copper coordination plane and the imidazole plane. This dependence results from interactions between the bridging imidazolate and the terminal ligand (AE in complex **2**). From Table V, it appears that the smooth variation of |2*J*| essentially reflects the small differences between corresponding ϕ values. The dependence of |2*J*| on the angle α is more difficult to detect since a rather large variation of this parameter does not significantly affect the singlet–triplet separation. More examples of closely related complexes are needed to clarify this point.

In conclusion, this work illustrates the use of the [(AE)CuImH]$^+$ unit to obtain homo- and heterodinuclear complexes. Works are in progress to extend the scope of these possibilities to other pairs of metal centers with identical [(AE)MImM′(AE)]$^{n+}$ or different [(AE)MImM′L]$^{n+}$ environments (L being a polydentate ligand different from AEH). The latter type of complexes may be valuable to probe the dependence of the exchange coupling on ligand–ligand interactions.[32]

Acknowledgment. We thank Dr. A. Mari for his contribution to the magnetic measurements.

Registry No. [(AE)CuImNi(AE)]ClO$_4$, 102575-61-1; [(AE)CuImCu(AE)]ClO$_4$, 102575-63-3; [(AE)CuImH]ClO$_4$, 102575-65-5; [(AE)NiPy]ClO$_4$, 97398-11-3; [(AE)CuBr]$_2$, 102629-50-5.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen parameters, and least-squares-planes equations (4 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973,
and Department of Chemistry and Biochemistry, James Cook University of North Queensland, Townsville, Queensland 4811, Australia

Coordination Mode of Tris(2-pyridyl)carbinol to Cobalt(III): Crystal Structure of $Li[Co\{(2\text{-}py)_3COH\}_2](S_2O_6)_2\cdot 10H_2O$

David J. Szalda*[1] and F. Richard Keene*[2]

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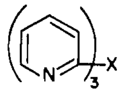
The bis[tris(2-pyridyl)carbinol]cobalt(III) complex was isolated as either of two linkage isomers, dependent on conditions of synthesis. A symmetrical form has all donor atoms being py N (i.e. ((py)$_3$COH-*N,N′,N″*)$_2$), while the unsymmetrical form has one deprotonated ligand which is coordinated through two py N atoms and the alkoxy O (i.e. ((py)$_3$COH-*N,N′,N″*)-((py)$_3$CO$^-$-*N,N′,O*)). The X-ray crystal structure of the symmetrical form as $Li[Co\{(2\text{-}py)_3COH\}_2](S_2O_6)_2\cdot 10H_2O$ is reported: the complex of formula $C_{32}H_{46}N_6O_{24}S_4LiCo$ is monoclinic, space group *C*2/*c*, β = 109.88 (2)°, with cell dimensions *a* = 19.177 (6) Å, *b* = 10.533 (2) Å, *c* = 23.390 (7) Å, and *Z* = 4. The cation has the six pyridine N atoms coordinated to the metal center in almost perfect octahedral geometry (Co(III)–N bond distances range between 1.931 (3) and 1.944 (3) Å). Electrochemical studies of this symmetric linkage isomer reveal similarities to the [Co(bpy)$_3$]$^{n+}$ species, with both the Co(III)/Co(II) and Co(II)/Co(I) redox couples apparent on the cyclic voltammetric time scale.

Introduction

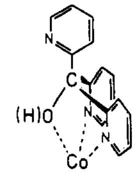
There have been a number of recent reports of the coordination of tripodal ligands in which the three ligating atoms belong to π-acceptor groups, such as N-heterocyclic ring systems. Boggess et al.[3-5] have synthesized first-row transition-metal complexes of the ligands



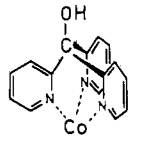
X = CH, COH, P, P=O, As, N

and have studied the spectral and electrochemical properties of these species. Canty et al.[6-8] have used a wide range of ligands of the types XY$_3$ (where the bridgehead atom X = CH or COH, and Y = 2-pyridyl, 1-pyrazolyl or *N*-methylimidazol-2-yl) to impose unusual coordination geometries on metal centers such as Hg(II) and Au(III).

We have been engaged on a study of the group VIII (groups 8–10[29]) complexes of these ligands, particularly with Ru[9] and Rh.[10] Within this group, reports of the coordination mode of tris(2-pyridyl)carbinol in the bis(ligand)cobalt(III) complex are conflicting. Boggess and Boberg[4] and White and Faller[11] have identified the complex to contain one deprotonated and one nondeprotonated ligand: the deprotonated ligand was considered to have an N,N′,O-coordination mode (i.e. two pyridine nitrogen atoms and the deprotonated hydroxyl oxygen atom being the ligating atoms, **1**). The reports differ however as to the nature of the coordination mode of the nondeprotonated ligand, viz. N,N′,O[4] or N,N′,N″ (**2**).[11] We also synthesized this bis(tridentate) complex as part of our studies and observed a form of the complex whose ^{13}C NMR spectrum was inconsistent with either of the two previous assignments. We report here an X-ray crystal structure of the complex $Li[Co\{(2\text{-}py)_3COH\}_2](S_2O_6)_2\cdot 10H_2O$ in which both ligands show N,N′,N″-coordination.



(py)$_3$CO(H)-*N,N′,O*
1



(py)$_3$COH-*N,N′,N″*
2

Experimental Section

Physical Measurements. Electronic spectra were recorded with a Cary 219 spectrophotometer, and NMR spectra were obtained in CD$_3$CN or D$_2$O solutions by using a Bruker AM-300 NMR spectrometer, with *p*-dioxane (δ = 66.5) as an internal standard.

All electrochemical measurements were made in acetonitrile/0.1 M tetraethylammonium perchlorate (TEAP) solution vs. an Ag/AgCl (3 M NaCl) reference electrode by using a Bioanalytical Systems Inc. (BAS) CV-27 voltammograph.

Elemental microanalyses were carried out by the Canadian Microanalytical Service, Vancouver, Canada.

Syntheses. Tris(2-pyridyl)carbinol, (2-py)$_3$COH, was prepared from bis(2-pyridyl)ketone and 2-lithiopyridine as detailed previously[11,12] in 48%

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(1) Brookhaven National Laboratory. Permanent address: Baruch College, New York, NY.
(2) James Cook University of North Queensland. On an approved Special Studies Program at Brookhaven National Laboratory.
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(11) White, D. L.; Faller, J. W. *Inorg. Chem.* **1982**, *21*, 3119–3122.

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Table I. Experimental Details of the X-ray Diffraction Study of $Li[Co\{(C_5H_4N)_3COH\}_2](S_2O_6)_2\cdot 10H_2O$

	(A) Crystal Parameters[a] at 21 °C		
a, Å	19.177 (6)	*Z*	4
b, Å	10.533 (2)	M_r	1092.85
c, Å	23.390 (7)	space group	*C*2/*c*
β, deg	109.88 (2)	*ρ*(exptl),[b] g cm^{-3}	1.63 (1)
V, Å^3	4443 (3)	*ρ*(calcd), g cm^{-3}	1.634
	(B) Measurement of Intensity Data		
instrument	Enraf-Nonius Cad-4 diffractometer		
radiation	Mo K*α* (0.7093 Å) graphite-monochromatized		
2*θ* limits, deg	1–55		
scan type	*θ*(cryst)–2*θ*(counter)		
stds	3 reflcns, ($\bar{5}14$), ($\bar{4}42$), and ($\bar{3}1\bar{8}$), measd after each 1 h of exposure time, showing variations of less than ±3.5% from the av value		
	(C) Treatment of Intensity Data[c]		
redcn to prelim F_o and $\sigma(F_o)$	cor for bkgd attenuators, and Lorentz–polarization effects of monochromated X-radiation in the usual manner,[c] with extinction effects not obsd in the data		
abs cor[d]	μ = 6.83 cm^{-1}; max and min transmission coeff 0.8470 and 0.7730, respectively		
no. of obsd data	5488 reflcns collcd; 3587 having $F_o > 3\sigma(F_o)$ used in the refinement		

[a] From a least-squares fit to the settings angles of 25 reflections with $2\theta > 20°$. [b] In carbon tetrachloride and bromoform. [c] Data reduction and corrections performed by using the program KAPPA, part of the CRYSNET system at Brookhaven National Laboratory. [d] Absorption correction computed by using ABSOR, part of the CRYSNET system at Brookhaven National Laboratory.

yield; mp 127 °C (lit.[12] 127–128 °C).

Preparation of the Bis[tris(2-pyridyl)carbinol]cobalt(III) Complex. Method A. The complex was prepared as the perchlorate salt in 1:1 ethanol/dimethoxyethane as detailed previously.[4] Recrystallization was achieved by stirring a suspension of perchlorate salt in water with Dowex 1-X2 resin (Cl^- form), filtering, and precipitating with $NaClO_4$. The resultant orange complex was washed with ice-cold water and ethanol and air-dried. Yield: 80%. Anal. Calcd for $[Co\{(C_5H_4N)_3COH\}\{(C_5H_4N)_3CO^-\}](ClO_4)_2\cdot 2H_2O$: C, 46.9; H, 3.56; N, 10.26. Found: C, 47.0; H, 3.42; N, 10.15.

The PF_6^- salt could also be obtained by precipitation with NH_4PF_6 rather than $NaClO_4$, in which case the product was washed with ice-cold water and 2-propanol.

Method B. Tris(2-pyridyl)carbinol (200 mg, 0.76 mmol) in methanol (3 mL) was added to a solution of $CoCl_2\cdot 6H_2O$ (100 mg, 42 mmol) in water (3 mL). The solution was reluxed for 15 min and cooled, and the cation was precipitated as the PF_6^- salt by the addition of NH_4PF_6. The filtered solid was washed with cold water. The products obtained by this method contained variable mixtures of the Co(II) and Co(III) species and were sometimes a mixture of linkage isomers. Isomeric purity was obtained by refluxing the product in aqueous solution over activated charcoal (as detailed below). Recrystallization was then achieved by using techniques detailed in method A. Anal. Calcd for $[Co\{(C_5H_4N)_3COH\}_2](ClO_4)_3\cdot 2H_2O$: C, 41.8, H, 3.29; N, 9.14. Found: C, 41.6; H, 3.31; N, 9.04.

Charcoal-Catalyzed Isomerizations of the Linkage Isomers of $[Co\{(2\text{-}py)_3COH\}_2]^{3+}$. Aqueous solutions of the complexes obtained in syntheses A and B were refluxed for 18 h in the presence of activated charcoal. The solutions were then cooled and filtered, and the products were precipitated by the addition of NH_4PF_6.

Structure Determination of $Li[Co\{(2\text{-}py)_3COH\}_2](S_2O_6)_2\cdot 10H_2O$. Collection and Reduction of X-ray Data. Crystals of the bis[tris(2-pyridyl)carbinol]cobalt(III) dithionate complex were prepared by mixing $CoCl_2\cdot 6H_2O$ (0.024 g; 0.1 mmol) and the ligand (0.053 g; 0.2 mmol) in distilled water (3 mL). The solution was filtered, and a solution of $Li_2S_2O_6$ (0.2 g) in ethanol (10 ml) was added without stirring. After the mixture was allowed to stand for several days, crystals formed at the diffusion layer. This compound crystallized as transparent orange prisms, which exhibited 2/*m* Laue symmetry and systematic absences *hkl* ($h + k = 2n + 1$) and *h*0*l* ($l = 2n + 1$) consistent with the monoclinic space groups *Cc* (No. 9, C_s^4)[13a] and *C*2/*c* (No. 15, C_{2h}^6).[13b]

Table II. Atomic Coordinates for $Li[Co\{(C_5H_4N)_3COH\}_2](S_2O_6)_2\cdot 10H_2O$[a,b]

atom	*x*	*y*	*z*
Co	0.0000	0.5000	0.0000
N(1)	0.08473 (16)	0.5018 (3)	0.07457 (13)
C(12)	0.1531 (2)	0.5197 (3)	0.07177 (17)
C(13)	0.2144 (2)	0.5253 (4)	0.12365 (19)
C(14)	0.2069 (2)	0.5110 (5)	0.18090 (19)
C(15)	0.1367 (3)	0.4935 (4)	0.18287 (18)
C(16)	0.0770 (2)	0.4891 (4)	0.12992 (17)
N(2)	0.05382 (16)	0.3871 (3)	−0.03598 (13)
C(22)	0.1263 (2)	0.4102 (4)	−0.02691 (16)
C(23)	0.1681 (2)	0.3308 (4)	−0.04900 (18)
C(24)	0.1347 (3)	0.2274 (4)	−0.0828 (2)
C(25)	0.0606 (3)	0.2031 (4)	−0.0931 (2)
C(26)	0.0222 (2)	0.2830 (4)	−0.06867 (19)
N3	0.04061 (16)	0.6447 (3)	−0.02852 (13)
C(32)	0.1127 (2)	0.6448 (4)	−0.02296 (16)
C(33)	0.1434 (2)	0.7441 (4)	−0.04469 (18)
C(34)	0.0997 (2)	0.8463 (4)	−0.0714 (2)
C(35)	0.0261 (2)	0.8467 (4)	−0.0760 (2)
C(36)	−0.0018 (2)	0.7454 (4)	−0.05455 (18)
O(10)	0.23350 (14)	0.5442 (3)	0.01678 (12)
C(10)	0.15807 (19)	0.5305 (4)	0.00888 (18)
S(1)	0.19851 (6)	−0.12560 (13)	0.64092 (6)
O(11)	0.1775 (2)	−0.1945 (4)	0.58444 (17)
O(12)	0.27639 (19)	−0.1348 (4)	0.67738 (17)
O(13)	0.1497 (2)	−0.1444 (4)	0.67584 (16)
S(2)	0.18606 (9)	0.06826 (14)	0.61619 (7)
O(21)	0.2079 (3)	0.1356 (4)	0.6741 (2)
O(22)	0.1101 (3)	0.0862 (5)	0.5791 (2)
O(23)	0.2390 (3)	0.0867 (4)	0.58547 (17)
O(1)	0.3771 (2)	0.2901 (4)	0.25714 (18)
O(2)	0.0752 (4)	−0.0012 (5)	0.7842 (4)
O(3)	0.0837 (3)	0.5200 (4)	−0.1653 (2)
O(4)	0.0036 (6)	−0.2743 (11)	0.7189 (4)
O(5)	0.0000	0.3437 (6)	−0.2500
O(6)	0.3570 (7)	−0.2729 (13)	0.2195 (5)
O(7)	0.1648 (7)	−0.2652 (13)	0.8038 (5)
Li	0.1050 (16)	−0.181 (2)	0.7405 (12)

[a] Numbers in parentheses are errors in the significant digit(s). [b] The site occupancy factor for O(4), O(5), O(6), O(7), and Li is 0.5.

A crystal (0.266 × 0.400 × 0.500 mm^3) mounted in a Lindemann glass capillary was used for data collection. The reflections in the $h,k,\pm l$ octants with $h + k = 2n$ were collected. Crystal data and details of the data collection and reduction are given in Table I.

Determination and Refinement of the Structure. The coordinates of the cobalt atom were determined from a Patterson map,[14] while the other atoms were located on subsequent difference Fourier maps. Space group *Cc* was assumed for the solution of the structure, but after all the atoms were located $\bar{1}$ symmetry was observed in the complex and between the anions and solvent molecules, so that the space group was changed to *C*2/*c* for the refinement of the structure.

Anisotropic temperature factors were used for all non-hydrogen atoms. The location of the hydrogen atoms on the ligand were calculated (C–H bond length = 0.95 Å). These hydrogen atoms were allowed to "ride"[14] on the atom to which they were attached. The hydrogen atoms on the ordered oxygen atoms were located on a difference Fourier map and fixed at these positions. A common isotropic temperature factor for all the hydrogen atoms refined to U = 0.062 (3) Å^2. The hydrogen atoms attached to oxygen atoms that were disordered (occupancy factor less than 1) were not included in the refinement.

The quantity $\sum w(|F_o| - |F_c|)^2$, where $w = 1.6085/(\sigma(F_o)^2 + 0.000563F_o^2)$, was minimized in the least-squares refinement.[15] During the final cycle of refinement the largest parameter shift was less than 0.01

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(14) Except where otherwise noted, all calculations were performed by using SHELX-76: Sheldrick, G. M. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.: Delft University: Delft, Holland, 1978; pp 34–42.

(15) (a) Neutral-atom scattering factors were used in the least squares refinement taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. 1, p 99. (b) Anomalous dispersion effects used in the least-squares refinement were included for all non-hydrogen atoms and were taken from: Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

Table III. Bond Distances (Å) and Angles (deg) for $Li[Co\{(C_5H_4N)_3COH\}_2](S_2O_6)_2\cdot 10H_2O$

	Cobalt–Ligand Distances		
Co–N(1)	1.938 (3)	Co–N(3)	1.931 (3)
Co–N(2)	1.944 (3)		
	Cobalt–Ligand Angles		
N(1)–Co–N(2)	89.4 (1)	N(2)–Co–N(3)	89.8 (1)
N(1)–Co–N(3)	89.4 (1)	N(2)–Co–N(2′)	180.0 (1)
N(1)–Co–N(1′)	180.0 (1)	N(2)–Co–N(3′)	90.2 (1)
N(1)–Co–N(2′)	90.7 (1)	N(3)–Co–N(3′)	180.0 (1)
N(1)–Co–N(3′)	90.6 (1)		

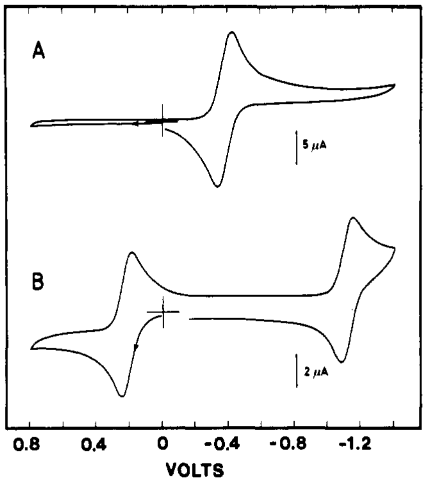

Figure 1. Cyclic voltammograms of the linkage isomers of the $[Co\{(2\text{-}py)_3COH\}_2]^{n+}$ cation in acetonitrile/0.1 M TEAP:[17] (A) unsymmetric form; (B) symmetric form. Scan rate = 100 mV/s.

of its error. The final R_1 value[16a] was 0.055, while the weighted discrepancy index R_2[16] was 0.068. The final difference Fourier map revealed a peak of 0.75 $e^-/Å^3$ near (~0.5 Å) an oxygen atom (O(2)), indicating some positional disorder, while the remaining peaks were all less than ±0.5 $e^-/Å^3$.

The non-hydrogen atomic coordinates are reported in Table II, and the Co–N distances and N–Co–N angles with their standard deviations are listed in Table III. The thermal parameters for the non-hydrogen atoms, the positional parameters for the hydrogen atoms, the interatomic distances and angles for the ligand/anions/lithium coordination sphere, the final observed and calculated structure factors, the hydrogen bonding interactions, and least-squares planes for the pyridine rings are all available as supplementary material.

Results and Discussion

Synthesis and Characterization of Linkage Isomers of the Bis[tris(2-pyridyl)carbinol]cobalt(III) Cation. Synthesis of the title cation in ethanol/dimethoxyethane using the method of Boggess and Boberg[4] yielded the Co(III) species $[Co((py)_3COH)((py)_3CO^-)](ClO_4)_2$. The electronic spectrum in acetonitrile showed absorption maxima at $\lambda = 387$ nm ($\epsilon = 340$ M^{-1} cm^{-1}) and 463 nm ($\epsilon = 84$ M^{-1} cm^{-1}). Cyclic voltammetry[17] of the complex in acetonitrile (Figure 1A) showed a quasi-reversible redox couple at $E_{1/2} = -0.38$ V ($\Delta E_p = 80$ mV), attributed to Co(III)/Co(II). Coulometry under inert conditions (argon) on the diffusion plateau of the reduction wave led to $n \sim 1$, however extensive decomposition of the complex occurred.

The ^{13}C NMR spectrum (75 MHz) of this Co(III) species in CD_3CN is shown in Figure 2A. Nineteen resonances are observed in the aromatic region, and the two resonances at $\delta = 93.1$ and 83.2 associated with the aliphatic bridging carbon atoms demonstrate that the two $(2\text{-}py)_3COH$ tripod ligands are in different environments. These data are consistent with either an asymmetric bis(N,N′,O) form of the cation (the symmetric form of this coordination mode would show no more than 15 pyridine C resonances) or the (N,N′,N″)(N,N′,O) species. The magnitude of the separation of the chemical shifts for the two bridging carbon atoms favors the latter assignment, as determined by White and Faller.[11]

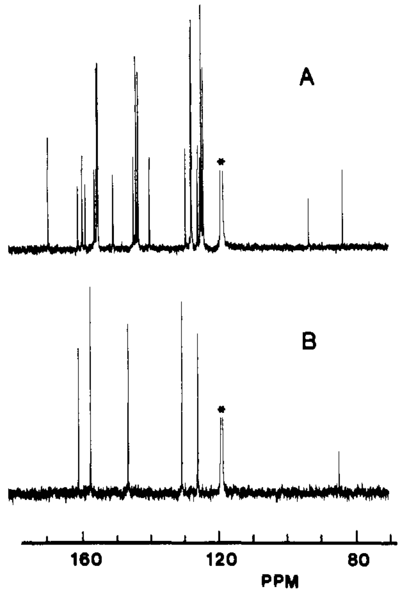

Figure 2. 75-MHz ^{13}C NMR spectra of the linkage isomers of the bis[tris(2-pyridyl)carbinol]cobalt(III) cation in CD_3CN: (A) unsymmetric form; (B) symmetric form. An asterisk indicates resonance due to solvent.

Syntheses of the complex in aqueous solution yielded products of varying composition: the species identified above is one (generally minor) component. However, an additional major product was obtained which had the following characteristics. The cyclic voltammetry[17] is shown in Figure 1B: there is a reversible one-electron couple at $E_{1/2} = +0.22$ V and a quasi-reversible couple at $E_{1/2} = -1.13$ V ($\Delta E_p = 70$ mV), which are assigned to Co(III)/Co(II) and Co(II)/Co(I), respectively. Using spectrocoulometric techniques, the electronic spectrum of the Co(III) form shows $\epsilon_{445}^{max} = 73$ M^{-1} cm^{-1} in acetonitrile solution, with the Co(II) species having $\epsilon_{381}^{max} = 2100$ M^{-1} cm^{-1}. The variable ratio of D_{381}/D_{345} for different syntheses indicates Co(II)/Co(III) variation for individual preparations and reflects some sensitivity of the Co(II) species to oxygen. Solutions of the Co(II) species oxidize to Co(III) over a period of days.

Coulometry under inert conditions (argon) of the pink Co(II) complex in acetonitrile solution was undertaken at −1.20 V at +25 and −10 °C, and also in the presence of a tenfold excess of the ligand at both temperatures. In all cases, a rapid formation of a bright blue species was observed up to $n = 0.5$–1.0, whereupon the solution reverted to a pink color with the gradual formation of a fine pink precipitate as n approached ca. 2. The initial blue color was more sustained at lower complex concentrations. These data are consistent with the initial formation of the Co(I) species on reduction (which might be expected to be deep blue in color by analogy with $Co(bpy)_3^+$ [18]), and it seems likely that it is the Co(II)/Co(I) couple that is observed at $E_{1/2} = -1.13$ V on the CV time scale. However, in the coulometry experiment, as the concentration of Co(I) builds up, it undergoes decomposition (presumably via a disproportionation process) to unknown products.

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(16) (a) $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. (b) $\sigma_{av} = \sum_m(l_m - l)^2/(m - l)^{1/2}$.

(17) All cyclic voltammetry data were recorded by using a glassy-carbon working electrode and are quoted vs. a Ag/AlCl (3 M NaCl) reference electrode (which is 35 mV anodic of the saturated sodium chloride calomel electrode, SSCE). All coulometric measurements were performed by using a Pt-gauze working electrode.

(18) (a) Waind, G. M.; Martin, B. *J. Inorg. Nucl. Chem.* **1958**, *8*, 551–556. (b) Kaizu, Y.; Torii, Y.; Kobayashi, H. *Bull, Chem. Soc. Jpn.* **1970**, *43*, 3296–3297. (c) Willett, B. C.; Anson, F. C. *J. Electrochem. Soc.* **1982**, *129*, 1260–1266. (d) Keene, F. R.; Creutz, C.; Sutin, N., unpublished work.

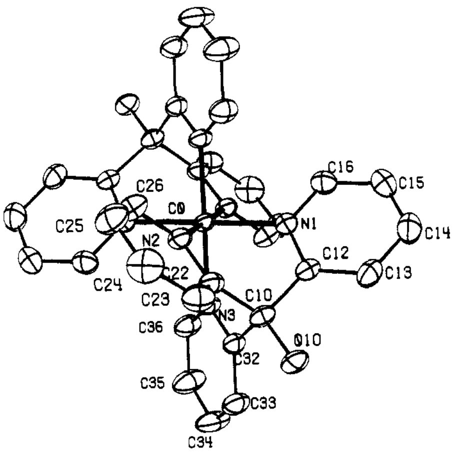

Figure 3. ORTEP drawing of the $[Co\{(C_5H_4N)_3COH\}_2]^{3+}$ cation, with thermal ellipsoids at 50% probability level. The atom-numbering scheme is shown. Hydrogen atoms are omitted for clarity.

The ^{13}C NMR spectrum of the Co(III) complex shows five resonances in the aromatic region, and one bridgehead carbon environment ($\delta = 84.2$). This is consistent only with a stereochemistry in which all pyridine rings are equivalent (i.e. point group symmetry D_{3d}) so that the coordination mode of both ligands is necessarily N,N′,N″.

Quite clearly there are two linkage isomers for this cation, and the X-ray structural analysis of the bis(N,N′,N″) form is detailed below.

Isomerization of Linkage Isomers. Isomers of Co(III) complexes may be equilibrated in the presence of activated charcoal.[19] In this instance, after being refluxed for 18 h in aqueous solution, the symmetrical isomer is observed to be the more stable form, as the unsymmetrical isomer will isomerize almost quantitatively to it under these conditions. Such methods constitute the most satisfactory way of obtaining the isomerically pure symmetric Co(III) complex.

Description of the Structure. A view of the $[Co\{(C_5H_4N)_3COH\}_2]^{3+}$ cation and the atom-labeling scheme used are presented in Figure 3. The cobalt atom lies on a center of inversion at (0, $^1/_2$, 0), and the two tridentate ligands attached to it are related to each other by this center of inversion. The six nitrogens coordinated to the cobalt are arranged in an almost perfect octahedral geometry with the Co–N bond distances ranging from 1.931 (3) to 1.944 (3) Å, and all the N–Co–N bond angles (both intra- and interligand) are within 0.7° of either 90 or 180° (Table III). These bond lengths are normal for a Co(III)–N bond, where N is part of a pyridine ring.[20-22]

The bond lengths and angles within the ligand are normal, with the average[16b] intrapyridine C–C bond length being 1.375 (10) Å and C–N bond length being 1.325 (5) Å,[20,23,24] and with an average C–COH bond length of 1.520 (9) Å.[8]

The average S–O distance in the $S_2O_6^{2-}$ anions is 1.445 (9) Å with an S–S distance of 2.114 (2) Å.

The lithium ion has an approximately tetrahedral coordination sphere of oxygen atoms, as expected,[25] with Li–O distances ranging between 1.77 (3) and 2.31 (2) Å and O–Li–O bond angles ranging between 98° and 121° with an average value of 109 (8)°.

Crystal Packing. The crystal is held together by a network of hydrogen bonds involving the alcohol group on the ligands, the dithionate anions, and the waters of crystallization. Each cation is surrounded by six dithionate ions. The four dithionate ions closest to the Co(III) center form two sets related by a center of inversion, with the shortest Co–S distances in the sets being 5.69 and 5.85 Å. These ion–ion interactions also help stabilize the crystal. In addition, there are two $S_2O_6^{2-}$ anions which are hydrogen bonded to the cation through the alcohol group of each ligand.

Comparisons with Other Structures. Structures of FeL_2^{2+}[23] and CoL_2^{2+},[24] where L = tris(2-pyridyl)amine, are known, and the ligand is found to be coordinated to the metal atom in a tridentate manner through the three pyridyl nitrogen atoms. The two complexes each contain a center of inversion about the metal center. The immediate ligand environment in the Fe(II) complex[23] is the more octahedral (average intraligand N–Fe–N angle = 88.1°, compared with 85.6° for N–Co(II)–N in CoL_2^{2+}[24]). In the present structure of the bis[tris(2-pyridyl)carbinol]cobalt(III) cation, both ligands are also coordinated through the three pyridyl nitrogen atoms, and the ligand environment is almost perfectly octahedral (average intraligand N–Co(III)–N angle = 89.5°). This may be the result of two factors: the decrease in the metal–nitrogen bond length from 2.100 (2) – 2.152 (2) Å in CoL_2^{2+}[23] to 1.98 (2) Å in FeL_2^{2+}[24] to 1.938 Å in the present case and the longer pyridine–bridging atom bond length (1.528 (9) Å) compared with 1.44 (1) Å for the tris(2-pyridyl)amine species.

Tris(2-pyridyl)methane has also been assigned a tridentate coordination mode in the bis(ligand) complexes of Co(II) and Co(III) from NMR studies.[11]

While tris(2-pyridyl)amine and tris(2-pyridyl)methane may only coordinate through the pyridyl nitrogen atoms, the coordination mode of tris(2-pyridyl)carbinol as a tridentate is ambiguous since it may also coordinate via the alcohol group. Canty et al.[8] have reported structural studies of a methylmercury(II) complex containing tris(2-pyridyl)carbinol. In this case, the coordination mode of the tripodal ligand is tridentate with binding occurring through the three pyridyl nitrogen atoms, although the geometry is somewhat distorted with one Hg–N bond being significantly shorter than the other two. No structures of octahedral complexes of this ligand have been described in detail, although White and Faller have given preliminary results of a structural determination of the title complex in a footnote to ref 11. In previous discussions of the bis[tris(2-pyridyl)carbinol]cobalt(III) ion, Boggess and Boberg[4] have claimed from spectroscopic studies (IR, electronic) that both tris(2-pyridyl)carbinol ligands coordinate to Co(III) in an N,N′,O fashion with one of the two coordinated alcohol groups being deprotonated, while White and Faller[11,26] subsequently determined one $(py)_3CO^-$-*N,N′,O* ligand and one $(py)_3COH$-*N,N′,N″* from their structure. It seems probable from the present work that the products observed in these two previous studies were the same, and that it does have (N,N′,N″)(N,N′,O)-coordination.[27] However, the present work has also identified and characterized a new symmetrical bis(N,N′,N″) linkage isomer of the title complex.

It is noted that the (N,N′,N″)(N,N′,O)-coordination mode is observed for this ligand in the bis(ligand)ruthenium(II) analogue, details of which will be published subsequently.[9]

Electrochemistry of the $[Co\{(2\text{-}py)_3COH\}_2]^{n+}$ Cation. Earlier electrochemical studies[3] of bis(ligand)cobalt(II) complexes of $(2\text{-}py)_3X$ (X = N, P, P=O, As) have shown that reduction produces a stable Co(I) species when X = P, P=O, or As, whereas for X = N a direct reduction from Co(II) to metallic Co(0) occurs. Since X is capable of $d\pi$–$p\pi$ bonding in the former cases, delocalization through the ligand is possible, and their electrochemical behavior was concluded[3] to be similar to that of $Co(bpy)_3^{n+}$, with the low-valent Co(I) species being stabilized by $t_{2g} \rightarrow \pi^*$ back-bonding. The relative instability of the Co(I) complex for X = N was therefore claimed to be due to the inability of the

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bridgehead atom to allow extensive delocalization.

However, the present study shows that for the analogous complexes where the bridgehead atom is carbon (i.e. X = COH in the title complex, and X = CH[10]) the cyclic voltammetric behavior parallels that of $Co(bpy)_3^{n+}$ and not $Co\{(2\text{-py})_3N\}_2^{n+}$. Furthermore, there is evidence from the coulometric studies reported above for the transient existance of the $[Co\{(2\text{-py})_3COH\}_2]^+$, and the $[Co\{(2\text{-py})_3CH\}_2]^+$ complex can be synthesized by sodium amalgam reduction of the Co(II) species and shows reasonable stability (several days) under inert conditions.[10a] Since delocalization via dπ–pπ bonding would not be anticipated in either of these ligands, the above observations argue against the necessity of extensive delocalization via the bridging atom to allow stabilization of the low-valent Co(I) species, unless there is a spatial electronic interaction between pyridine rings in these tripodal ligands.[28]

Further studies of the Co(I) and Rh(I) complexes of a number of these tripodal ligands are in progress[10b] and will be reported subsequently.

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Registry No. $[Co\{(2\text{-py})_3COH\}\{(2\text{-py})_3CO^-\}](ClO_4)_2$, 73580-28-6; $[Co\{(2\text{-py})_3COH\}_2](ClO_4)_3$, 102630-75-1; $Li[Co\{(2\text{-py})_3COH\}_2](S_2O_6)_2 \cdot 10H_2O$, 102630-77-3.

Supplementary Material Available: Tables of thermal parameters for the non-hydrogen atoms, positional parameters for the hydrogen atoms, interatomic distances and angles for the ligand, the anions, and the lithium coordination sphere, hydrogen bonding interactions, and least-squares planes (9 pages). Ordering information is given on any current masthead page.

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[28] In this case, the complex of tris(2-pyridyl)amine may be the exception because of ligand distortion induced by the relative shortness of the bridgehead (N)–pyridine bonds.

[29] The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13).

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Structural and Theoretical Discussion of $[Bi_4Fe_4(CO)_{13}]^{2-}$: Application of MO and TEC Theories to a Zintl–Metal Carbonylate

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The reaction of $[Et_4N][BiFe_3(CO)_{10}]$ with CO in CH_2Cl_2 cleanly produces $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$ and iron pentacarbonyl. The complex crystallizes in the centrosymmetric orthorhombic space group *Pcab* (No. 61), with $a = 14.128$ (3) Å, $b = 15.567$ (4) Å, $c = 39.816$ (18) Å, $V = 8756$ (5) Å^3, and $D(\text{calcd}) = 2.55$ g cm^{-3} for $Z = 8$ and $M_r = 1683.96$. Diffraction data (Mo Kα, $2\theta = 6$–$40°$) were collected with a Syntex $P2_1$ automated diffractometer; the structure was solved and refined to $R_F = 7.8\%$ for those 2926 reflections with $|F_o| > 3.0\sigma(|F_o|)$. The $[Bi_4Fe_4(CO)_{13}]^{2-}$ dianion can be described as a hybrid Zintl ion–metal carbonyl, with three $Fe(CO)_3$ units capping faces of a Bi_4 tetrahedron. An additional $Fe(CO)_4$ fragment is apically bonded to that unique bismuth atom which is bonded to all three $Fe(CO)_3$ units. The $[Bi_4Fe_4(CO)_{13}]^{2-}$ dianion is involved in some significant intermolecular Bi–Bi contacts. Molecular orbital calculations have been carried out and are discussed along with qualitative electron-counting formalisms.

Introduction

The interest in metal cluster chemistry has dramatically increased during the last decade. The structures, the nature of the bonding, and the reactivity of metal cluster compounds are generally well established by synthetic, spectroscopic, and theoretical studies.[1-3] There are a number of transition-metal complexes that contain A_3 or A_4 groups, where A is phosphorus or arsenic, bonded to the transition-metal atoms. Most of the complexes show η^3-A_3–ML_3, η^3-A_3–M_2L_6 and η^1,η^2-A_4–ML_3 geometries.[4] Among the group 15 elements, unfortunately, bismuth–transition-metal cluster chemistry is not well-known. A few cationic or anionic polybismuth clusters have been known for some time,[5] and a few organic derivatives containing Bi–Bi bonds have also been reported recently.[6]

A preliminary account of the structure of a $[Bi_4Fe_4(CO)_{13}]^{2-}$ cluster compound has appeared[7] and has encouraged us to undertake MO studies to understand the bonding in it. This cluster compound is an electron-rich Zintl–metal carbonylate that is based on a p-block cluster framework. The complete structural details

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