from hot water. It was necessary to filter the hot solution through a warm glass filter to prevent premature precipitation of the product but to remove any of the orange cobalt(II) complex which had formed. The filtrate was cooled in an ice bath to precipitate the final product. Any unreacted ligand which still remained tended to float on the surface of the solution and was removed by decantation. The product was filtered and air dried, yielding 0.37 g (7% of theoretical).

Physical Measurements

Infrared spectra were obtained as Nujol mulls between sodium chloride disks on a Beckman IR-8 spectrometer. All spectra were calibrated with known bands of polystyrene. Electronic absorption spectra were obtained as aqueous or methanol solutions using a Beckman DB-GT spectrometer with 1 cm matched cells. Dq values were calculated using the equations described by Lever [13] with the assumption C = 4B. Magnetic susceptibility measurements were obtained at 25 °C and 7000 gauss using an instrument constructed from an Ainsworth balance and an Ealing electromagnet. The compound $HgCo(SCN)_4$ was used as calibrant. Molar conductance measurements were made in methanol solution using a General Radio Company 650-A Impedance Bridge. Equivalent weight determinations were done by cation exchange chromatography using Dowex 50W-X8 20 - 50 mesh hydrogen form resin and standard sodium hydroxide solution. Carbon, hydrogen, and nitrogen analyses were performed by M-H-W Laboratories, Phoenix, Arizona.

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