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Contribution from the Chemistry Department,
Tehran University, Tehran, Iran

## New Route to the Preparation of $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2{\cdot}4H_2O$

Mansour Abedini

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A binuclear complex, μ-carbonato-bis(pentaamminecobalt(III)) sulfate tetrahydrate, has been reported by Kremer and Mac-Coll[1] and Kranig.[2] They have obtained this salt by mixing $CoSO_4$, $(NH_4)_2CO_3$, and $NH_4OH$ at low temperatures and bubbling air through the mixture for a period of 24 h.

It has been shown[3,4] that in the reaction of aquopentaamminecobalt(III) ion with carbon dioxide, hydroxopentaamminecobalt(III) species, which is in equilibrium with the aquopentaamminecobalt(III) ion in aqueous solution, plays an important role in the rate-determining step. In the process of carbon dioxide uptake, formation of $[(NH_3)_5CoCO_3H]^{2+}$ has been proposed as a possible intermediate step. Now, in the same way that a proton is split from this intermediate to form the $[(NH_3)_5CoCO_3]^+$ ion, we could also imagine the splitting of a water molecule between the above-mentioned intermediate and the $[(NH_3)_5CoOH]^{2+}$ ion, to form a binuclear complex

$$[(NH_3)_5CoCO_3H]^{2+} + [HOCo(NH_3)_5]^{2+} \\ \rightarrow [(NH_3)_5CoCO_3Co(NH_3)_5]^{4+} + H_2O$$

In order to examine the possibility of the occurrence of this reaction, $[Co(NH_3)_5H_2O]I_3$, prepared according to the method described by Schlessinger,[5] was employed as a starting material in the reaction

$$2[Co(NH_3)_5H_2O]I_3 + 3Ag_2CO_3 + 2(NH_4)_2SO_4 \xrightarrow[H_2O]{CO_2} 6AgI\downarrow \\ + 2(NH_4)_2CO_3 + [(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2{\cdot}4H_2O$$

Reaction of $[Co(NH_3)_5H_2O]I_3$ (32.7 mmol), $(NH_4)_2SO_4$ (65.7 mmol), and $Ag_2CO_3$ (48.9 mmol) in 200 ml of water at 0 °C, with constant stirring and bubbling of $CO_2$ gas for a period of 2 h, produced an oily liquid, which was then crystallized into deep red crystals, by addition of absolute alcohol. An acidified solution of this product showed no reaction with $K_2S_2O_8$, therefore excluding $[Co(NH_3)_5H_2O]ISO_4$ as a possible reaction product. Yield of the binuclear complex was 49%, based on the amount of $[Co(NH_3)_5H_2O]I_3$ used. Anal. Calcd: $NH_3$, 27.75; Co, 19.19; $SO_4$, 31.38. Found: $NH_3$, 27.50; Co, 19.10; $SO_4$, 31.40. A sample of this complex salt (0.5 g) was heated at 600 °C to a constant weight (0.2501 g). The loss of weight according to the reaction

$$[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2{\cdot}4H_2O \rightarrow 2CoSO_4 + 10NH_3 \\ + CO_2 + {}^1/_2O_2 + 4H_2O$$

corresponded to 49.98% volatiles ($NH_3$, $CO_2$, $H_2O$, and $O_2$) in the compound (calcd 49.34%). In addition, the deep violet residue ($CoSO_4$) was analyzed for its sulfate content (exptl 61.57%; calcd 61.93%).

Potentiometric titration of a $1.63 \times 10^{-3}$ M solution of the complex, which showed an initial pH of 7.2, gave a mole ratio of $H^+$:Co equal to 0.93 which is consistent with the reaction

$$[(NH_3)_5CoCO_3Co(NH_3)_5]^{4+} + 2H^+ \xrightarrow{H_2O} 2[(NH_3)_5CoH_2O]^{3+} + CO_2$$

The electronic spectrum of the complex showed a d–d transition at 505 mμ ($\log \epsilon = 2.14$) and a shoulder growing at 350 mμ on a uv band consistent with the data expected of a $N_5Co{-}O{-}CO{-}O$ chromophore.[6] The near-uv band showed a maximum at 255 mμ.

Adding $H_2SO_4$ to the complex for a complete conversion to the $[(NH_3)_5CoH_2O]^{3+}$ ion shifted the bands to 490 mμ ($\log \epsilon = 1.69$) and 340 mμ, respectively, which are values reported for the aquopentaamminecobalt(III) complex ion.[7]

The DTA curve of the complex was obtained by a Netzch 404 instrument. It showed, against Kaolin as reference, three endothermic peaks at 170, 310, and 490 °C corresponding to the loss of water of crystallization, ammonia, and carbon dioxide, respectively.

These experimental data conclusively prove the formation of a binuclear complex. Furthermore, this reaction is found to be a more convenient synthetic procedure for the formation of the binuclear complex and probably would be suitable for the preparation of similar complexes of Rh and Ir.

**Registry No.** $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2$, 49731-04-6; $[Co(NH_3)_5H_2O]I_3$, 15612-06-3.

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Contribution from the Physics and Chemistry Departments,
Kent State University, Kent, Ohio 44242

## Correlation of Electron Paramagnetic Resonance Line Intensities with Magnetic Moments for Some Spin-Crossover Systems

Cathy Flick, Edward Gelerinter,* Julia B. Zimmerman,
and Norman V. Duffy

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In 1973 we reported observation of separate paramagnetic resonance (EPR) lines due to the $S = {}^1/_2$ and $S = {}^5/_2$ states in the spin-crossover system of tris(dicyclohexyldithiocarbamato)iron(III) (CHDF) at room temperature and 127 K.[1] Identification of these lines was based primarily on the temperature dependence of the line intensities. In particular we identified a broad asymmetric line at $g_{\mathrm{eff}} \simeq 4.3$ that decreased in intensity at low temperature as due to the $S = {}^5/_2$ state; this is consistent with the observation that shortening the metal–ligand bond[2] and decreasing the thermal energy available favors the low-spin case. Also, theory predicts a broad line in the region of $g_{\mathrm{eff}} \simeq 4.3$ for reasonable values of the fine-structure parameters in the $S = {}^5/_2$ system.[3]

Recently Hall and Hendrickson[4] have reported EPR spectra of similar compounds at much lower temperatures than were

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* To whom correspondence should be addressed at Physics Department, Kent State University.

**Table I.** Relative Intensities[a] of the Low-Field Line (Arbitrary Units) and Solid $\mu_{eff}$ (Both at Room Temperature)

| | $\mu_{eff}$,[b] $\mu_B$ | % of population in high-spin state[e] | Intensity/mol |
|---|---|---|---|
| BBDF (di-*n*-butyl) | 5.32[d] | 79 | 540 ± 50 |
| MMDF (methylmethoxy) | 5.34[c] | 80 | 360 ± 50 |
| MBDF (methylbenzyl) | 4.98[c] | 68 | 670 ± 300 |
| ETDF (ethyl-*p*-tolyl) | 4.24[c] | 47 | 130 ± 30 |
| CPDF (dicyclopentyl) | 2.72[c] | 14 | 9 ± 4 |
| CHDF (dicyclohexyl) | 1.8[c] | 1 | 1.7 ± 0.5 |
| | 2.75[d] | 15 | |

[a] Approximated as height × (width)$^2$. [b] Maximum error ±0.1 $\mu_B$. [c] This work. [d] Measured in ref 5. [e] $\chi_M = \chi_{5/2}x + \chi_{1/2}(1 - x)$ where $\chi_{5/2} = (35/3)N\mu^2/kT$ and $\chi_{1/2} = N\mu^2/kT$.[7]

available in our study (4.2–85 K). However, they were unable to observe any lines at room temperature for any of the compounds, including tris(di-*n*-butyldithiocarbamato)iron(III) (BBDF). We have seen room-temperature EPR spectra for BBDF and other tris(*N*,*N'*-diorganodithiocarbamato)iron(III) compounds. In each case, a dominant feature of the spectrum is a broad low-field line such as that observed in CHDF. Here we present evidence that the intensity of this room-temperature line can be roughly correlated with the effective solid-state magnetic moments ($\mu_{eff}$) of these compounds. This further strengthens the identification of the line as due to an $S = {}^5/_2$ state.

Although Hall and Hendrickson do not give much detail concerning their EPR experimental parameters, possibly their failure to observe such lines at room temperature merely reflects a difference in apparatus sensitivity. Although the lines are quite intense, their broadness might prevent observation when conditions are unfavorable.

## Experimental Section

The compounds studied were tris(*N*,*N'*-diorganodithiocarbamato)iron(III) where the substituents on the nitrogen of the dithiocarbamate portion were di-*n*-butyl (BBDF), methylmethoxy (MMDF), methylbenzyl (MBDF), ethyl-*p*-tolyl (ETDF), dicyclopentyl (CPDF), and dicyclohexyl (CHDF). All were prepared by a standard method.[5] The crude compound was recrystallized from chloroform solution by the slow addition of ethanol under nitrogen. Elemental analyses were not obtained, but this method of purification routinely gives acceptably pure samples.[6]

The solid magnetic moments of freshly recrystallized samples (except for CHDF) were measured at room temperature using a Faraday magnetic susceptibility apparatus and Cahn electrobalance with a $HgCo(SCN)_4$ standard. Sample sizes were on the order of a few milligrams.

The derivative EPR spectra were observed at X band (~$10^{10}$ Hz) using a Varian V-4500-10A spectrometer with a 100-kHz modulation field of 5 G. The dc magnetic field was swept from 0 to 12 000 G. We used a Varian dual cavity with the sample in the first cavity and a diphenylpicrylhydrazyl (DPPH) marker in the second cavity. The EPR powder samples were freshly recrystallized and sealed in a 3-mm i.d. quartz tube under vacuum. Sample size ranged from 60 to 120 mg.

## Results

Figure 1 shows the room-temperature spectra for the compounds listed above. The arrow marks the position of the DPPH signal ($g_{eff} = 2.0$). Table I lists the relative intensities of the broad low-field line and $\mu_{eff}$, together with conservative error estimates. Since the position of the baseline is unclear, we have calculated the intensities of the absorption derivative lines as the height × (width)$^2$ rather than attempt a first-moment integration. Despite difficulties in assigning line widths, a trend is apparent: the intensity of the line identified as $S = {}^5/_2$ generally decreases (within experimental limits) with decreasing $\mu_{eff}$. We should note that we measured $\mu_{eff} = 1.8$ $\mu_B$ for CHDF, considerably lower than the value $\mu_{eff} = 2.75$ $\mu_B$ reported by others using the Gouy method.[5] Although the EPR data were taken from a freshly recrystallized preparation, the magnetic moment measurement was made several months later from the same preparation (stored under nitrogen). However, the intensity measurement is consistent with the lower value for $\mu_{eff}$.

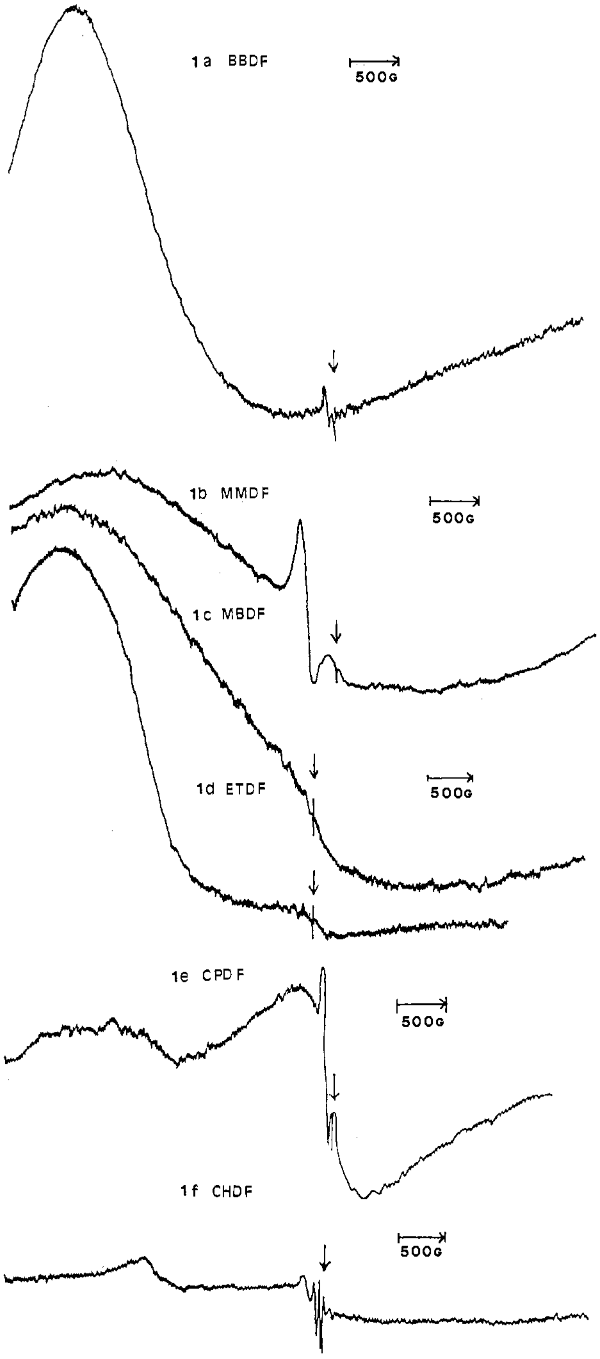

**Figure 1.** Derivative EPR spectra of tris(*N*,*N'*-diorganodithiocarbamato)iron(III) powder samples at room temperature. Starting field 5 G for 1a, 1f; 50 G for others. The arrow marks the position of DPPH ($g_{eff} = 2.0$).

We have also observed EPR spectra (0–12 000 G) from impurities removed by recrystallization of some of these compounds. These gave a broad line centered at $g_{eff} \simeq 2.0$. This impurity line most noticeably interferes with the CPDF spectrum (Figure 1e); its intensity corresponds to approximately ${}^1/_2$% by weight impurity.

We also observed some spectra at lower temperatures (down to 95 K); the low-field line narrows and eventually structure begins to be resolved around $g_{\text{eff}} \simeq 4.3$ as expected from theory for the $S = {}^5/_2$ state.[3]

In summary, we have identified the broad low-field line in the room-temperature EPR spectra of several spin-crossover compounds as due to the $S = {}^5/_2$ state. The decrease in line intensity with decreased $\mu_{\text{eff}}$ is consistent with the decreased contribution from the $S = {}^5/_2$ state.

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**Registry No.** BBDF, 14526-32-0; MMDF, 60282-50-0; MBDF, 23674-41-1; ETDF, 35944-38-8; CPDF, 36763-00-5; CHDF, 21288-88-0.

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Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

# Molecular Structure of *trans*-Bis(benzeneselenido)[difluoro-3,3′-(trimethylenedinitrilo)bis(2-pentanone oximato)borate]rhodium(III)

James P. Collman,* Richard K. Rothrock, Judith P. Sen,
Thomas D. Tullius, and Keith O. Hodgson

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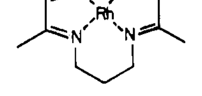
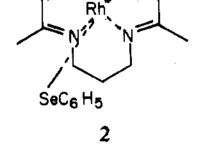
The development of new superconducting materials has aroused considerable interest among physicists and chemists. The speculative mechanism for superconductivity proposed by Little[1] suggests that "excitonic" interactions could result upon placing a one- or two-dimensional metal in the proximity of a readily polarizable medium. We are presently engaged in the synthesis and characterization of compounds comprised of a backbone of atoms of heavy elements covalently bound in a linear array. Our synthetic approach to this problem has centered about the oxidative addition of disulfides and diselenides to a square-planar, macrocyclic rhodium(I) complex. We wish to report here the x-ray crystal structure of a transition metal complex which serves as the simplest model for our future study in this area.

The oxidative addition of diphenyl diselenide to the square-planar [difluoro-3,3′-(trimethylenedinitrilo)bis(2-pentanone oximato)borate]rhodium(I),[2,3] **1** (commonly abbreviated as $Rh[C_2(DO)(DOBF_2)]$) affords the $Rh(C_2(DO)(DOBF_2)](SeC_6H_5)_2$ complex, **2**. With respect to the oxidative addition reaction, the low-valent rhodium compound **1** is one of the most reactive $d^8$ transition metal complexes yet isolated. Substrates, including alkyl and acyl halides, alkyl tosylates, and alkyl and aryl disulfides and diselenides, generally undergo the addition by an $S_N2$ mechanism.[2]



**1**



**2**

Table I. Root-Mean-Square Amplitudes of Vibration

| Atom | Axis 1 | Axis 2 | Axis 3 | Atom | Axis 1 | Axis 2 | Axis 3 |
|---|---|---|---|---|---|---|---|
| Rh | 0.145 | 0.176 | 0.203 | C13 | 0.170 | 0.246 | 0.301 |
| Se1 | 0.173 | 0.198 | 0.270 | C1P1 | 0.163 | 0.200 | 0.237 |
| Se2 | 0.170 | 0.210 | 0.247 | C2P1 | 0.184 | 0.239 | 0.259 |
| N1 | 0.163 | 0.183 | 0.199 | C3P1 | 0.175 | 0.233 | 0.336 |
| N2 | 0.163 | 0.182 | 0.235 | C4P1 | 0.180 | 0.215 | 0.370 |
| N3 | 0.162 | 0.188 | 0.224 | C5P1 | 0.196 | 0.255 | 0.337 |
| N4 | 0.151 | 0.191 | 0.240 | C6P1 | 0.202 | 0.241 | 0.262 |
| C1 | 0.185 | 0.242 | 0.360 | C1P2 | 0.186 | 0.202 | 0.221 |
| C2 | 0.150 | 0.210 | 0.226 | C2P2 | 0.170 | 0.192 | 0.244 |
| C3 | 0.141 | 0.197 | 0.243 | C3P2 | 0.168 | 0.228 | 0.276 |
| C4 | 0.140 | 0.213 | 0.230 | C4P2 | 0.181 | 0.251 | 0.334 |
| C5 | 0.191 | 0.213 | 0.283 | C5P2 | 0.132 | 0.265 | 0.361 |
| C6 | 0.173 | 0.229 | 0.287 | C6P2 | 0.180 | 0.233 | 0.291 |
| C7 | 0.191 | 0.266 | 0.329 | O1 | 0.166 | 0.201 | 0.313 |
| C8 | 0.161 | 0.244 | 0.276 | O2 | 0.185 | 0.196 | 0.292 |
| C9 | 0.185 | 0.255 | 0.357 | B | 0.192 | 0.214 | 0.290 |
| C10 | 0.175 | 0.237 | 0.259 | F1 | 0.270 | 0.296 | 0.348 |
| C11 | 0.167 | 0.180 | 0.227 | F2 | 0.190 | 0.234 | 0.390 |
| C12 | 0.165 | 0.176 | 0.258 | | | | |

## Experimental Section

**Preparation of $Rh[C_2(DO)(DOBF_2)](SeC_6H_5)_2$, 2.** To a solution of $Rh[C_2(DO)(DOFB_2)]$, **1**, (100 mg, 0.239 mmol), in dry tetrahydrofuran (10 ml) under a nitrogen atmosphere was added a tetrahydrofuran solution (5 ml) of diphenyl diselenide (80.0 mg, 0.256 mmol). After stirring of the solution for 1 h at room temperature, the solvent was removed under reduced pressure. The residue was recrystallized from acetonitrile affording ruby red crystals (110 mg, 62%). Ir (KBr pellet): $\bar{\nu}_{CN}$ 1590, 1515 cm$^{-1}$; $\bar{\nu}_{NO}$ 1112 cm$^{-1}$; $\bar{\nu}_{BO}$ 1155, 808 cm$^{-1}$; $\bar{\nu}_{BF}$ 995 cm$^{-1}$; $\bar{\nu}_{Ph}$ 1562, 1450, 1424, 742, 690 cm$^{-1}$; $\bar{\nu}_{Se-Ph}$ 467 cm$^{-1}$. NMR (60 MHz in $CDCl_3$): $\delta$ 1.00 (t, $J$ = 8 Hz), 1.80 (s), 2.35 (q on m, $J$ = 8 Hz), 4.00 (m), 7.20 (m). Anal. Calcd for $C_{25}H_{32}BF_2N_4O_2RhSe_2$: C, 41.12; H, 4.42; N, 7.67; Se, 21.63. Found: C, 41.14; H, 4.38; N, 7.52; Se, 21.60.

The compound crystallized as long, ruby red parallelepipeds, one of which was cleaved to a size (0.20 × 0.20 × 0.20 mm) suitable for diffraction studies. Data were collected on a Syntex $P2_1$ four-circle diffractometer equipped with a single-crystal graphite monochromator (Bragg $2\theta$ angle 12.2°) using Mo K$\bar{\alpha}$ radiation ($\lambda_{K\bar{\alpha}}$ 0.71073 Å) at a takeoff angle of 3.0°. Least-squares refinement of the setting angles of 15 machine-centered reflections resulted in parameters for a monoclinic unit cell of $a$ = 15.361 (6) Å, $b$ = 11.44 (1) Å, $c$ = 16.374 (4) Å, $\beta$ = 105.16 (4)°, and $V$ = 2778 (4) Å$^3$. The crystal was found to belong uniquely to space group $P2_1/c$, with four molecules per unit cell ($\rho_{\text{calcd}}$ = 1.75 g/ml; $\rho_{\text{obsd}}$ = 1.73 g/ml, obtained by flotation in 1,2-dibromoethane/heptane).

Intensity data were collected employing variable-speed $\theta$–$2\theta$ scans ($2\theta_{\text{max}}$ = 60°). A total of 8147 unique reflections ($h,k,\pm l$) were collected, of which 3659 had $|F_o|^2 > 3\sigma(|F_o|)^2$. Corrections were made for background and Lorentz–polarization. An absorption correction was not applied as the maximum and minimum values of $\mu t$ for the very symmetric crystal vary only a few percent.

The coordinates of the Rh and one Se atom were determined from a three-dimensional Patterson map.[4] The positions of the other nonhydrogen atoms were determined by a subsequent difference Fourier. The structure was refined using full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ in which $w$ is given by $4F_o^2/\sigma^2(F_o^2)$. The agreement factors $R$ and $R_w$ are defined as $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.

Including all nonhydrogen atoms with anisotropic temperature factors and fixed calculated H atom positions, the final values of $R$ and $R_w$ were both 0.052. The final error in an observation of unit weight was 1.66.

The rms amplitudes of vibration for all nonhydrogen atoms are given in Table I. [The observed and calculated structure factors are given in Table III and Table IV lists the positional and thermal parameters from the final refinement.[5]]