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Cobalt Monothiobenzoate

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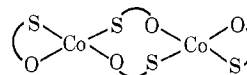
Monothiobenzoate ($C_6H_5COS^- = mtb^-$), long known as a complexing agent,^{1,2} has only recently aroused interest in structural studies, mainly because transition metal complexes with this ligand show varying stereochemistries. Besides chelating bidentate behavior (as in monomeric $Cr(mtb)_3$),³ the bifunctional ligating group may also effect binuclear complexation by bridging between two metal centers, as in $Ni_2(mtb)_4 \cdot C_2H_5OH$.⁴⁻⁶ Apart from a brief report⁷ mentioning their difficult formation and instability, cobalt(II) and -(III) monothiobenzoate complexes have been little investigated.

We have found that addition of aqueous $Kmtb$, in a stoichiometric ratio, to dilute aqueous cobalt(II) sulfate produces, besides large amounts of an ill-defined brown product, a mother liquor, which on careful concentration under vacuum deposits small amounts ($\sim 10\%$) of emerald green crystals of tetra(monothiobenzoato)dnicobalt(II), mp $134-135^\circ$. *Anal.* Calcd for $C_{28}H_{20}O_4S_4Co_2$: C, 50.45; H, 3.04; S, 19.24; Co, 17.68. Found: C, 50.26; H, 3.09; S, 19.09; Co, 17.40. The molecular weight (osmometric) in a 0.265% w/w solution in 1,2-dichloroethane was 680 ± 15 ; calcd, 667. The compound is stable in the solid state, but decomposes fairly rapidly in solution, which made it impossible to purify by recrystallization. The best specimens were collected by careful selection of fractions obtained from the mother liquors. The compound is moderately soluble in several polar and non-polar organic solvents, but only in 1,2-dichloroethane are fresh solutions sufficiently stable to allow reliable electronic spectra and molecular weight measurements to be recorded.

Attempts to prepare cobalt(III) monothiobenzoates from either the reaction of $Co_2(mtb)_4$ or cobalt(II) sulfate with excess monothiobenzoate and oxygen in the presence of carbon or that of cobalt(III) carbonate or oxalate complexes with $Hmtb$ or $Na(mtb)$ failed. These reactions gave mainly ill-defined products from which some small amounts of dibenzoyl disulfide, $(C_6H_5COS)_2$, could be recovered (mp $129-130^\circ$).⁸ Hence, in contrast to anionic 1,1-dithiolate ligands—

such as dithiocarbamates and dithiocarboxylates—monothiobenzoate seems unable to promote oxidation to Co(III) and rather resembles the mono- and dithiophosphinates, which stabilize Co(II) species in polynuclear coordination.⁹⁻¹²

The electronic spectrum in $C_2H_4Cl_2$ shows maxima at 6.5 ($\log \epsilon$ 1.28), 7.7 (1.30), and 16.25 (2.38) kK, together with shoulders at ~ 17.5 , ~ 15.0 , 14.1 (2.10), and 12.1 (1.05) kK. This is consistent with the presence of a pseudotetrahedral structure (average values of spectral parameters: $10Dq = -4.10$ kK, $B = 0.67$ kK) and suggests a chromophore of the type



Although other forms of bridging, e.g., through a three-coordinate sulfur atom, in which case the Co(II) ion would be five-coordinate, cannot be ruled out, they appear less likely in view of the typical pseudotetrahedral aspect of the electronic spectrum (Figure 1). Thus, a

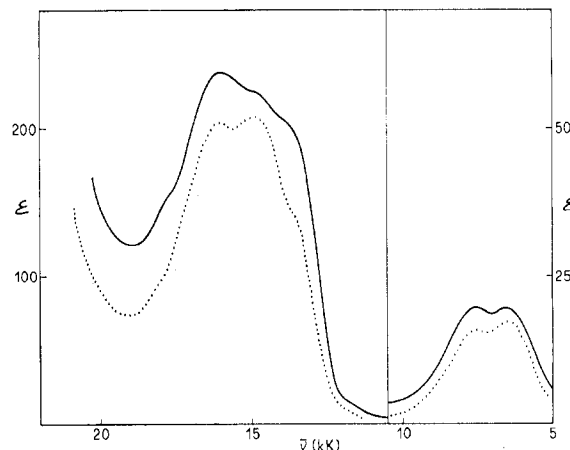


Figure 1.—Absorption spectrum of $Co_2(mtb)_4$: —, in $C_2H_4Cl_2$ solution; ····, unpolarized crystal spectrum (arbitrary ordinate scale).

structural similarity to the double-bridged polynuclear structures found among some phosphinato and mono- and dithiophosphinato complexes of Co(II) and Zn(II) might be expected. However, in the present case molecular weight data imply the presence of only the dimer, and the constancy of the ϵ data, which follow Beer's law over the range 10^{-5} – 10^{-2} M in $C_2H_4Cl_2$, seems to exclude any other form of association.

There are further electronic transitions in the uv spectrum, with maxima at 41.6 kK ($\log \epsilon$ 4.55) preceded by shoulders at 19.2, 21.3, 30.0, 33.4, and 37.0 kK. The electronic spectrum in $CHCl_3$ (although instability

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in this solvent makes the spectrum less reliable) is quite similar to that in $C_2H_4Cl_2$, as are also the reflectance and single-crystal spectra, except that, in the latter, the 15.1-kK band becomes the main maximum with shoulders at 13.7, 15.9, and 17.8 kK, and the onset of uv absorption is less intense.

Infrared spectra, with strong absorptions at 1565 and 1500 cm^{-1} (attributable to C=O stretching), 960, 935, and 915 cm^{-1} (CS stretching), and 655 cm^{-1} (OCS bending)—compare ref 7—add little information as to the stereochemistry present. However, magnetic susceptibility data offer evidence for the presence of magnetic coupling between Co(II) centers in the dimer units. In fact μ_{eff} is strongly temperature dependent, ranging from approximately 1.8 BM at 90°K to 3.1 BM at room temperature, as shown in Figure 2. The ob-

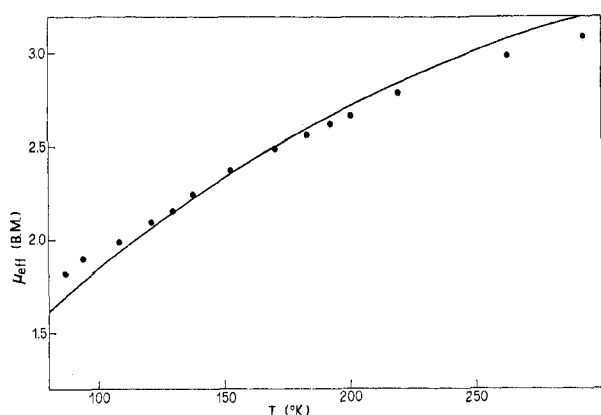


Figure 2.— μ_{eff} values for $Co_2(mtb)_4$: circles, experimental values (corrected for diamagnetism but not for TIP); full line, calculated for a binuclear cluster of $S = 3/2$ ions according to eq 1 with $g = 2.31$ and $J = -63^\circ$.

served μ_{eff} values approximately fit the temperature dependence expected (Figure 2) according to an obvious extension of the spin-coupling model proposed by Earnshaw, Figgis, and Lewis¹³ which leads, in the present case, to the equation

$$\mu_{eff}^2 \text{ (per gram-atom of Co)} = \frac{g^2(3x + 15x^3 + 42x^5)}{(1 + 3x + 5x^3 + 7x^5)} \quad (1)$$

where $x = \exp(2J/kT)$.

Assuming, tentatively, that $g = 2 - (8\lambda/10Dq) = 2.31$ (which would correspond to $\lambda = -0.16$ kK, and $|Dq| = 0.41$ kK, hence the order of g commonly observed for pseudotetrahedral Co(II) complexes), experimental data are consistent with $J \approx -63^\circ$ (see Figure 2). This appears to be a unique case of magnetic coupling in polynuclear pseudotetrahedral Co(II) complexes. Despite the uncertainties, due to neglect of TIP contributions to the experimental magnetic susceptibility and to the arbitrary values assigned to the orbital g corrections, the order of magnitude of J is probably correct. It may be noted that it is in line with J values observed¹³⁻¹⁵ in several polynuclear complexes of first-row transition metals having carboxylate bridges, such as formates, acetates, propionates, and benzoates of Cr(III) ($-J \approx 10-20^\circ$)¹³ and Fe(III)

($-J \approx 40-50^\circ$).¹³ Thus, monothiobenzoate $C_6H_5-COS^-$ in its ligand behavior resembles, on the one hand, the mono- and dithiophosphinates (ability to promote bridged coordination) and, on the other, carboxylate ligands (efficiency of magnetic coupling through the bridging groups). This is strikingly different from the polynuclear cobalt(II) phosphinates and mono- and dithiophosphinates, which have been reported to exhibit the normal paramagnetism of tetrahedral Co(II), and it may be concluded that phosphorus-containing bridges do not allow any significant magnetic coupling to occur.

Last, monothiobenzoate is quite different from both dithiocarboxylate and dithiophosphate ligands in that it promotes pseudotetrahedral coordination of Co(II) and lacks any pronounced oxidation effect on cobalt. Instead, the dithiophosphates strongly prefer¹⁶ pseudo-octahedral coordination, and to Co(III), while the dithiocarboxylates give this coordination geometry and oxidation state exclusively.

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Hindered-Ligand Systems. VI. Trigonal-Prismatic to Octahedral Coordination via Hydrogenation of Acyclic C=N Functional Groups

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The hexadentate ligand, *cis,cis*-1,3,5-tris(pyridine-2-carboxylaldimino)cyclohexane, ((py)₃tach), undergoes trigonal-prismatic coordination with Zn(II), Mn(II), and Co(II) ions^{1,2} but may be capable of near-octahedral coordination in the Fe(II) and Ni(II) derivatives.^{2,3} It is now found that the reaction of the Co(II), Ni(II), and Zn(II) complexes with BH_4^- , which affects the hydrogenation of the acyclic C=N bonds, gives the corresponding complexes of *N,N',N''*-tris(2-picolyl)-*cis,cis*-1,3,5-triaminocyclohexane ((pic)₃tach) which are basically octahedral. Although the hydrogenation of Schiff's bases with BH_4^- is fairly well known,⁴ these reaction products have a greater significance. If only conformational restraints of the acyclic C=N functional groups are responsible for the unusual coordination geometries in complexes of (py)₃tach, then removal of these restraints by hydrogenation of those groups should lead exclusively to chiral and basically octahedral coordination. This conclusion is consistent with experimental observations. It has also been found

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