during the reduction process. A band at 1450 cm$^{-1}$ was observed on rehydrated silica–alumina and was assigned to the formation of ammonium ions by Eischens and Pliskin.[23] Note that in the present study, the zeolite had always been treated at temperatures below 400°. According to Naccache and Ben Taarit,[24] Lewis acid centers were formed if Cu(II)Y was reduced by carbon monoxide at 500°. They proposed a scheme in which Cu$^{2+}$ ions were reduced to Cu$^{+}$ ions by carbon monoxide. The scheme cannot explain satisfactorily the present observation. At any rate, further investigation would be necessary to understand more about the reduction process.

[23] R. P. Eichens and W. A. Pliskin, *Advan. Catal. Relat. Subj.*, 1 (1958).

[24] C. M. Naccache and Y. Ben Taarit, *J. Catal.*, **22**, 171 (1972).

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# Complexes as Ligands. Structure and Metal Exchange of β-Diketonate–Schiff's Base Adducts Containing Copper(II) and Cobalt(II)

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**Abstract:** In the course of investigating adducts formed by bis(hexafluoroacetylacetonato)copper(II), the reaction of this Lewis acid with the Lewis base, *N,N'*-ethylenebis(salicylideniminato)cobalt(II), was investigated. During the characterization of this structure by mass spectroscopy, magnetic susceptibility, and X-ray crystal structure determination, it was discovered that the metals had interchanged primary coordination spheres. The interchange is rapid in methylene chloride at room temperature. The identical adduct is formed by the addition of *N,N'*-ethylenebis(salicylideniminato)copper(II) to bis(hexafluoroacetylacetonato)cobalt(II). The crystals of $Cu(C_{16}H_{14}N_2O_2)Co(C_5HF_6O_2)_2$ are triclinic with $a$ = 18.412 (5) Å, $b$ = 9.419 (3) Å, $c$ = 12.044 (3) Å, $\alpha$ = 113.90 (2)°, $\beta$ = 123.25 (2)°, and $\gamma$ = 89.20 (2)°; the unit cell, space group $P\bar{1}$, contains two molecules. The molecule contains a copper atom with square-planar coordination and an octahedrally coordinated cobalt atom. The two phenolic oxygen atoms function as bridging atoms between the metal centers.

The cobalt(II) complex of *N,N'*-ethylenebis(salicylidenimine), salen, is one of the first cobalt complexes reported to coordinate molecular oxygen.[1] Accordingly, we are interested in the acid–base chemistry of this complex and its 1:1 adducts. During these studies, we encountered interesting binuclear complexes formed by the reaction of Co(salen) and fluorinated β-ketoenolate copper(II) complexes. Reports of salen complexes acting as ligands to form binuclear compounds have appeared in the literature.[2] These binuclear complexes are believed to form because of the ability of the salen phenolic oxygen atoms to function as bridging atoms. However, no confirmatory crystal and molecular structure data have been reported. Because of our interest in Co(salen) and fluorinated β-ketoenolate copper(II), we have investigated the physical properties, structure, and reactivities of these copper–cobalt systems.

Our investigations have shown that reactions between Co(salen) and fluorinated β-ketoenolate copper(II) complexes produce binuclear compounds in which the metals have exchanged coordination spheres. These products are therefore best described as addition compounds of Cu(salen) and fluorinated β-ketoenolate cobalt(II) complexes. For most of the studies reported here, the adduct was prepared directly by the addition of Cu(salen) to bis(hexafluoroacetylacetonato)cobalt(II).

## Experimental Section

*N,N'*-Ethylenebis(salicylideniminato)cobalt(II) [Co(salen)],[3] bis(hexafluoroacetylacetonato)copper(II) [Cu(hfa)$_2$],[4] and diaquobis(hexafluoroacetylacetonato)cobalt(II) [$Co(hfa)_2 \cdot 2H_2O$][5] were prepared by methods described in the literature. *N,N'*-Ethylenebis(salicylideniminato)copper(II) [Cu(salen)] and the nickel analog, Ni(salen), were prepared by substituting copper acetate or nickel acetate for cobalt acetate in the procedure described for Co(salen).[3]

**Cu(salen)Co(hfa)$_2$.** The adduct was originally prepared using a Soxhlet extractor because of the low solubility of Co(salen) in methylene chloride. Co(salen) (3.0 g, 9.3 mmol) was placed in the extraction thimble; Cu(hfa)$_2$ (4.4 g, 9.3 mmol) was dissolved in 100 ml of methylene chloride. The extraction was allowed to continue until most of the Co(salen) had been removed from the thimble (48 hr). The methylene chloride was pumped off and the residue washed with carbon tetrachloride to remove unreacted Cu(hfa)$_2$. The product was recrystallized from methylene chloride.

The adduct was best prepared, however, by stirring 1 mmol (330 mg) of Cu(salen) and 1 mmol (493 mg) of $Co(hfa)_2 \cdot 2H_2O$ in 100 ml of methylene chloride for 2 hr. Partial evaporation of the solvent and overnight storage in a refrigerator produced small, dark red crystals. The product was recrystallized from methylene chloride. *Anal.* Calcd: C, 38.89; H, 2.01; Co, 7.34; Cu, 7.91. Found: C, 39.15; H, 2.06; Co, 7.39; Cu, 7.67.

**Ni(salen)Co(hfa)$_2$.** This orange-red complex can be prepared using the procedure described for Cu(salen)Co(hfa)$_2$. *Anal.* Calcd: C, 39.13; H, 2.02; Co, 7.38; Ni, 7.31. Found: C, 39.09; H, 1.81; Co, 7.52; Ni, 7.15.

**Magnetic Susceptibility.** Solution susceptibilities were measured with a JELCO 60-MHz nmr using the Evans method.[6] Temperature-dependent studies on the solid complex were done with a PAR

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[1] T. Tsumaki, *Bull. Chem. Soc. Jap.*, **13**, 252 (1938).

[2] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968), and references therein.

[3] R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, **69**, 1880 (1947).

[4] W. R. Walker and N. C. Li, *J. Inorg. Nucl. Chem.*, **27**, 2255 (1965).

[5] F. A. Cotton and R. H. Holm, *J. Amer. Chem. Soc.*, **82**, 2979 (1960).

[6] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

vibrating sample magnetometer. Susceptibilities were corrected for diamagnetism using a combination of reported diamagnetic susceptibilities and Pascal's constants.[7]

**Molecular Weight.** Molecular weights were measured in methylene chloride using a vapor pressure osmometer.

**Mass Spectroscopy.** Mass spectra were recorded on a Varian-MAT CH-5 spectrometer. A source temperature of 220° and an ionizing voltage of 70 eV were used. Peak heights were measured from an oscillographic trace. Fragmentation of the compounds was extensive.

**X-Ray Diffraction.** Clear, well-formed, maroon platelets of $C_{26}H_{16}F_{12}N_2O_6CoCu$ were grown from methylene chloride. Crystal data: $M = 802.9$; triclinic; $a = 18.412\ (5)$, $b = 9.419\ (3)$, $c = 12.044\ (3)$ Å; $\alpha = 113.90\ (2)$, $\beta = 123.25\ (2)$, and $\gamma = 89.20\ (2)°$; $V = 1536 \times 10^{-24}$ cm$^3$, $\rho_{\text{measd}}$ (flotation in bromoform and hexane) $= 1.74$ g cm$^{-3}$, $Z = 2$, $\rho_{\text{calcd}} = 1.74$ g cm$^{-3}$, $F(000) = 796$, $\mu$(Mo K$\alpha$) $= 28.12$ cm$^{-1}$. There were no systematic absences, space group $P1$ or $P\bar{1}$ (the latter confirmed by results of the analysis).

Initial cell parameters and the assignment of the crystal system were obtained from a precession and Weissenberg photographic examination of the crystals. The final cell data were obtained from a least-squares fit to the hand-centered settings for the four angles of ten reflections on a Picker FACS-1 diffractometer (Mo K$\alpha$, $\lambda = 0.71070$ Å). Intensity data were collected on the diffractometer (Mo K$\alpha$ radiation) on a platelet approximately 0.4 mm on each face and 0.1 mm thick. The intensities were measured with a scintillation counter, employing pulse height analysis and with attenuation being inserted when the count rate exceeded 10,000 counts/sec. The 6935 symmetry-nonequivalent reflections in the $2\theta$ range 0–55° were measured at least once using a moving crystal–moving counter method with a $2\theta$ scan rate of 2°/min. Background measurements for 10 sec were recorded at the two limits of the scan. The base width of the scan was 2°, but a dispersion factor was applied to take account of the $\alpha_1$–$\alpha_2$ splitting. Three standard reflections, $6\bar{4}0$, 340, and $03\bar{5}$, were measured after every 100 reflections; the maximum deviation among the values for these three reflections was less than $\pm 2\%$ of their original values. Lorentz and polarization corrections were applied to the data. Of the 6935 unique reflections, 4368 were judged above background. A peak was judged above background if the net intensity was more than 7% of background or more than 45 net counts, whichever was higher.[8] No correction was made for absorption. The maximum transmission factors that could result were calculated to be 0.76 and 0.20 as applied to the intensities.

The structure was determined by the heavy-atom method based on the cobalt and copper atoms. Three cycles of full-matrix least-squares refinement on positional and isotropic thermal parameters using all of the data gave crystallographic $R$ and $R_2$[9] factors of 0.18 and 0.17. In this and subsequent least-squares refinements, unit weights were employed and the quantity minimized was $\Sigma w\|F_o| - |F_c\|^2$. Anisotropic thermal parameters were now introduced for all the nonhydrogen atoms and two cycles of full-matrix least-squares refinement reduced $R$ to 0.120 and $R_2$ to 0.117.

When solution of the X-ray structure was begun, we were not certain if the compound was Co(salen)Cu(hfa)$_2$ or Cu(salen)Co(hfa)$_2$. Up to this point in the solution, the molecule was assumed to be Co(salen)Cu(hfa)$_2$. When calculations were made assuming Cu(salen)Co(hfa)$_2$, there was some improvement in the fit: $R = 0.106$, $R_2 = 0.103$. Within experimental error, the atom positions were unchanged; however, anisotropic thermal parameters did change significantly. In the first solution, the thermal parameters of the four-coordinate metal were approximately 50% larger than those for the six-coordinate metal. In the second solution, these parameters were nearly equal. Although not conclusive, we consider this as additional evidence that the compound under study is, indeed, Cu(salen)Co(hfa)$_2$. This formulation was used for all subsequent refinements.

**Table I.** Fractional Coordinates[a]

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Co | 0.2852 (1) | 0.1711 (1) | 0.0374 (1) |
| Cu | 0.4916 (1) | 0.2728 (1) | 0.2350 (1) |
| O1 | 0.2862 (4) | 0.2051 (7) | −0.1233 (6) |
| O2 | 0.1836 (4) | 0.2858 (7) | −0.0092 (6) |
| O3 | 0.1944 (4) | −0.0451 (7) | −0.1429 (6) |
| O4 | 0.2533 (4) | 0.1243 (6) | 0.1607 (5) |
| O5 | 0.3976 (4) | 0.0792 (6) | 0.1028 (6) |
| O6 | 0.3988 (4) | 0.3715 (6) | 0.2221 (6) |
| N1 | 0.5794 (5) | 0.1712 (8) | 0.2244 (7) |
| N2 | 0.5880 (5) | 0.4625 (8) | 0.3753 (8) |
| C1 | 0.2171 (6) | 0.2158 (11) | −0.2300 (9) |
| C2 | 0.1434 (7) | 0.2582 (13) | −0.2404 (10) |
| C3 | 0.1323 (6) | 0.2964 (11) | −0.1280 (11) |
| C4 | 0.2172 (8) | 0.1796 (16) | −0.3644 (12) |
| C5 | 0.0557 (7) | 0.3604 (15) | −0.1403 (13) |
| C6 | 0.1337 (6) | −0.1226 (10) | −0.1548 (10) |
| C7 | 0.1220 (6) | −0.0909 (12) | −0.0418 (11) |
| C8 | 0.1821 (6) | 0.0271 (10) | 0.1032 (10) |
| C9 | 0.0710 (7) | −0.2654 (13) | −0.3043 (11) |
| C10 | 0.1615 (7) | 0.0506 (12) | 0.2144 (11) |
| C11 | 0.4137 (6) | −0.0625 (10) | 0.0966 (8) |
| C12 | 0.3488 (6) | −0.1819 (10) | 0.0596 (9) |
| C13 | 0.3631 (7) | −0.3282 (11) | 0.0492 (10) |
| C14 | 0.4409 (8) | −0.3641 (12) | 0.0696 (11) |
| C15 | 0.5047 (7) | −0.2500 (14) | 0.1057 (10) |
| C16 | 0.4947 (6) | −0.0965 (11) | 0.1216 (9) |
| C17 | 0.5716 (6) | 0.0192 (11) | 0.1745 (9) |
| C18 | 0.6604 (6) | 0.2855 (12) | 0.2842 (11) |
| C19 | 0.6744 (6) | 0.4364 (13) | 0.4116 (11) |
| C20 | 0.5811 (6) | 0.5967 (11) | 0.4468 (10) |
| C21 | 0.5004 (8) | 0.6363 (10) | 0.4239 (10) |
| C22 | 0.5081 (8) | 0.7971 (13) | 0.5154 (11) |
| C23 | 0.4348 (11) | 0.8474 (13) | 0.4990 (13) |
| C24 | 0.3503 (8) | 0.7401 (14) | 0.3897 (12) |
| C25 | 0.3387 (6) | 0.5826 (11) | 0.3000 (10) |
| C26 | 0.4131 (7) | 0.5263 (11) | 0.3125 (9) |
| F1 | 0.2860 (6) | 0.2894 (13) | −0.3214 (9) |
| F2 | 0.1508 (5) | 0.1757 (14) | −0.4756 (8) |
| F3 | 0.2434 (6) | 0.0522 (12) | −0.4017 (8) |
| F4 | 0.0260 (6) | 0.3307 (13) | −0.0785 (12) |
| F5 | −0.0098 (6) | 0.3284 (18) | −0.2675 (10) |
| F6 | 0.0793 (8) | 0.5134 (11) | −0.0689 (16) |
| F7 | −0.0047 (5) | −0.3272 (9) | −0.3339 (7) |
| F8 | 0.0440 (6) | −0.2406 (10) | −0.4156 (6) |
| F9 | 0.1066 (6) | −0.3834 (8) | −0.3214 (8) |
| F10 | 0.1584 (6) | 0.1929 (10) | 0.2795 (9) |
| F11 | 0.2287 (6) | 0.0372 (12) | 0.3290 (8) |
| F12 | 0.0913 (6) | −0.0402 (12) | 0.1656 (9) |
| H2 | 0.095 | 0.266 | −0.332 |
| H7 | 0.067 | −0.159 | −0.070 |
| H12 | 0.291 | −0.158 | 0.041 |
| H13 | 0.313 | −0.414 | 0.020 |
| H14 | 0.449 | −0.473 | 0.061 |
| H15 | 0.562 | −0.275 | 0.124 |
| H17 | 0.628 | −0.013 | 0.184 |
| H18A | 0.720 | 0.267 | 0.303 |
| H18B | 0.649 | 0.308 | 0.205 |
| H19A | 0.715 | 0.430 | 0.500 |
| H19B | 0.723 | 0.533 | 0.455 |
| H20 | 0.638 | 0.684 | 0.528 |
| H22 | 0.569 | 0.878 | 0.593 |
| H23 | 0.443 | 0.961 | 0.562 |
| H24 | 0.295 | 0.778 | 0.377 |
| H25 | 0.278 | 0.503 | 0.223 |

[a] Positional parameters for Cu(salen)Co(hfa)$_2$. Hydrogen positions were calculated using standard criteria. Estimated standard deviation in parentheses.

Because the structure factors for a large number of reflections with small intensities were consistently undercalculated, the original data were reduced a second time using a $2\sigma$ criterion for inclusion as observed. This resulted in 3377 significantly nonzero reflections. Further full-matrix least-squares refinements which included calculated hydrogen positions and anomalous scattering factors[10] for copper and cobalt resulted in $R = 0.083$ and $R_2 = 0.065$ for the nonzero reflections. Computer storage limitations required refinements to be done in two parts; parameters for 24 atoms were permitted to vary in each part. Positional and isotropic thermal parameters for hydrogen atoms were held constant. A final difference map showed regions of electron density near the cobalt and copper atoms; the highest positive peak corresponded to 0.82 e/Å$^3$ and

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[7] G. Foëx, "Tables de Constantes et Donnees Numeriques," Vol. 7, Masson, Paris, 1957.

[8] A program, NRC-2A, written by F. R. Ahmed, was used to process the data.

[9] $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

[10] D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 215.

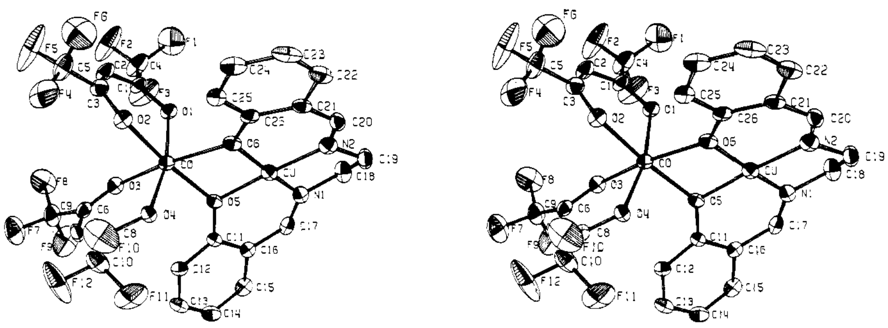

Figure 1. Stereoscopic drawing of Cu(salen)Co(hfa)$_2$.

Table II. Anisotropic Thermal Parameters[a]

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Co | 54 (1) | 147 (2) | 101 (2) | 27 (1) | 52 (1) | 61 (2) |
| Cu | 54 (1) | 154 (2) | 115 (2) | 16 (1) | 51 (1) | 57 (2) |
| O1 | 59 (4) | 227 (13) | 138 (9) | 39 (6) | 62 (5) | 114 (9) |
| O2 | 64 (4) | 202 (13) | 144 (10) | 41 (6) | 67 (6) | 80 (10) |
| O3 | 59 (4) | 168 (12) | 106 (9) | 20 (6) | 49 (5) | 44 (9) |
| O4 | 49 (3) | 160 (11) | 89 (8) | 3 (5) | 41 (5) | 45 (8) |
| O5 | 55 (4) | 115 (11) | 129 (9) | 23 (5) | 58 (5) | 56 (9) |
| O6 | 66 (4) | 114 (11) | 121 (9) | 23 (5) | 57 (5) | 52 (8) |
| N1 | 56 (5) | 181 (15) | 105 (11) | 13 (7) | 51 (6) | 51 (11) |
| N2 | 65 (5) | 183 (16) | 131 (12) | 24 (7) | 60 (7) | 76 (12) |
| C1 | 51 (6) | 237 (22) | 128 (15) | 48 (9) | 49 (8) | 115 (15) |
| C2 | 65 (7) | 332 (27) | 143 (16) | 61 (11) | 55 (9) | 158 (18) |
| C3 | 66 (7) | 201 (21) | 187 (18) | 41 (10) | 73 (10) | 108 (16) |
| C4 | 96 (8) | 588 (40) | 229 (21) | 136 (15) | 116 (12) | 276 (25) |
| C5 | 66 (8) | 424 (34) | 332 (26) | 105 (14) | 110 (13) | 186 (25) |
| C6 | 48 (6) | 151 (17) | 112 (14) | 23 (8) | 29 (8) | 53 (13) |
| C7 | 41 (5) | 223 (22) | 139 (16) | −13 (9) | 34 (8) | 78 (16) |
| C8 | 37 (5) | 173 (19) | 137 (15) | 15 (8) | 38 (8) | 80 (15) |
| C9 | 64 (7) | 257 (24) | 130 (16) | −16 (10) | 31 (9) | 25 (16) |
| C10 | 102 (8) | 268 (25) | 192 (19) | 0 (11) | 107 (11) | 80 (18) |
| C11 | 52 (6) | 114 (16) | 87 (12) | 16 (8) | 49 (7) | 34 (12) |
| C12 | 61 (6) | 160 (18) | 135 (15) | 41 (9) | 69 (8) | 80 (14) |
| C13 | 87 (8) | 136 (18) | 167 (17) | 17 (10) | 85 (10) | 63 (15) |
| C14 | 93 (9) | 138 (20) | 190 (19) | 51 (11) | 91 (12) | 78 (16) |
| C15 | 69 (8) | 208 (23) | 145 (17) | 49 (11) | 66 (10) | 64 (17) |
| C16 | 53 (6) | 130 (17) | 93 (13) | 27 (8) | 49 (8) | 31 (12) |
| C17 | 42 (5) | 252 (21) | 108 (14) | 35 (9) | 47 (8) | 76 (14) |
| C18 | 56 (6) | 281 (22) | 161 (18) | 9 (9) | 74 (9) | 67 (17) |
| C19 | 48 (6) | 268 (25) | 146 (17) | −16 (10) | 28 (9) | 90 (18) |
| C20 | 51 (6) | 174 (21) | 109 (16) | −14 (9) | 27 (8) | 53 (15) |
| C21 | 77 (8) | 98 (16) | 96 (13) | 14 (9) | 50 (9) | 42 (12) |
| C22 | 104 (9) | 140 (22) | 136 (16) | 5 (11) | 70 (11) | 59 (16) |
| C23 | 147 (13) | 127 (22) | 183 (21) | 51 (14) | 126 (15) | 85 (18) |
| C24 | 111 (9) | 164 (22) | 187 (19) | 66 (12) | 113 (12) | 96 (17) |
| C25 | 68 (7) | 148 (19) | 125 (15) | 26 (9) | 57 (9) | 59 (14) |
| C26 | 63 (7) | 166 (10) | 97 (13) | 28 (10) | 52 (8) | 86 (14) |
| F1 | 171 (8) | 768 (33) | 383 (19) | 50 (13) | 182 (11) | 350 (22) |
| F2 | 133 (6) | 1348 (44) | 282 (14) | 280 (15) | 146 (9) | 544 (23) |
| F3 | 204 (8) | 733 (30) | 244 (14) | 212 (14) | 186 (10) | 275 (18) |
| F4 | 148 (7) | 835 (33) | 789 (31) | 254 (13) | 303 (14) | 619 (28) |
| F5 | 114 (7) | 1361 (54) | 350 (19) | 307 (17) | 112 (10) | 382 (29) |
| F6 | 216 (11) | 430 (24) | 1080 (46) | 216 (14) | 397 (21) | 381 (29) |
| F7 | 99 (5) | 379 (18) | 214 (13) | −60 (8) | 50 (7) | 8 (12) |
| F8 | 160 (7) | 469 (22) | 114 (10) | −87 (10) | 14 (7) | 80 (13) |
| F9 | 150 (7) | 267 (16) | 274 (15) | 46 (9) | 63 (8) | −62 (12) |
| F10 | 214 (8) | 481 (22) | 453 (19) | 92 (12) | 281 (12) | 160 (18) |
| F11 | 176 (8) | 826 (30) | 370 (17) | 189 (13) | 208 (10) | 438 (21) |
| F12 | 176 (8) | 719 (29) | 312 (16) | −179 (12) | 180 (10) | −4 (18) |

[a] Thermal parameters ($\times 10^4$) for Cu(salen)Co(hfa)$_2$. The form of the anisotropic thermal parameter is $\exp(-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl])$.

occurred near the copper position. The fact that neutral scattering curves were used for all atoms may have contributed to the size of these peaks. Some disorder was apparent in the $-CF_3$ groups. At positions corresponding to a 60° rotation of the fluorine atoms about the $C-CF_3$ bond, the difference map showed areas of positive electron density. The highest peaks, occurring in the F10, F11, F12 group, were 0.5 e/Å$^3$. Since the major purpose of this work was the determination of molecular structure, the investigation of this disorder was not pursued further. Scattering curves for the nonhydrogen atoms were those of Cromer and Mann;[11] for hydrogen, the scattering curve of Stewart, *et al.*,[12] was used. Final

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(11) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Table III. Bond Lengths and Angles[a]

| Bond | Å | Bond | A | Bond | Å | Bond | Å |
|---|---|---|---|---|---|---|---|
| Co–O1 | 2.095 (7) | C11–C16 | 1.41 (2) | C2–C3 | 1.38 (2) | C21–C26 | 1.42 (2) |
| Co–O2 | 2.065 (8) | C15–C16 | 1.40 (2) | C1–C4 | 1.51 (2) | C25–C26 | 1.41 (2) |
| Co–O3 | 2.046 (10) | N1–C17 | 1.28 (1) | C3–C5 | 1.48 (2) | C4–F1 | 1.35 (2) |
| Co–O4 | 2.059 (6) | C16–C17 | 1.45 (2) | O3–C6 | 1.25 (1) | C4–F2 | 1.21 (2) |
| Co–O5 | 2.090 (7) | N1–C18 | 1.46 (1) | C6–C7 | 1.41 (2) | C4–F3 | 1.29 (2) |
| Co–O6 | 2.120 (10) | N2–C19 | 1.45 (1) | O4–C8 | 1.25 (1) | C5–F4 | 1.25 (2) |
| Cu–O5 | 1.889 (9) | C18–C19 | 1.46 (2) | C7–C8 | 1.36 (2) | C5–F5 | 1.23 (2) |
| Cu–O6 | 1.896 (7) | N2–C20 | 1.26 (1) | C6–C9 | 1.48 (2) | C5–F6 | 1.27 (2) |
| Cu–N1 | 1.905 (8) | C20–C21 | 1.43 (2) | C8–C10 | 1.52 (2) | C9–F7 | 1.31 (2) |
| Cu–N2 | 1.884 (13) | C21–C22 | 1.42 (2) | O5–C11 | 1.34 (1) | C9–F8 | 1.27 (2) |
| Cu–Co | 3.060 (1) | C22–C23 | 1.36 (2) | C11–C12 | 1.39 (1) | C9–F9 | 1.28 (2) |
| O1–C1 | 1.26 (1) | C23–C24 | 1.38 (2) | C12–C13 | 1.37 (1) | C10–F10 | 1.27 (2) |
| C1–C2 | 1.36 (2) | C24–C25 | 1.37 (2) | C13–C14 | 1.38 (2) | C10–F11 | 1.31 (2) |
| O2–C3 | 1.26 (2) | O6–C26 | 1.34 (1) | C14–C15 | 1.35 (2) | C10–F12 | 1.24 (2) |

| Angle | Degrees | Angle | Degrees | Angle | Degrees | Angle | Degrees |
|---|---|---|---|---|---|---|---|
| O1–Co–O2 | 85.6 (3) | C3–C5–F4 | 116.6 (14) | Co–O5–Cu | 100.4 (1) | O5–C11–C12 | 120.3 (6) |
| O1–Co–O3 | 84.1 (3) | C3–C5–F5 | 116.7 (14) | Co–O5–C11 | 136.1 (6) | O5–C11–C16 | 121.2 (8) |
| O1–Co–O4 | 167.1 (3) | C3–C5–F6 | 111.2 (13) | Cu–O5–C11 | 121.7 (6) | C12–C11–C16 | 118.4 (7) |
| O1–Co–O5 | 94.5 (3) | F4–C5–F5 | 106.7 (9) | Co–O6–Cu | 99.2 (2) | C11–C12–C13 | 121.2 (9) |
| O1–Co–O6 | 93.4 (3) | F4–C5–F6 | 99.8 (10) | Co–O6–C26 | 136.5 (6) | C12–C13–C14 | 120.9 (10) |
| O2–Co–O3 | 91.1 (3) | F5–C5–F6 | 103.7 (16) | Cu–O6–C26 | 124.3 (6) | C13–C14–C15 | 118.7 (8) |
| O2–Co–O4 | 84.8 (3) | O3–C6–C7 | 127.1 (8) | Cu–N1–C17 | 124.9 (5) | C14–C15–C16 | 122.8 (13) |
| O2–Co–O5 | 173.9 (3) | O3–C6–C9 | 114.2 (7) | Cu–N1–C18 | 113.1 (5) | C11–C16–C15 | 117.9 (9) |
| O2–Co–O6 | 100.0 (3) | C7–C6–C9 | 118.6 (7) | C17–N1–C18 | 122.0 (9) | C11–C16–C17 | 124.8 (7) |
| O3–Co–O4 | 87.5 (3) | C6–C7–C8 | 122.5 (11) | Cu–N2–C19 | 114.0 (5) | C15–C16–C17 | 117.0 (10) |
| O3–Co–O5 | 95.0 (3) | O4–C8–C7 | 129.3 (11) | Cu–N2–C20 | 123.4 (8) | N1–C17–C16 | 123.6 (9) |
| O3–Co–O6 | 168.5 (3) | O4–C8–C10 | 113.1 (6) | C19–N2–C20 | 121.9 (10) | N1–C18–C19 | 106.3 (6) |
| O4–Co–O5 | 95.9 (3) | C7–C8–C10 | 117.5 (10) | O1–C1–C2 | 129.3 (11) | N2–C19–C18 | 109.8 (11) |
| O4–Co–O6 | 96.7 (3) | C6–C9–F7 | 115.9 (12) | O1–C1–C4 | 115.2 (10) | N2–C20–C21 | 127.2 (9) |
| O5–Co–O6 | 73.9 (3) | C6–C9–F8 | 114.5 (9) | C2–C1–C4 | 115.5 (11) | C20–C21–C22 | 117.6 (10) |
| O5–Cu–O6 | 83.9 (3) | C6–C9–F9 | 111.9 (8) | C1–C2–C3 | 123.4 (12) | C20–C21–C26 | 124.1 (9) |
| O5–Cu–N1 | 94.6 (3) | F7–C9–F8 | 102.8 (12) | O2–C3–C2 | 125.9 (6) | C22–C21–C26 | 118.2 (9) |
| O5–Cu–N2 | 176.8 (3) | F7–C9–F9 | 104.3 (12) | O2–C3–C5 | 114.3 (9) | C21–C22–C23 | 121.9 (13) |
| O6–Cu–N1 | 173.0 (3) | F8–C9–F9 | 106.3 (6) | C2–C3–C5 | 119.8 (8) | C22–C23–C24 | 119.4 (8) |
| O6–Cu–N2 | 97.1 (3) | C8–C10–F10 | 113.5 (7) | C1–C4–F1 | 109.4 (13) | C23–C24–C25 | 121.4 (13) |
| N1–Cu–N2 | 84.7 (4) | C8–C10–F11 | 110.0 (12) | C1–C4–F2 | 119.2 (7) | C24–C25–C26 | 120.9 (10) |
| Co–O1–C1 | 122.0 (7) | C8–C10–F12 | 117.1 (12) | C1–C4–F3 | 111.5 (11) | O6–C26–C21 | 122.8 (11) |
| Co–O2–C3 | 126.7 (6) | F10–C10–F11 | 101.6 (9) | F1–C4–F2 | 106.2 (8) | O6–C26–C25 | 119.0 (6) |
| Co–O3–C6 | 125.7 (5) | F10–C10–F12 | 105.8 (9) | F1–C4–F3 | 98.6 (12) | C21–C26–C25 | 118.2 (8) |
| Co–O4–C8 | 123.8 (6) | F11–C10–F12 | 107.6 (8) | F2–C4–F3 | 109.9 (15) | | |

[a] Bond lengths (Å) and angles (deg) for Cu(salen)Co(hfa)$_2$. Estimated standard deviation in parentheses.

positional parameters for the 48 nonhydrogen atoms along with calculated hydrogen positions are listed in Table I.[13] The anisotropic thermal parameters appear in Table II.

## Results and Discussion

The molecular structure as determined by X-ray diffraction (Figure 1) consists of six-coordinate cobalt and a four-coordinate copper. As proposed for other binuclear salen compounds,[2] the phenolic oxygen atoms act as bridging atoms. The copper–cobalt distance of 3.060 (1) Å excludes the possibility of any significant metal–metal bonding. Bond lengths and angles for the nonhydrogen atoms are listed in Table III.

The Cu(salen) portion of the molecule is somewhat distorted from the planar configuration that might be expected. The two phenyl rings are not in the best plane formed through the nitrogen and oxygen atoms coordinated to copper. In fact, the entire salen moiety has a convex shape; the angle between the planes of the two phenyl rings is 143°39′. The best plane, through the atoms Co, O2, O3, O5, and O6, makes an angle of 161°53′ with the best plane through Cu, O5, O6, N1, and N2. If we arbitrarily describe the phenyl rings as being above the plane of the copper and its coordinating atoms then the cobalt lies below this plane.

Cu(salen)[14] is dimeric in the solid state resulting in five-coordinate copper atoms. The copper(II) salen fragment in the Cu(salen)·Co(hfa)$_2$ adduct is strictly four coordinate; the closest approach of a neighboring molecule to the copper atom is 3.3 Å. The atom to which this distance refers is not a phenolic oxygen atom as in Cu(salen), but a carbon atom on a phenyl ring. The arrangement of molecules in the crystal is illustrated in Figure 2.

Visible spectroscopy could not distinguish unambiguously between compounds Co(salen)Cu(hfa)$_2$ and Cu(salen)Co(hfa)$_2$ because of overlap of the d–d transitions with strong charge transfer bands. Mass spectroscopy was employed to compare results with the conclusions from the X-ray study. Spectra were taken of samples prepared from Co(salen) and Cu(hfa)$_2$, sample I, and from Cu(salen) and Co(hfa)$_2$·2H$_2$O, sample II. In each case, all metal containing molecular ion peaks were identified as arising from M(salen) or from M(hfa)$_2$ parts of the molecule. In sample I, 97.6% of the M(hfa)$_2$ peaks came from cobalt fragments; 85.8% of the M(salen) peaks were produced by copper containing fragments. For sample II, the respective results were 96.0 and 87.0%.

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(13) See paragraph at end of paper regarding supplementary material.

(14) E. N. Baker, D. Hall, A. J. McKinnon, and T. N. Waters, *Chem. Commun.*, 134 (1967).

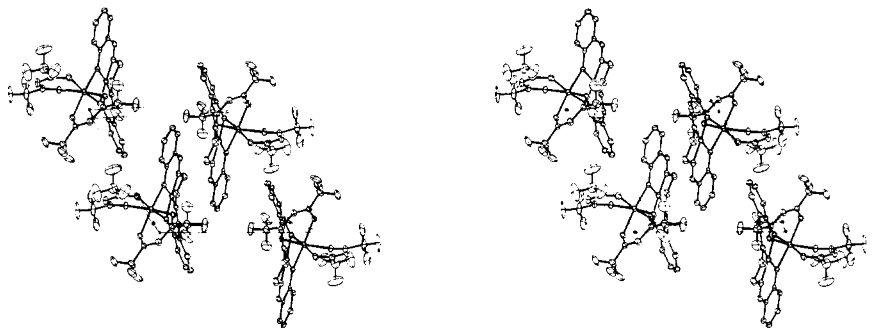

Figure 2. Stereoview of the arrangement of Cu(salen)Co(hfa)$_2$ molecules in the crystal. The origin is in the lower left corner: *a*, into the plane of the page; *b*, vertical; *c*, horizontal.

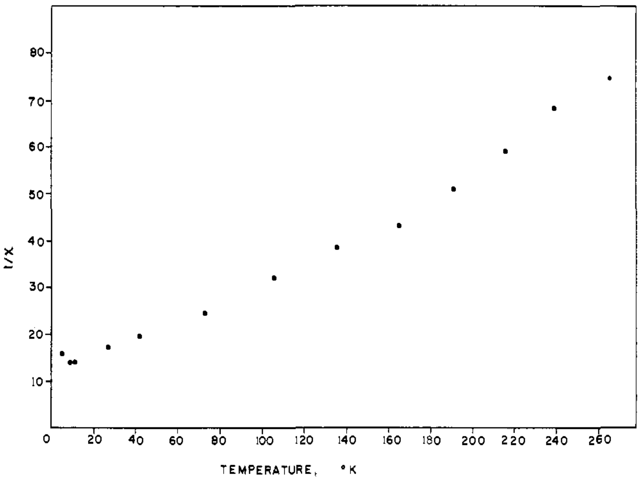

Figure 3. Temperature dependence of the magnetic susceptibility of Cu(salen)Co(hfa)$_2$.

These data are consistent with the formulation of the adduct as Cu(salen)Co(hfa)$_2$. There are alternative explanations for the deviation of the above percentages from 100%. The possible existence in the solid of a small percentage of Co(salen)Cu(hfa)$_2$ is not inconsistent with the X-ray or magnetic data. The 220° source temperature and 70 eV ionizing voltage produce a spectrum in which most peaks correspond to low *m/e* ratios. Consequently, there is a relatively high concentration of small fragments which could recombine with either metal to account for the observed peaks.

That the complex Cu(salen)Co(hfa)$_2$ can be made from Co(salen) and Cu(hfa)$_2$ as well as from Cu(salen) and Co(hfa)$_2$ is somewhat unusual. The first reaction requires copper and cobalt to exchange coordination spheres. The surprising feature of this exchange is that when both reactants are in $10^{-4}$ *M* concentration in methylene chloride, the exchange is completed in less than 20 sec at room temperature.

If bis(trifluoroacetylacetonato)copper(II), Cu(tfa)$_2$, is used instead of Cu(hfa)$_2$, the exchange rate is slow enough to be measured in a spectrometer cell. At concentrations of $10^{-4}$ *M*, the half-life for the reaction is approximately 15 min at room temperature. Preliminary studies indicate that the rate of exchange is dependent upon the concentration of the limiting reagent. A mechanism in which a Co(salen)Cu(hfa)$_2$ binuclear complex is formed very rapidly, followed by the exchange of metals as the rate-determining step, is consistent with this observation. The solvent methylene chloride is not expected to participate in the exchange. Addition of Lewis bases such as pyridine, DMSO, or bipyridine to solutions of the binuclear complex results in cleavage of the molecule and formation of Co(hfa)$_2$B$_x$ and Cu(salen).

With bis(acetylacetonato)copper(II), no binuclear complex is formed nor is any metal exchange observed. The metal–ligand bonds in the four-coordinate copper complexes have relative stabilities in the order Cu(acac)$_2$ > Cu(tfa)$_2$ > Cu(hfa)$_2$.[4] Therefore, less energy would be required to break the copper β-diketonate bond as hydrogen atoms are replaced by fluorine atoms and rearrangement might be more facile. Furthermore, if a binuclear complex is the first step in the exchange mechanism, then the observation of no adduct formation with the Lewis acid Cu(acac)$_2$ is consistent with the fact that no interchange occurs. The absence of adduct formation with bis(acetylacetonato)copper(II) parallels the decreased ability of this copper complex to pick up fifth and sixth ligands (*i.e.*, the two phenolic oxygens in this case) when compared with Cu(tfa)$_2$ and Cu(hfa)$_2$. The observed order of coordinating ability is Cu(hfa)$_2$ > Cu(tfa)$_2$ > Cu(acac)$_2$.[4]

The magnetic susceptibility of Cu(salen)Co(hfa)$_2$ was measured as a function of temperature over the range 4–265°K. The Curie–Weiss plot (Figure 3) is nonlinear as would be expected for a complex containing two paramagnetic centers with different Weiss constants. At 265°K, the magnetic moment is 5.3 BM. This is consistent with high-spin octahedral cobalt(II) and square-planar copper(II). Copper(II) usually has a magnetic moment of 1.9 BM. Assuming coupling to be negligible at this temperature, a calculated moment of 4.9 BM for the cobalt(II) contribution is obtained from the observed susceptibility of 5.3 BM and that expected for Cu(II) of 1.9 BM using the formula $(5.3^2 - 1.9^2)^{1/2}$. This calculated value for cobalt(II) falls in the center of the range expected for octahedral Co(II) complexes (4.7–5.2 BM).[15]

If the copper atom is replaced by a nickel atom, then the resulting complex, Ni(salen)Co(hfa)$_2$, has a magnetic moment which is due entirely to the paramagnetism of Co(II) since square-planar Ni(II) is diamagnetic. At 290°K, the observed moment for the nickel analog is 4.83 BM. Measurement of the susceptibility over the temperature range 4–290°K showed a Curie–Weiss temperature dependence: $\chi = 3.13/(T + 16.3)$. Adding the susceptibility of a monomeric copper(II)

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[15] R. L. Carlin, "Transition Metal Chemistry," Vol. I, Marcel Dekker, New York, N. Y., 1965, pp 1–31.

complex to that for Ni(salen)Co(hfa)$_2$ should give us the measured moment for Cu(salen)Co(hfa)$_2$ in the absence of coupling. When this was done, the calculated susceptibility closely approximated the measured susceptibility above 45°K. Below this temperature, the measured susceptibility is smaller than the calculated one. The difference increases as the temperature approaches 4°K, indicative of a small amount of antiferromagnetic coupling. The coupling could be intermolecular or intramolecular involving copper and cobalt. Since the amount of coupling is small, a calculation of the coupling constant would not be accurate because of the nonnegligible orbital contributions from the cobalt.

The adduct Cu(salen)Co(hfa)$_2$ exists in solution as well as the solid state. The visible spectrum of the complex is not an addition of the spectra of Cu(salen) and Co(hfa)$_2$. The molecular weight in methylene chloride measured by vapor pressure osmometry gave a value of 725 (theoretical 803), indicating extensive association of the two metal species in solution. The solution magnetic moment of 5.1 BM at room temperature also is consistent with the cobalt atom being in an octahedral high-spin d$^7$ configuration.

Also, there is no detectable solution esr signal at room temperature. When the esr spectrum of Cu(salen) is observed on a series of solutions to which varying quantities of Co(hfa)$_2$ are added, it is found that the signal strength decreases with addition of the cobalt until stoichiometric quantities are added. At this point, the signal disappears completely. Apparently, the cobalt becomes coupled to the copper causing very rapid relaxation of the unpaired spin. One would expect that a nmr signal could be observed if this is the case. Unfortunately, this proposal cannot be tested because Cu(salen)Co(hfa)$_2$ is only sparingly soluble in noncoordinating solvents like methylene chloride.

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**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-6640.

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# Evaluation of the Thermodynamic Data Reported for the Reversible Oxygenation of the Amine Complexes of Cobalt(II) Protoporphyrin IX Dimethyl Ester

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**Abstract:** Recently, Stynes and Ibers, *et al.*, reported thermodynamic data, determined from visible spectroscopic measurements, for the reversible oxygenation of various amine complexes of cobalt(II) protoporphyrin IX dimethyl ester. In evaluating the equilibrium constants for their systems, they employed the Hill equation in a way that appeared questionable. This, coupled with the fact that Walker has challenged one of the essential conclusions of Ibers, *et al.*, caused us to report our reexamination of the data for this system. The method employed in the reexamination involved rigorously solving for both $K^{-1}$ and $\epsilon_C - \epsilon_A$ with numerical techniques and representing the solution graphically as we have strongly advocated in the past. It was found that, on the whole, the systems investigated by Ibers, *et al.*, were poorly defined and in most instances no numerical data can be obtained.

Stynes and Ibers,[1] and others[2] reported thermodynamic data, determined from visible spectroscopic measurements, for the reversible oxygenation of various amine complexes of cobalt(II) protoporphyrin IX dimethyl ester.

$$\mathrm{LCoP} + \mathrm{O_2(g)} \overset{K_{eq}}{\rightleftharpoons} \mathrm{LCoP(O_2)} \qquad (1)$$

The equilibrium constant expression for a system such as described by eq 1 can be written as

$$K = \frac{[C_C]}{[C_B - C_C][C_A - C_C]} \qquad (2)$$

where $C_A$ is the initial molar concentration of acid, $C_B$ is the initial molar concentration of base, and $C_C$ is the equilibrium molar concentration of complex. The Benesi–Hildebrand (B-H) analysis[3,4] is one of the most common procedures for manipulating eq 2 to arrive at a linear form of the equilibrium constant expression. Ibers, *et al.*, employed an approach referred to as the Hill equation.[1-3] The application of this equation in the calculation of thermodynamic parameters from spectroscopic observables can be shown to suffer from many of the pitfalls which have been described in the literature for B-H type analyses.[4-7] These procedures

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[1] H. C. Stynes and J. A. Ibers, *J. Amer. Chem. Soc.*, **94**, 1559 (1972).

[2] D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, **95**, 1142 (1973).

[3] A. V. Hill, *J. Physiol. (London)*, **40**, IVP (1910).

[4] N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, **81**, 6138 (1959).

[5] N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, **81**, 6142 (1959).