is clearly evident (Figure 1). As earlier work has shown, $(CH_3)_4C_4B_8H_8$ exists in solution[22] as an equilibrium mixture of two forms (evidently types 2 and 3, Figure 1) and in the solid[23] as type 3 only; the compound does not rearrange up to its decomposition temperature. Thus, the presence of one or more metal atoms in the cage can have a profound influence on the cage geometry even when the formal skeletal electron count is held constant.

Acknowledgment. This work was supported by the Office of Naval Research and the National Science Foundation (Grant No. CHE 79-09948).

Registry No. III, 76377-03-2.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Properties and Structures of Five-Coordinated Cobalt(II) and Copper(II) Complexes of *N*,*N'*-Bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-oxaheptane-1,7-diamine

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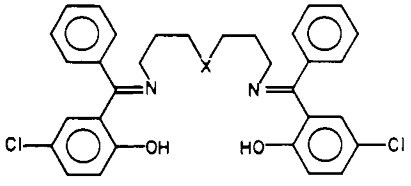
Received February 26, 1980

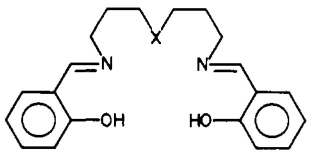
The title complexes, [Co(cbpO)] and [Cu(cbpO)], have been synthesized and studied by single-crystal X-ray diffraction. The copper complex contains the metal atom in a distorted square pyramid whose apex is formed by the Cu–O bond to the ether oxygen atom. The O_2N_2 base of the square pyramid is distorted so as to give some trigonal-bipyramidal character to the geometry, the N atoms being raised above (0.35 Å) the base and the Cu atom and the O atoms below it (0.06 and 0.35 Å, respectively). The Cu–O bond to the ether oxygen is markedly elongated (2.575 Å), indicating a rather weak linkage. This compares with apical bond elongations of 2.374 (10) and 2.686 (1) Å, respectively, in the related five-coordinated [Cu(mbpN)] and [Cu(cbpS)]. If the long Cu–O bond were absent, the copper environment would approximate a flattened tetrahedron. The metal environment in [Co(cbpO)] is distorted trigonal bipyramidal with the two Co–N bonds axial and the three Co–O bonds equatorial. The Co–O bond to the ether oxygen is relatively strong (2.124 (3) Å) in contrast with the [Cu(cbpO)] analogue. The observation of metal to ether oxygen bonding at all in these complexes contrasts with the apparent absence of such bonds in a series of related salicylaldimine complexes. [Co(cbpO)] readily forms a six-coordinated pyridine adduct, while [Cu(cbpO)] appears not to do so, even in pyridine solution. Crystal data for [Cu(cbpO)]: space group $C2/c$, $Z = 8$, $a = 13.993$ (5) Å, $b = 13.652$ (8) Å, $c = 29.40$ (1) Å, $\beta = 91.46$ (3)°, $V = 5615$ Å^3, $R = 5.8\%$ for 1840 reflections. Crystal data for [Co(cbpO)]: space group $C2/c$, $Z = 8$, $a = 13.914$ (7) Å, $b = 13.477$ (4) Å, $c = 29.86$ (1) Å, $\beta = 90.57$ (3)°, $V = 5599$ Å^3, $R = 6.1\%$ for 3397 reflections.

Introduction

Bivalent metal complexes of potentially pentadentate ligands of the type H_2cbpX (**1**) and H_2salX (**2**) may form either four-coordinated or five-coordinated structures, depending on whether the central donor atom X is bonded to the metal. For H_2salX complexes, where X = S, O, Taylor et al. have suggested, on the basis of spectral data, that the central X group does not usually coordinate to the metal in salX complexes, producing distorted square-planar copper(II) complexes,[2] tetrahedral cobalt(II) complexes,[3] and possibly weakly coordinated low-spin five-coordinated nickel(II) complexes.[4] These suggested structures have not yet been confirmed by X-ray crystal structural data. Subsequent experiments have provided evidence of M–X bonding in complexes of H_2salX (X = NR, PCH_3),[3,5,6] H_2cbpX (X = NH, S)[7-10] and H_2mbpX (X = NH).[7,9-12] In most cases the M–X bonding has been confirmed by X-ray crystal structure data.[5-8,10,11] Due to the weak donor properties of ether oxygen atoms, the X = O ligand gives



1, H_2cbpX



2, H_2salX

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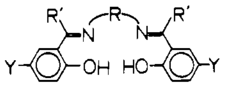
Table I

compd		anal. data		magnetic moment[d]	visible-near-infrared spectra[a]		
		calcd	found		solid state	dichloromethane	pyridine[b]
$Cu(cbpO)\cdot{}^1/_2H_2O$	C	60.84	60.96	1.80	16 000 br	16 400 (131), 14 500 sh[b]	14 500 (136)
	H	4.62	4.65				
	N	4.43	4.97				
Co(cbpO)	C	62.17	62.37	4.78	15 000, 13 500 sh, 6600	15 000 (18)	9500 (20)
	H	4.56	4.58			6700 (12)[b]	
	N	4.53	4.42				
$[Cu(3,4\text{-}cbpN)]\cdot{}^1/_2H_2O$				1.96	17 500 sh, 15 000	16 500 sh, 14 200 (151.5)[c]	16 500 sh, 13 500 (151.5)
Cu(2,3-cbpN)				1.92	12 500	12 800 (194)[c]	12 100 (211)
$[Cu(2,3\text{-}mbpN)]\cdot H_2O$				1.87	12 000	12 800 (216)[c]	12 200 (300)
$[Cu(2,3\text{-}mmbpN)]\cdot 2H_2O$				1.89	12 000	12 800 (252)[c]	12 200 (222)
Cu(3,3-cbpN)					13 300	14 300 (200)[c]	12 700 (192)
Cu(3,3-mbpN)					13 500 br	14 500 (190)[c]	13 100 (185)

[a] $cm^{-1} \times 10^{-3}$. Key: br, broad; sh, shoulder. Extinction coefficients in parentheses. [b] 0.01 M. [c] 0.005 M. [d] μ in μ_B.

the best chance of obtaining McbpX complexes without M–X bonds, as in the corresponding MsalX complexes, or complexes with significantly weakened M–X bonds. The complexes are also models for analogous tetradentate Schiff base complexes (3) with NMNR rings which range from 5-membered to



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15-membered, where R is a methylene chain.[13,14] We report here the crystal structures and physicochemical data of two cbpO complexes, [Cu(cbpO)] and [Co(cbpO)], each of which is five-coordinated, with a fifth bond which is greatly weakened with Cu(II) but only slightly so with Co(II).

The "blue" (type I) copper sites of the electron-transfer proteins azurin, plastocyanin, and stellacyanin probably contain four-coordinated copper(II).[15,16] Many studies have examined the relationship between the physical properties of four-coordinated copper(II) and the structural details,[17-22] and the electronic and ESR spectra of the blue copper sites can be partially but not completely simulated with small-molecule model comdplexes.[22-24] The synthesis of complexes such as [Cu(cbpO)] and [Cu(cbpS)] is of particular interest because they represent modified four-coordinated complexes with a perturbation in the form of a weak fifth bond.

Experimental Section

Preparation of the Complexes. 5-Chloro-2-hydroxybenzophenone was obtained from the Aldrich Chemical Co.

Bis(3-aminopropyl) Ether. This compound was obtained from the lithium aluminum hydride reduction of 3,3′-oxybis(propionitrile) (Fluka Chemical Co.). The preparation method was similar to that described previously[9] for bis(3-aminopropyl) sulfide. The compound was obtained as a pale yellow oil which was used without further purification.

Schiff Base. 5-Chloro-2-hydroxybenzophenone (2 mmol) and bis(3-aminopropyl) ether (1.3 mmol) were refluxed together for 30 min. 2,2-Dimethoxypropane (100 mL) was added to the resulting melt, and the solution was used to prepare the metal complexes.

Cobalt Complex. The Schiff base solution (1 mmol in 100 mL) was added to a hot methanol solution of cobalt(II) acetate tetrahydrate (1 mmol in 100 mL) and the volume reduced by heating until the tan compound precipitated.

Copper Complex. The Schiff base solution (1 mmol in 100 mL) was added to a hot methanol solution of copper(II) acetate monohydrate (1 mmol in 100 mL). Piperidine (2 mL) was added to the solution, and the volume was reduced by heating until the green compound precipitated.

Physical Measurements. C, H, and N analyses were carried out by the Australian Microanalytical Service, Melbourne, Australia. Solid-state reflectance spectra were measured on Zeiss PMQII spectrophotometer with an RA3 reflectance attachment. Solution spectra were recorded on a Hitachi EPS-3T spectrophotometer. Room-temperature magnetic moments were measured by the Gouy method. These data are shown in Table I.

Crystal Data and Data Collection. [Cu(cbpO)]: $CuCl_2O_3N_2C_{32}H_{28}$, mol wt 623, space group $C2/c$, $Z = 8$, $a = 13.993\ (3)$ Å, $b = 13.652\ (8)$ Å, $c = 29.40\ (1)$ Å, $\beta = 91.46\ (3)°$, $V = 5615$ Å^3, $\rho_{calcd} = 1.49$ g cm^{-3}, $\rho_{obsd} = 1.47$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 10.6$ cm^{-1}. Crystal dimensions (distances in mm of faces from centroid): (100) 0.13, $(\bar{1}00)$ 0.13, $(11\bar{1})$ 0.11, $(\bar{1}\bar{1}1)$ 0.11, $(1\bar{1}\bar{1})$ 0.115, $(\bar{1}11)$ 0.115, (010) 0.095, $(0\bar{1}0)$ 0.095, (001) 0.045, $(00\bar{1})$ 0.045. Maximum and minimum transmission coefficients: 0.97, 0.93.

[Co(cbpO)]: $CoCl_2O_3N_2C_{32}H_{28}$, mol wt 519, space group $C2/c$, $Z = 8$, $a = 13.914\ (7)$ Å, $b = 13.477\ (4)$ Å, $c = 29.86\ (1)$ Å, $\beta = 90.57\ (3)°$, $V = 5599$ Å^3, $\rho_{calcd} = 1.47$ g cm^{-3}, $\rho_{obsd} = 1.48$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 8.7$ cm^{-1}. Crystal dimensions (mm from centroid): (100) 0.325, $(\bar{1}00)$ 0.325, (010) 0.49, $(0\bar{1}0)$ 0.49, (001) 0.03, $(00\bar{1})$ 0.03. Maximum and minimum transmission coefficients: 0.96, 0.70.

Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius four-circle CAD-4 diffractometer. The θ–2θ scan technique was used, as previously described,[7] to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 48°$ for [Cu(cbpO)] and $1° < 2\theta < 50°$ for [Co(cbpO)]. Scan widths were calculated as $(A + B \tan \theta)°$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to $K\alpha_1$–$K\alpha_2$ splitting. The values of A and B were 0.9 and 0.35°, respectively, for both complexes.

The intensities of four standard reflections, monitored for each crystal at 100-reflection intervals, showed no greater fluctuations than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and absorption. Of the 3852 independent intensities for [Cu(cbpO)] and 4121 for [Co(cbpO)],

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Table II

A. Positional and Thermal Parameters and Their Estimated Standard Deviations for [Co(cbpO)]

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.22037 (8)	0.79072 (8)	0.25117 (4)	0.0533 (6)	0.0366 (5)	0.0372 (5)	0.0016 (6)	0.0022 (5)	−0.0008 (5)
Cl1	0.0917 (2)	0.4697 (2)	0.06212 (9)	0.104 (2)	0.063 (1)	0.062 (1)	−0.006 (1)	0.002 (1)	−0.026 (1)
Cl2	0.5320 (2)	0.5948 (2)	0.42886 (9)	0.083 (2)	0.099 (2)	0.066 (1)	0.013 (2)	−0.010 (1)	0.032 (1)
O1	0.1349 (4)	0.6868 (4)	0.2313 (2)	0.073 (4)	0.044 (3)	0.033 (3)	−0.011 (3)	0.005 (3)	−0.003 (3)
O1′	0.3546 (4)	0.7820 (4)	0.2718 (2)	0.054 (3)	0.055 (3)	0.035 (3)	0.000 (3)	0.001 (3)	0.008 (3)
O2	0.1572 (4)	0.9333 (4)	0.2581 (2)	0.045 (3)	0.044 (3)	0.066 (4)	0.005 (3)	−0.000 (3)	−0.002 (3)
N1	0.2463 (5)	0.8249 (5)	0.1833 (2)	0.070 (5)	0.041 (4)	0.041 (4)	−0.011 (4)	0.005 (3)	0.001 (3)
N1′	0.1774 (5)	0.7684 (5)	0.3177 (2)	0.059 (4)	0.043 (4)	0.039 (3)	0.001 (3)	0.010 (3)	−0.002 (3)
C1	0.1656 (6)	0.6820 (6)	0.1515 (3)	0.048 (4)	0.035 (4)	0.037 (4)	0.001 (4)	0.005 (4)	0.004 (3)
C2	0.1264 (6)	0.6447 (6)	0.1919 (3)	0.048 (5)	0.038 (4)	0.039 (4)	0.002 (4)	−0.000 (4)	0.003 (4)
C3	0.0747 (6)	0.5539 (6)	0.1896 (3)	0.051 (5)	0.049 (5)	0.044 (5)	−0.009 (4)	−0.001 (4)	0.006 (4)
C4	0.0656 (7)	0.5008 (6)	0.1506 (3)	0.071 (6)	0.038 (4)	0.061 (6)	−0.012 (4)	−0.002 (5)	−0.001 (4)
C5	0.1050 (6)	0.5375 (6)	0.1117 (3)	0.051 (5)	0.045 (5)	0.047 (5)	0.004 (4)	−0.002 (4)	−0.011 (4)
C6	0.1537 (6)	0.6261 (6)	0.1119 (3)	0.054 (5)	0.045 (5)	0.040 (4)	0.003 (4)	0.002 (4)	0.002 (4)
C7	0.2143 (5)	0.7782 (6)	0.1484 (3)	0.034 (4)	0.040 (4)	0.040 (4)	0.003 (4)	0.002 (3)	0.004 (4)
C8	0.2230 (6)	0.8213 (6)	0.1018 (3)	0.054 (5)	0.037 (4)	0.042 (4)	0.000 (4)	0.004 (4)	0.006 (4)
C9	0.3078 (7)	0.8249 (7)	0.0792 (3)	0.057 (5)	0.070 (6)	0.055 (5)	0.010 (5)	0.007 (4)	0.018 (5)
C10	0.3117 (7)	0.8651 (8)	0.0362 (3)	0.077 (6)	0.080 (7)	0.053 (5)	0.009 (6)	0.024 (5)	0.017 (5)
C11	0.2323 (8)	0.9030 (8)	0.0168 (3)	0.092 (7)	0.076 (6)	0.043 (5)	0.014 (6)	0.010 (5)	0.023 (5)
C12	0.1493 (8)	0.9007 (9)	0.0387 (3)	0.084 (7)	0.096 (7)	0.045 (5)	0.027 (6)	−0.001 (5)	0.020 (5)
C13	0.1443 (7)	0.8590 (8)	0.0814 (3)	0.075 (6)	0.075 (6)	0.050 (5)	0.011 (6)	0.015 (5)	0.013 (5)
C14	0.2979 (7)	0.9208 (8)	0.1771 (4)	0.067 (6)	0.060 (6)	0.077 (7)	−0.023 (5)	0.007 (5)	0.001 (5)
C15A^{i} ^{b}	0.2978 (11)	0.9903 (10)	0.2142 (5)	0.070 (9)	0.041 (7)	0.067 (9)	−0.009 (7)	−0.001 (8)	−0.002 (7)
C15B^{ii}	0.2314 (23)	0.9993 (20)	0.1905 (10)	0.101 (20)	0.037 (14)	0.082 (17)	0.024 (14)	0.054 (14)	0.019 (13)
C16	0.2006 (9)	1.0151 (7)	0.2340 (5)	0.091 (8)	0.033 (5)	0.136 (10)	−0.002 (5)	0.005 (8)	0.005 (6)
C1′	0.3337 (6)	0.7229 (6)	0.3480 (3)	0.054 (4)	0.031 (4)	0.037 (4)	−0.000 (4)	0.008 (4)	−0.002 (3)
C2′	0.3869 (5)	0.7452 (6)	0.3091 (3)	0.038 (4)	0.035 (4)	0.042 (4)	−0.001 (3)	0.006 (3)	−0.004 (4)
C3′	0.4883 (6)	0.7281 (6)	0.3110 (3)	0.053 (5)	0.046 (5)	0.044 (4)	−0.001 (4)	0.011 (4)	−0.006 (4)
C4′	0.5307 (6)	0.6827 (6)	0.3472 (3)	0.047 (5)	0.047 (5)	0.053 (5)	0.003 (4)	0.003 (4)	−0.006 (4)
C5′	0.4773 (7)	0.6565 (6)	0.3834 (3)	0.064 (5)	0.043 (5)	0.042 (4)	0.006 (4)	0.001 (4)	0.003 (4)
C6′	0.3798 (6)	0.6767 (6)	0.3848 (3)	0.056 (5)	0.049 (5)	0.043 (4)	−0.001 (4)	0.012 (4)	0.003 (4)
C7′	0.2314 (6)	0.7437 (6)	0.3523 (3)	0.056 (5)	0.037 (4)	0.036 (4)	−0.004 (4)	0.014 (4)	−0.001 (4)
C8′	0.1872 (6)	0.7390 (6)	0.3984 (3)	0.058 (5)	0.046 (5)	0.038 (4)	−0.000 (4)	0.011 (4)	−0.002 (4)
C9′	0.1420 (8)	0.6550 (7)	0.4139 (3)	0.091 (7)	0.053 (5)	0.044 (5)	−0.022 (5)	0.015 (5)	−0.006 (4)
C10′	0.1009 (8)	0.6546 (8)	0.4559 (3)	0.094 (7)	0.067 (6)	0.060 (6)	−0.021 (6)	0.022 (5)	0.011 (5)
C11′	0.1024 (8)	0.7363 (9)	0.4823 (3)	0.089 (7)	0.086 (7)	0.042 (5)	0.001 (6)	0.020 (5)	0.003 (5)
C12′	0.1471 (9)	0.8195 (8)	0.4671 (3)	0.116 (9)	0.069 (6)	0.050 (5)	−0.005 (6)	0.016 (6)	−0.020 (5)
C13′	0.1904 (8)	0.8222 (7)	0.4255 (3)	0.091 (7)	0.055 (6)	0.054 (5)	−0.013 (5)	0.019 (5)	−0.010 (5)
C14′	0.0781 (7)	0.7909 (8)	0.3240 (3)	0.054 (5)	0.082 (7)	0.061 (5)	0.007 (5)	0.012 (5)	0.001 (6)

atom	*x*	*y*	*z*	*U*, Å^2	atom	*x*	*y*	*z*	*U*, Å^2
C15B′^{iv}	0.472 (3)	0.356 (3)	0.1989 (12)	4.4 (7)	C16A″^{vi}	0.068 (2)	0.953 (3)	0.2785 (11)	3.6 (6)
C15A′^{iii}	0.434 (1)	0.406 (1)	0.1767 (5)	6.2 (3)	C16A′^{v}	0.141 (1)	0.964 (1)	0.3051 (6)	4.4 (4)
C16B′^{vii}	0.094 (3)	0.964 (3)	0.2903 (15)	6.1 (10)					
H3^{c}	0.039 (7)	0.534 (7)	0.218 (3)		H3′	0.532 (7)	0.748 (7)	0.286 (3)	
H4	0.028 (7)	0.447 (7)	0.149 (3)		H4′	0.595 (7)	0.669 (7)	0.346 (3)	
H6	0.189 (7)	0.650 (7)	0.084 (3)		H6′	0.344 (7)	0.661 (7)	0.409 (3)	
H9	0.359 (7)	0.802 (7)	0.092 (3)		H9′	0.134 (7)	0.601 (7)	0.395 (3)	
H10	0.379 (7)	0.868 (7)	0.023 (3)		H10′	0.069 (7)	0.600 (7)	0.466 (3)	
H11	0.240 (7)	0.929 (7)	−0.011 (3)		H11′	0.065 (7)	0.737 (7)	0.510 (3)	
H12	0.091 (7)	0.925 (7)	0.027 (3)		H12′	0.156 (7)	0.872 (7)	0.488 (3)	
H13	0.081 (7)	0.856 (7)	0.095 (3)		H13′	0.231 (7)	0.882 (7)	0.415 (3)	
H141	0.360 (7)	0.909 (7)	0.167 (3)		H141′	0.040 (7)	0.765 (7)	0.299 (3)	
H142	0.263 (7)	0.956 (7)	0.152 (3)		H142′	0.057 (7)	0.765 (7)	0.350 (3)	
H161	0.158 (7)	1.034 (7)	0.211 (3)		H151′	0.047 (7)	0.914 (7)	0.351 (3)	
H162	0.200 (7)	1.066 (7)	0.253 (3)		H152′	−0.002 (7)	0.907 (7)	0.309 (3)	

B. Positional and Thermal Parameters and Their Estimated Standard Deviations for [Cu(cbpO)]^{a}

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.2263 (2)	0.7636 (2)	0.24967 (8)	0.037 (1)	0.033 (1)	0.023 (1)	−0.002 (2)	−0.009 (1)	0.002 (1)
Cl1	0.0902 (5)	0.4673 (5)	0.0568 (2)	0.097 (6)	0.060 (4)	0.047 (3)	−0.010 (4)	−0.015 (4)	−0.023 (3)
Cl2	0.5280 (5)	0.5898 (5)	0.4290 (2)	0.076 (5)	0.092 (5)	0.052 (4)	0.016 (4)	−0.030 (3)	0.023 (4)
O1	0.1243 (9)	0.677 (1)	0.2298 (4)	0.036 (9)	0.051 (8)	0.013 (6)	−0.012 (9)	−0.003 (6)	−0.001 (7)
O1′	0.3543 (9)	0.796 (1)	0.2722 (5)	0.021 (8)	0.048 (9)	0.058 (9)	−0.020 (8)	−0.026 (7)	0.007 (8)
O2	0.1461 (12)	0.933 (1)	0.2524 (5)	0.070 (12)	0.034 (8)	0.060 (10)	0.006 (9)	−0.008 (9)	0.004 (9)
N1	0.255 (1)	0.804 (1)	0.1854 (5)	0.05 (1)	0.030 (9)	0.017 (8)	−0.017 (10)	0.004 (8)	0.003 (8)
N1′	0.174 (1)	0.759 (1)	0.3125 (5)	0.04 (1)	0.016 (8)	0.034 (9)	−0.009 (9)	0.005 (8)	−0.011 (8)
C1	0.165 (2)	0.669 (2)	0.1500 (7)	0.09 (2)	0.03 (1)	0.031 (12)	−0.03 (1)	−0.013 (13)	0.015 (11)
C2	0.116 (2)	0.637 (2)	0.1906 (6)	0.04 (1)	0.06 (1)	0.019 (10)	−0.02 (1)	−0.015 (10)	−0.005 (11)
C3	0.068 (2)	0.546 (2)	0.1867 (7)	0.06 (2)	0.06 (2)	0.027 (12)	−0.03 (1)	0.012 (12)	−0.003 (12)
C4	0.057 (2)	0.497 (2)	0.1465 (7)	0.03 (1)	0.05 (1)	0.045 (13)	−0.02 (1)	−0.001 (12)	−0.002 (12)
C5	0.103 (2)	0.530 (2)	0.1089 (7)	0.13 (2)	0.05 (1)	0.020 (11)	−0.02 (2)	−0.026 (13)	−0.012 (11)
C6	0.153 (2)	0.617 (2)	0.1083 (7)	0.09 (2)	0.05 (1)	0.020 (11)	−0.04 (1)	−0.009 (13)	−0.000 (11)

Table II (*Continued*)

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C7	0.211 (2)	0.766 (2)	0.1498 (6)	0.13 (2)	0.03 (1)	0.007 (9)	−0.01 (2)	−0.002 (12)	0.010 (10)
C8	0.224 (2)	0.812 (2)	0.1018 (7)	0.08 (2)	0.03 (1)	0.022 (11)	0.00 (1)	−0.001 (12)	−0.001 (11)
C9	0.310 (2)	0.815 (2)	0.0791 (8)	0.03 (1)	0.09 (2)	0.055 (15)	0.05 (1)	0.005 (12)	0.010 (15)
C10	0.313 (2)	0.861 (2)	0.0378 (7)	0.05 (2)	0.11 (2)	0.029 (12)	0.05 (2)	0.012 (12)	0.025 (14)
C11	0.229 (2)	0.901 (2)	0.0184 (7)	0.09 (2)	0.08 (2)	0.027 (12)	0.00 (2)	0.017 (13)	0.031 (13)
C12	0.146 (2)	0.896 (2)	0.0417 (8)	0.06 (2)	0.08 (2)	0.046 (13)	0.01 (2)	−0.026 (12)	0.032 (13)
C13	0.137 (2)	0.852 (2)	0.0845 (7)	0.05 (2)	0.08 (2)	0.036 (12)	0.04 (1)	−0.012 (12)	−0.008 (13)
C14	0.303 (2)	0.900 (2)	0.1840 (7)	0.08 (2)	0.04 (1)	0.031 (12)	−0.04 (1)	−0.002 (13)	0.019 (11)
C15	0.233 (2)	0.986 (2)	0.1911 (11)	0.03 (2)	0.02 (1)	0.173 (27)	−0.02 (1)	0.017 (18)	0.040 (15)
C16	0.200 (2)	1.005 (2)	0.2357 (8)	0.12 (2)	0.09 (2)	0.066 (15)	−0.05 (2)	0.073 (14)	−0.049 (15)
C1′	0.333 (1)	0.721 (1)	0.3470 (6)	0.01 (1)	0.03 (1)	0.026 (9)	0.01 (1)	0.000 (8)	−0.022 (9)
C2′	0.388 (1)	0.749 (2)	0.3102 (6)	0.04 (1)	0.04 (1)	0.029 (10)	−0.01 (1)	−0.016 (9)	−0.013 (11)
C3′	0.487 (1)	0.732 (2)	0.3103 (6)	0.03 (1)	0.04 (1)	0.034 (11)	−0.00 (1)	−0.007 (9)	0.009 (11)
C4′	0.530 (2)	0.684 (2)	0.3481 (7)	0.05 (2)	0.04 (1)	0.040 (13)	−0.02 (1)	0.001 (12)	−0.001 (12)
C5′	0.472 (1)	0.654 (1)	0.3829 (7)	0.02 (1)	0.04 (1)	0.044 (12)	0.01 (1)	−0.018 (10)	−0.000 (11)
C6′	0.381 (2)	0.674 (1)	0.3854 (7)	0.04 (1)	0.03 (1)	0.032 (11)	−0.01 (1)	−0.010 (10)	0.001 (10)
C7′	0.234 (2)	0.741 (1)	0.3499 (6)	0.08 (2)	0.01 (1)	0.019 (9)	−0.01 (1)	0.010 (11)	−0.011 (10)
C8′	0.182 (1)	0.741 (2)	0.3959 (7)	0.02 (1)	0.06 (1)	0.039 (11)	−0.01 (1)	−0.004 (10)	−0.007 (13)
C9′	0.135 (2)	0.661 (2)	0.4115 (7)	0.07 (2)	0.06 (1)	0.036 (12)	−0.04 (1)	0.037 (12)	−0.015 (12)
C10′	0.093 (2)	0.663 (2)	0.4527 (8)	0.07 (2)	0.09 (2)	0.040 (14)	−0.06 (2)	0.007 (14)	0.008 (15)
C11′	0.098 (2)	0.744 (2)	0.4796 (7)	0.07 (2)	0.08 (2)	0.034 (12)	−0.02 (2)	0.003 (12)	−0.001 (15)
C12′	0.144 (2)	0.823 (2)	0.4648 (8)	0.08 (2)	0.09 (2)	0.045 (14)	0.01 (2)	−0.008 (14)	−0.032 (14)
C13′	0.192 (2)	0.825 (2)	0.4223 (7)	0.10 (2)	0.05 (1)	0.032 (13)	−0.02 (2)	0.026 (14)	−0.005 (12)
C14′	0.070 (1)	0.781 (2)	0.3157 (7)	0.02 (1)	0.06 (2)	0.049 (13)	0.02 (1)	−0.004 (10)	−0.021 (12)
C15′	0.054 (2)	0.887 (2)	0.3195 (8)	0.10 (2)	0.10 (2)	0.047 (15)	0.05 (2)	0.026 (15)	0.029 (16)
C16′	0.121 (2)	0.952 (2)	0.3006 (10)	0.15 (3)	0.08 (2)	0.072 (19)	0.06 (2)	−0.029 (19)	−0.025 (18)

atom	x	y	z	atom	x	y	z
H3[c]	0.00 (1)	0.52 (1)	0.215 (6)	H3′	0.53 (1)	0.75 (1)	0.281 (6)
H4	−0.00 (1)	0.44 (1)	0.150 (6)	H4′	0.57 (1)	0.67 (1)	0.346 (6)
H6	0.18 (1)	0.62 (1)	0.083 (6)	H6′	0.35 (1)	0.68 (1)	0.410 (6)
H9	0.36 (1)	0.78 (1)	0.087 (6)	H9′	0.11 (1)	0.61 (1)	0.396 (6)
H10	0.38 (1)	0.86 (1)	0.023 (6)	H10′	0.05 (1)	0.61 (1)	0.462 (6)
H11	0.23 (1)	0.94 (1)	−0.011 (6)	H11′	0.08 (1)	0.75 (1)	0.513 (6)
H12	0.09 (1)	0.93 (1)	0.035 (6)	H12′	0.14 (1)	0.88 (1)	0.478 (6)
H13	0.08 (1)	0.86 (1)	0.106 (6)	H13′	0.23 (1)	0.88 (1)	0.417 (6)
H141	0.36 (1)	0.91 (1)	0.154 (6)	H141′	0.03 (1)	0.76 (1)	0.278 (6)
H142	0.38 (1)	0.91 (1)	0.211 (6)	H142′	0.02 (1)	0.74 (1)	0.343 (6)
H151	0.13 (1)	0.97 (1)	0.167 (6)	H151′	−0.04 (1)	0.89 (1)	0.304 (6)
H152	0.28 (1)	1.03 (1)	0.183 (6)	H152′	0.03 (1)	0.90 (1)	0.341 (6)
H161	0.16 (1)	1.08 (1)	0.237 (6)	H161′	0.18 (1)	0.96 (1)	0.307 (6)
H162	0.26 (1)	1.03 (1)	0.252 (7)	H162′	0.06 (1)	1.02 (1)	0.303 (6)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] Occupancy: (i) C15A, 0.667; (ii) C15B, 0.333; (iii) C15A′, 0.75; (iv) C15B′, 0.25; (v) C16A′, 0.45; (vi) C16A″, 0.30; (vii) C16B, 0.25. [c] U for all hydrogen atoms is 5.0 Å^2.

there were 1840 and 3397, respectively, with $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[25] These data were used in the final refinement of the structural parameters.

Structure Determination. [Co(cbpO)]. The position of the cobalt atom was determined from a three-dimensional Patterson function. The intensity data were phased sufficiently well by these positional coordinates to permit location of the other nonhydrogen atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described.[7] Slight positional disorder was observed in the alkyl-chain atoms, and for these the occupancy factors were refined. Anisotropic temperature factors were introduced for all nonhydrogen atoms, except for those exhibiting positional disorder. Further difference functions permitted location of the hydrogen atoms, which were included in the refinement for three cycles of least-squares and then held fixed.

[Cu(cbpO)]. Despite the somewhat different structures of the two complexes in detail, [Cu(cbpO)] and [Co(cbpO)] are sufficiently similar to the nearly isomorphous. Therefore solution of the [Cu(cbpO)] structure was carried out by refinement of the [Co(cbpO)] atom positions. There was evidence of slight positional disorder in the alkyl chains, as observed in the cobalt complex, but in this case the disorder could not be fully resolved into partially occupied positions. This is presumably because these positions are quite close to each other. Thus, the anisotropic thermal parameters reflect a slight disorder of these flexible chains.

The models converged with R = 5.8% and R_w = 6.8% for [Cu(cbpO)] and R = 6.1% and R_w = 7.2% for [Co(cbpO)]. A structure factor calculation with all observed and unobserved reflections include (no refinement) gave R = 7.0% and 7.9% for the two complexes, respectively; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference function was featureless. Tables of the observed and calculated structure factors are available.[26] The principal programs used are as previously described.[7]

Discussion

Visible–Near-Infrared Spectra. Copper Complex. The copper complex has a very broad absorption band in the 18 000–13 000-cm^{-1} range. In dichloromethane there is a maximum at 16 400 cm^{-1} and a shoulder at 14 500 cm^{-1}. In pyridine there is a broad maximum at 14 500 cm^{-1}. This latter spectrum is similar to those of Cu(mbpN) and Cu(cbpS) in the solid state and dichloromethane and pyridine solution. Both these compounds have been shown to have a distorted square-pyramidal geometry in the solid state.[10,11] The spectra

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(25) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(26) Supplementary material.

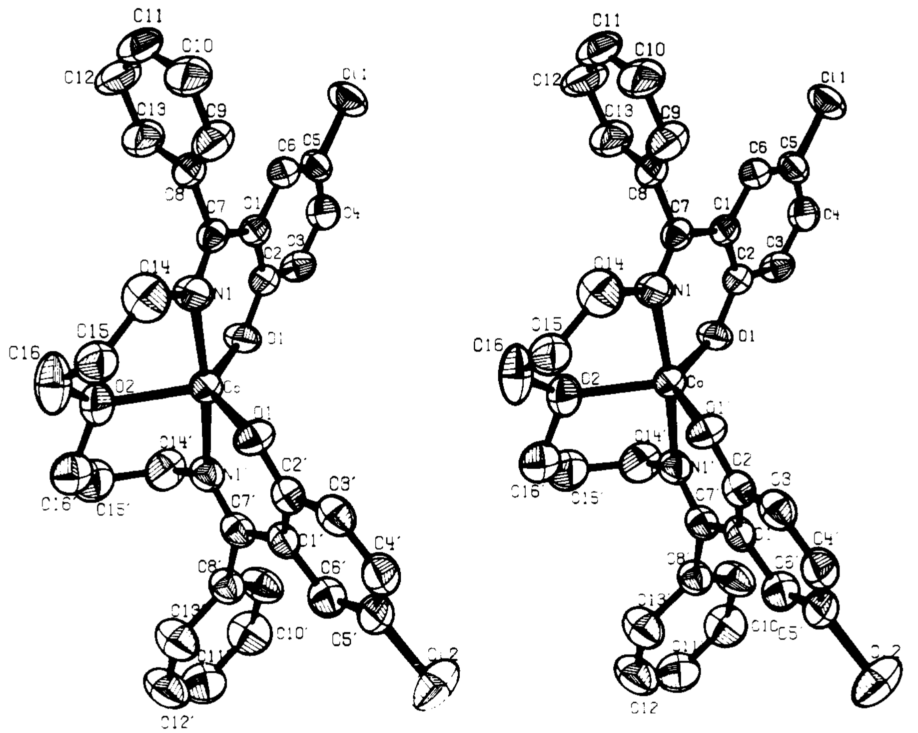

Figure 1. Stereopair view of the [Co(cbpO)] molecule.

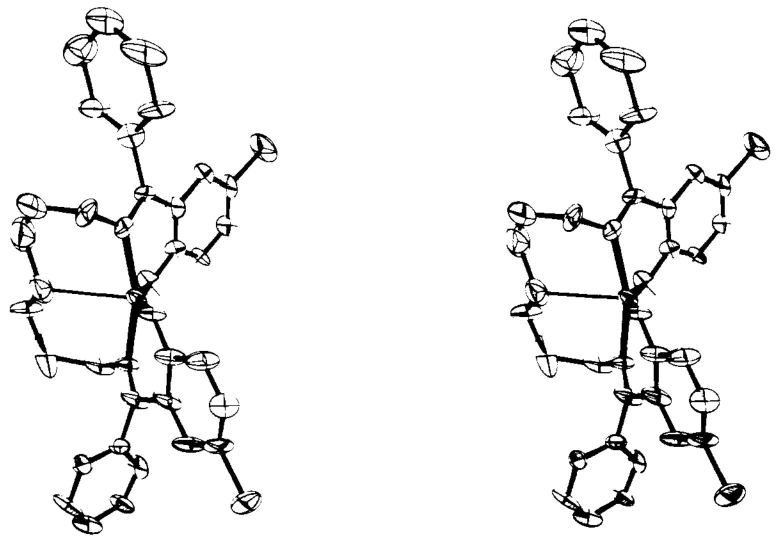

Figure 2. Stereopair view of the [Cu(cbpO)] molecule. The atom labels are analogous to those of the cobalt complex.

are not greatly different from those expected for equivalent four-coordinated complexes. Somewhat similar spectra are observed with a series of copper(II) complexes with closely related cbp ligands when these complexes have the most important features of the Cu(cbpO) geometry (vide infra): four strongly bonded ligands in pseudotetrahedral environment distorted toward tetrahedral.[27] The [Cu(cbpO)] spectrum is also similar to those of related Cu(cbpX) complexes containing a weakly bonded fifth ligand, which are also listed in Table I for comparison.[9-11,32,33] These spectra are quite different from that of trigonal bipyramidal [[Cu(2,3-mmbp)]$\cdot$2H_2O]$_\infty$ in which all five metal-ligand bonds are relatively strong (H_2[mmbp] = *N,N'*-bis[(2-hydroxy-5-methylphenyl)(4-methylphenyl)methylene]-3-azaheptane-1,6-diamine). No pyridine adduct has been isolated from solution, and it would appear that the solution spectral change is due to some solvent effect on the relative intensities of the component bands rather than a change from five- to six-coordination.

Cobalt Complex. The cobalt complex has spectral bands at 15 000, 13 500 (shoulder), and 6600 cm^{-1} in the solid state and a similar spectrum is dichloromethane solution. These spectra are consistent with compounds' five-coordinate geometry and very similar to the spectra reported for Co(cbpN)[9] and Co(cbpS),[9] which indicates that these two compounds are also five-coordinated. In pyridine solution, a spectrum typical of six-coordinate cobalt(II) is obtained, and the adduct [Co(cbpO)$\cdot$py] can be isolated from the pyridine solution. This compound has a solid-state spectrum (a maximum at 9600 cm^{-1}) similar to that of the pyridine solution.

Molecular Structures

Figure 1 shows a stereopair view of the [Co(cbpO)] complex. There is positional disorder in the alkyl chain of the ether linkages (see above), but only one of these positions is shown in the figures. Figure 2 shows a stereopair view of the [Cu-

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(27) Chia, P. C.; Freyberg, D. P.; Mockler, G. M.; Sinn, E. *Inorg. Chem.* **1977**, *16*, 254.

Table III. Bond Distances and Closest Intermolecular Contacts (Å)

	M = Cu	M = Co		M = Cu	M = Co
M–O(1)	1.934 (6)	1.927 (3)	C(14)–C(15B)	1.56 (2)	1.46 (2)
M–O(1′)	1.944 (6)	1.964·(3)	C(15A)–C(16)	1.42 (2)	1.52 (1)
M–O(2)	2.575 (7)	2.124 (3)	C(15B)–C(16)	1.42 (2)	1.39 (2)
M–N(1)	2.020 (7)	2.113 (4)	C(1′)–C(2′)	1.39 (1)	1.413 (6)
M–N(1′)	2.004 (7)	2.101 (4)	C(1′)–C(6′)	1.45 (1)	1.414 (7)
O(1)–C(2)	1.28 (1)	1.310 (5)	C(1′)–C(7′)	1.42 (1)	1.458 (6)
O(1′)–C(2′)	1.36 (1)	1.296 (5)	C(2′)–C(3′)	1.41 (1)	1.430 (6)
O(2)–C(16)	1.34 (1)	1.450 (7)	C(3′)–C(4′)	1.41 (1)	1.372 (7)
O(2)–C(16A′)	1.47 (2)	1.48 (1)	C(4′)–C(5′)	1.39 (1)	1.364 (7)
N(1)–C(7)	1.31 (1)	1.293 (6)	C(5′)–C(6′)	1.31 (1)	1.385 (7)
N(1)–C(14)	1.47 (1)	1.491 (6)	C(5′)–Cl(2)	1.778 (9)	1.758 (5)
N(1′)–N(7′)	1.39 (1)	1.316 (6)	C(7′)–C(8′)	1.55 (1)	1.514 (6)
N(1′)–N(14′)	1.50 (1)	1.430 (6)	C(8′)–C(9′)	1.35 (1)	1.378 (7)
C(1)–C(2)	1.46 (1)	1.421 (6)	C(8′)–C(13′)	1.39 (1)	1.383 (7)
C(1)–C(6)	1.43 (1)	1.410 (6)	C(9′)–C(10′)	1.36 (2)	1.381 (7)
C(1)–C(7)	1.47 (1)	1.466 (6)	C(10′)–C(11′)	1.35 (2)	1.354 (8)
C(2)–C(3)	1.41 (1)	1.421 (6)	C(11′)–C(12′)	1.34 (2)	1.361 (8)
C(3)–C(4)	1.36 (1)	1.371 (7)	C(12′)–C(13′)	1.43 (2)	1.386 (8)
C(4)–C(5)	1.38 (2)	1.381 (7)	C(14′)–C(15A′)	1.49 (2)	
C(5)–Cl(1)	1.76 (1)	1.748 (5)	C(14′)–C(15B′)	1.49 (2)	
C(5)–C(6)	1.37 (2)	1.373 (7)	C(15A′)–C(16A′)	1.41 (2)	2.32 (2)
C(7)–C(8)	1.57 (1)	1.513 (6)	C(15B′)–C(16B′)	1.41 (2)	
C(8)–C(9)	1.38 (2)	1.365 (7)	C(15A′)–C(16A″)		2.11 (3)
C(8)–C(13)	1.42 (1)	1.348 (7)	O(2)–C(16A″)		1.42 (2)
C(9)–C(10)	1.37 (2)	1.395 (7)	O(2)–C(16B′)		1.37 (3)
C(10)–C(11)	1.41 (2)	1.342 (8)	Cl(1)–C(11)		3.532 (6)
C(11)–C(12)	1.36 (2)	1.332 (8)	Cl(1)–C(10′)	3.545 (8)[a]	
C(12)–C(13)	1.40 (2)	1.395 (7)	O(1)–C(14′)	3.311 (9)[b]	
C(14)–C(15A)	1.56 (2)	1.45 (1)	C(2)–C(14′)	3.258 (11)[b]	

[a] $x, 1 - y, z - {}^1/_2$. [b] $-x, y, {}^1/_2 - z$.

(cbpO)] complex. The atom names are analogous to those used in the cobalt complex. The final positional and thermal parameters for the two complexes are given in Table II. Tables III and IV contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Both of these complexes consist of separated monomeric molecules, the nearest intermolecular distances being 3.545 (8) and 3.532 (6) Å for [Cu(cbpO)] and [Co(cbpO)], respectively. There is some positional disorder in the alkyl chains (vide supra and Table II).

Although the complexes are nearly isomorphous, there are significant differences for the two structures, in keeping with the different geometrical requirements of the two metals. Each of the complexes are five-coordinate, with the ether oxygens forming the fifth and weakest bond. However in the copper complex the bond is much weaker (2.575 (4) Å) than in the cobalt analogue (2.124 (3) Å). The copper to ether bond, Cu–O(2), is 0.64 Å longer than the average Cu–O bonds with the phenolic oxygens. This contrasts with some of the copper complexes of several related ligands. The Cu–X bonds are 2.686 (1) and 2.374 (10) Å, respectively, for X = S and X = NH in [Cu(cbpS)] and [Cu(mbpN)], where mbpX is equivalent to cbpX with the phenyl ring Cl atoms replaced with CH_3. In each case this represents a smaller relative elongation compared to the other four normal (strong) metal–ligand bonds. The elongation of Cu–X in [Cu(mbpN)] is 0.41 Å over the average distance of 1.967 Å for the other two Cu–N bonds in the complex. The elongation of the Cu–S bond is about the same when the greater size of the sulfur atom is taken into account: from a series of literature values, the "normal" distance for a short Cu–S bond in a five-coordinated complex is about 2.31 Å.[10,28-30]

[Cu(cbpO)] and [Cu(cbpS)] are chemically identical except for the fifth donor atom. Therefore a direct comparison of copper–thioether sulfur and -ether oxygen bonding can be made from the two structures. Given elongation of about 0.38 Å above "normal" in [Cu(cbpS)] and of about 0.64 Å in [Cu(cbpO)], the Cu–O bond must be considered weaker, although both complexes have sufficient metal–ligand interaction with the fifth donor atom to be classed as five-coordinate. The relatively shorter Cu–S distance, when the greater size of the sulfur atom is taken into account, demonstrates that the coordination of copper to a thioether sulfur is somewhat stronger than to the analogous ether group.

In contrast with the [Cu(cbpO)] structure, the bond between cobalt and the ether oxygen atom in [Co(cbpO)] is elongated only 0.18 Å over the Co–O bonds with the phenolic oxygens. The elongation is 0.10 Å compared to the average of the other four cobalt–ligand bonds.

The copper complex contains the metal atom in a very distorted square pyramid whose apex is formed by the Cu–O bond to the ether oxygen atom. The O_2N_2 base of the square pyramid is distorted so as to give some trigonal-bipyramidal character to the geometry, the N atoms being raised above (0.35 Å) the base and the Cu atom and the O atom below it (0.06 and 0.35 Å, respectively). The elevation of 0.06 Å for the Cu atom is quite small: if the apical Cu–O bond were not present, the copper environment would approximate a flattened tetrahedron. The metal environment in [Co(cbpO)] is distorted trigonal bipyramidal with the two Co–N bonds axial andthe three Co–O bonds equatorial. The Co–O bond to the ether oxygen is relatively strong (2.124 (3) Å) in contrast with the [Cu(cbpO)] analogue. The observation of metal to ether oxygen bonding at all in these complexes contrasts with the apparent inability to form such bonds in a series of related salicylaldimine complexes: the only significant difference in the ligands in this context is the electron-withdrawing power

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Table IV. Bond Angles (Deg)

	M = Cu	M = Co		M = Cu	M = Co
O(1)–M–O(1′)	155.3 (3)	129.4 (2)	N(1)–C(14)–C(15B)	112.1 (9)	106.6 (9)
O(1)–M–O(2)	103.9 (3)	115.6 (1)	C(14)–C(15A)–C(16)	119 (1)	116.6 (7)
O(1)–M–N(1)	92.8 (3)	88.5 (1)	C(14)–C(15B)–C(16)	119 (1)	125 (2)
O(1)–M–N(1′)	88.7 (3)	90.4 (1)	O(2)–C(16)–C(15A)	119 (1)	113.8 (5)
O(1′)–M–O(2)	100.6 (3)	114.6 (1)	O(2)–C(16)–C(15B)	114 (1)	118.7 (9)
O(1′)–M–N(1)	93.0 (3)	98.2 (2)	C(2′)–C(1′)–C(6′)	118.4 (9)	119.7 (4)
O(1′)–M–N(1′)	92.8 (3)	88.5 (1)	C(2′)–C(1′)–C(7′)	123.3 (9)	123.5 (4)
O(2)–M–N(1)	82.9 (3)	88.3 (2)	C(6′)–C(1′)–C(7′)	118.3 (9)	116.8 (4)
O(2)–M–N(1′)	80.3 (3)	85.2 (1)	O(1′)–C(2′)–C(1′)	125.7 (9)	127.4 (4)
N(1)–M–N(1′)	163.0 (3)	172.1 (2)	O(1′)–C(2′)–C(3′)	113.4 (9)	115.4 (4)
M–O(1)–C(2)	125.9 (6)	129.8 (3)	C(1′)–C(2′)–C(3′)	120.9 (8)	117.2 (4)
M–O(1′)–C(2′)	118.0 (6)	127.8 (3)	C(2′)–C(3′)–C(4′)	118.5 (9)	121.3 (4)
M–O(2)–C(16)	113.1 (8)	117.7 (3)	C(3′)–C(4′)–C(5′)	118 (1)	120.4 (5)
M–O(2)–C(16A′)	107.5 (7)	114.3 (5)	Cl(2)–C(5′)–C(4′)	117.2 (8)	119.9 (4)
M–N(1)–C(7)	122.2 (7)	127.4 (3)	Cl(2)–C(5′)–C(6′)	118.1 (9)	119.1 (4)
M–N(1)–C(14)	112.1 (6)	113.2 (3)	C(4′)–C(5′)–C(6′)	124.7 (9)	121.0 (5)
C(7)–N(1)–C(14)	122.7 (8)	119.0 (4)	C(1′)–C(6′)–C(5′)	118.7 (9)	120.0 (4)
M–N(1′)–C(7′)	120.6 (7)	127.9 (3)	N(1′)–C(7′)–C(1′)	124.0 (8)	121.9 (4)
M–N(1′)–C(14′)	115.6 (6)	112.3 (3)	N(1′)–C(7′)–C(8′)	113.9 (9)	119.5 (4)
C(7′)–N(1′)–C(14′)	123.8 (8)	119.7 (4)	C(1′)–C(7′)–C(8′)	122.1 (8)	118.7 (4)
C(2)–C(1)–C(6)	120.1 (9)	118.7 (4)	C(7′)–C(8′)–C(9′)	122.5 (9)	122.0 (4)
C(2)–C(1)–C(7)	119.2 (9)	123.3 (4)	C(7′)–C(8′)–C(13′)	116.0 (9)	119.1 (4)
C(6)–C(1)–C(7)	119.4 (9)	118.0 (4)	C(9′)–C(8′)–C(13′)	121.2 (9)	118.8 (4)
O(1)–C(2)–C(1)	124.8 (9)	125.3 (4)	C(8′)–C(9′)–C(10′)	120 (1)	120.1 (5)
O(1)–C(2)–C(3)	118.9 (9)	117.2 (4)	C(9′)–C(10′)–C(11′)	121 (1)	121.4 (5)
C(1)–C(2)–C(3)	115.5 (9)	117.5 (4)	C(10′)–C(11′)–C(12′)	119 (1)	118.7 (5)
C(2)–C(3)–C(4)	123.1 (9)	122.2 (5)	C(11′)–C(12′)–C(13′)	123 (1)	121.6 (5)
C(3)–C(4)–C(5)	119.5 (9)	119.6 (5)	C(8′)–C(13′)–C(12′)	115 (1)	119.3 (5)
C(4)–C(5)–C(6)	122.6 (9)	120.4 (5)	N(1′)–C(14′)–C(15′)	109 (1)	
Cl(1)–C(5)–C(4)	120.2 (9)	119.1 (4)	C(14′)–C(15′)–C(16′)	120 (1)	
Cl(1)–C(5)–C(6)	116.7 (9)	120.5 (4)	O(2)–C(16′)–C(15′)	116 (1)	
C(1)–C(6)–C(5)	118.1 (9)	121.5 (4)	C(16)–O(2)–C(16′)		110.7 (9)
N(1)–C(7)–C(1)	123.7 (8)	122.3 (4)	M–O(2)–C(16A″)		125 (1)
N(1)–C(7)–C(8)	119.2 (9)	121.7 (4)	M–O(2)–C(16B′)		117.7 (3)
C(1)–C(7)–C(8)	115.8 (8)	116.1 (4)	C(16)–O(2)–C(16A′)		108.9 (6)
C(7)–C(8)–C(9)	124 (1)	123.1 (4)	C(16)–O(2)–C(16A″)		116.2 (1)
C(7)–C(8)–C(13)	111 (1)	119.2 (4)	C(16)–O(2)–C(16B′)		113.1 (2)
C(9)–C(8)–C(13)	124 (1)	117.7 (5)	N(1′)–C(14′)–C(15A′)		
C(8)–C(9)–C(10)	119 (1)	120.7 (5)	N(1′)–C(14′)–C(15B′)		
C(9)–C(10)–C(11)	120 (1)	120.2 (5)	C(14′)–C(15A′)–C(16A′)		
C(10)–C(11)–C(12)	119 (1)	119.7 (5)	C(14′)–C(15A′)–C(16A″)		
C(11)–C(12)–C(13)	125 (1)	120.5 (6)	O(2)–C(16A′)–C(15A′)		114.5 (6)
C(8)–C(13)–C(12)	113 (1)	121.2 (5)	O(2)–C(16A″)–C(15A′)		123.7 (8)
N(1)–C(14)–C(15A)	112.1 (9)	117.5 (5)	O(2)–C(16B′)–C(15B′)		

of the phenyl chlorine in cbpX. [Co(cbpO)] is strongly five-coordinated and readily forms a six-coordinated pyridine adduct, while [Cu(cbpO)] is very weakly five-coordinated and does not readily increase the coordination number, even in pyridine solution.

The two cbpO complexes, especially [Cu(cbpO)], represent the long-chain (small *n*) form of the complexes [M(tsb)] with ligands 3, where R = $(CH_2)_n$.[13,14] The phenyl oxygen atoms are trans about the metal, as are the imine nitrogens. The trans arrangement in monomeric, long-chain, M(tsb) complexes (tsb = 3) mimics the trans structure of the bis(bidentate) Schiff base complexes.[31] If the weakly bound ether oxygen were completely uncoordinated, the $MN(CH_2)_3O(CH_2)_3N$ linkage would form a 10-membered ring. An examination of the structure suggests that a similar arrangement of the ligand atoms could be retained if the ether oxygen atom were replaced by a CH_2 group and moved ≥0.5 Å from the metal atom. The [Cu(cbpO)] structure is therefore a model (except for the weak Cu–O bond) for the [M(tsb)] complexes, with M = Ni, Cu, R = $(CH_2)_n$, and $n \geq 7$, which contain rings of 10 or more atoms. It seems likely that the [Cu(cbpO)] arrangement, or R = $(CH_2)_n$, with $n = 7$ represents the minimum chain length for which trans complexes of copper and nickel with approximately square-planar geometries can be formed. When the chain in mbpN is lengthened to $N(CH_2)_3NH(CH_2)_4N$ in [Cu(3,4-cbpN)], the geometry remains square pyramidal with an elongated Cu–N bond (2.29 Å),[32] but when the chain is shortened to $N(CH_2)_2NH(CH_2)_3N$ in $[[Cu(2,3\text{-mmbpN})]\cdot 2H_2O]_\infty$ the five-coordinated Cu(II) species is in a trigonal-bipyramidal environment, with a relatively much stronger Cu–N bond (2.077 Å).[33] The latter complex is an example of sterically enforced tbp geometry and Cu–N bond shortening, since the ligand 2,3-mmbpN differs importantly from cbpN and mbpN in the methylene chain length and unimportantly in its ring methyl substitutents. Thus $n = 7$ appears to be the minimum chain length of $(CH_2)_n$ that allows trans arrangement of the donor atoms without requiring great distortion from planarity. The short-chain M(tsb) complexes have a well-known cis arrangement of the donor atoms.[31,34] The consideration of monomeric long-chain M(tsb) complexes is relevant because such complexes have been shown to foorm with *n* values up to 12, when rings of 15-member atoms are formed,[13,14] even though polymeric structures with no NMNR rings had been variously proposed.[35,36] Even when

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the monomeric [Ni(tsb)] molecules associate in solution, it is reversible via intermonomer bonds, rather than via the two ends of tsb ligands acting as bidentates on two different metals.

Although [Cu(cbpO)], with its weak Cu–O ether linkage, can model the behavior of four-coordinated Cu^{II} and Ni^{II} complexes of type **3** ligands, it is unlikely that [Ni(cbpO)] would be equally appropriate. Comparison of complexes with ligand **1** indicates a generally much stronger M–X bonding in the Ni^{II} complexes than in their Cu^{II} analogues. This difference in structural behavior between d^8 and d^9 (and the equally dramatic difference between d^7 and d^9) is readily explained in terms of the crystal field stabilizing energies (CFSE) of these electronic configurations in various ligand environments.[7,11]

Magnetic Moments. The observed value of 1.80 μ_B for [Cu(cbpO)] is typical for Cu(II) in an orbitally nondegenerate ground state and corresponds to an effective *g* value of 2.08. In [Co(cbpO)], the moment, 4.78 μ_B, indicates high-spin d^7, which is the only result compatible with the observed trigonal-bipyramidal structure. Five-coordinated low-spin d^7 would gain considerable CFSE by a tetragonal distortion which elongates the M–X bond, as would d^9. This strong stabilization does not apply for high-spin d^7, and electrostatic repulsion is important in forcing the observed trigonal-bipyramidal environment of [Co(cbpO)].

Acknowledgment. Support received for instrumentation under NSF Grant Gp-41679 is gratefully acknowledged.

Registry No. Cu(cbpO), 76136-67-9; Co(cbpO), 76136-66-8; 5-chloro-2-hydroxybenzophenone, 85-19-8; bis(3-aminopropyl) ether, 2157-24-6.

Supplementary Material Available: Tables of observed and calculated structure factors and calculated least-squares planes (24 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, University of Virginia, Charlottesville, Virginia 22901, and William Marsh Rice University, Houston, Texas 77001

Electronic and Molecular Structure of Variable-Spin Metal Complexes. Spin State Dependent Crystal and Molecular Structures of $[Fe^{III}(5\text{-}OCH_3Salmeen)_2]PF_6$ ($S = {}^5/_2$), $[Fe^{III}(3\text{-}OCH_3Salmeen)_2]PF_6$ ($S = {}^1/_2$), and $[Fe^{III}(5\text{-}NO_2Salmeen)_2]PF_6$ ($S = {}^1/_2$)

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Received August 13, 1980

Spin state dependent crystal structure determinations of three six-coordinate $3d^5$ complexes of the $[Fe^{III}(X\text{-}Salmeen)_2]PF_6$ series of spin-equilibrium compounds (X = 5-OCH_3, 3-OCH_3, and 5-NO_2) are reported. At room temperature, the 5-OCH_3 derivative is a $S = {}^5/_2$ high-spin species ($\mu_{eff}{}^{295} = 5.75\ \mu_B$), whereas the 5-$NO_2$ ($\mu_{eff}{}^{295} = 2.58\ \mu_B$) and 3-$OCH_3$ ($\mu_{eff}{}^{298} = 3.20\ \mu_B$) derivatives are at or near the $S = {}^1/_2$ low-spin extreme. The structural determinations reveal that the three $[Fe^{III}(X\text{-}Salmeen)_2]^+$ cations possess the same general structure with an N_4O_2 donor atom set from two tridentate X–Salmeen ligands forming a distorted octahedron about the metal ion. In each case the terminal oxygen atoms occupy cis positions and the remaining four nitrogen atoms (two cis amines and two trans imines) complete the coordination sphere. The fine structural details for the three compounds reveal significant differences in the metal atom environments which can be largely attributed to the differing $S = {}^5/_2$ and $S = {}^1/_2$ spin states. For the $S = {}^5/_2$ complex, the average Fe–ligand bond length (δ_{av}) is longer by about 0.12 Å relative to the two $S = {}^1/_2$ cases, but the difference is not uniform: the Fe–N bonds vary far more [δ(amino) = 0.16 Å; δ(imino) = 0.16 Å] than the Fe–O bonds (δ = 0.02 Å). The spin state dependent structural changes observed for the $[Fe^{III}(X\text{-}Salmeen)_2]^+$ spin-equilibrium cations are compared to results previously reported for the electronically and structurally related hexadentate cations $[Fe^{III}(Sal)_2trien]^+$ and $[Fe^{III}(Acac)_2trien]^+$, for which δ_{av} is also 0.12–0.13 Å. In addition, variable-spin structural information now available for a variety of other $3d^5$ (and $3d^6$) spin-equilibrium compounds is also discussed in the context of the present results for the $[Fe^{III}(XSalmeen)_2]^+$ series of complexes. Crystal data for $[Fe^{III}(5\text{-}OCH_3Salmeen)_2]PF_6$: $FePF_6O_4N_4C_{22}H_{30}$, space group *Pbca*, $Z = 8$, $a = 10.263$ (3) Å, $b = 19.696$ (6) Å, $c = 26.768$ (6) Å, $V = 5411$ Å^3, $R = 5.1\%$ for 2712 reflections. Crystal data for $[Fe^{III}(3\text{-}OCH_3Salmeen)_2]PF_6$: $FePF_6O_4N_4C_{22}H_{30}$, space group $P2_1/c$, $Z = 4$, $a = 11.627$ (2) Å, $b = 10.412$ (5) Å, $c = 21.632$ (9) Å, $\beta = 92.62$ (2)°, $V = 2616$ Å^3, $R = 6.3\%$ for 2341 reflections. Crystal data for $[Fe^{III}(5\text{-}NO_2Salmeen)_2]PF_6$: $FePF_6O_6N_6C_{20}H_{24}$, space group *Pbcn*, $Z = 4$, $a = 12.609$ (7) Å, $b = 12.927$ (4) Å, $c = 16.122$ (2) Å, $V = 2628$ Å^3, $R = 4.7\%$ for 1648 reflections.

Introduction

The high-spin and low-spin magnetic isomeric forms of spin-equilibrium transition-metal complexes are now well-known to possess different average metal–ligand bond lengths, with the bonds of the low-spin form being significantly shorter.[2-12] Accordingly, spin-equilibrium species with ligands having bulky substituents and significient *inter*ligand steric interactions have a marked tendency to produce elongated metal–ligand bonds associated with the high-spin configuration. In addition, since such complexes lie near the (high spin) ⇄ (low spin) crossover, environmental effects such as changes in temperature,[13-16] pressure,[17,18] counterions,[9,19-21] occluded

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