# A Ligand-Induced Proton Shift (LIPS) in Two Cobaloxime Complexes. The Crystal and Molecular Structures of Chloro(dimethylglyoximato)-(dimethylglyoxime)(sulfanilamide)cobalt(III) Monohydrate and Chloro(dimethylglyoximato)-(dimethylglyoxime)(4-chloroaniline)cobalt(III) Dihydrate

**Gus J. Palenik,* Douglas A. Sullivan, and Datta V. Naik**

*Contribution from the Center for Molecular Structure, Department of Chemistry, University of Florida, Gainesville, Florida, 32611.* *Received October 11, 1974*

**Abstract:** Crystal structure studies of the compounds reported to be chlorobis(dimethylglyoximato)(ligand)cobalt(III), where the ligand is sulfanilamide or 4-chloroaniline, have been completed. An unusual ligand-induced proton shift (LIPS) has occurred so that the complexes are best formulated as chloro(dimethylglyoximato)(dimethylglyoxime)(ligand)cobalt-(III), where both neutral and dianionic dimethylglyoxime groups are found in one complex. The crystals of I, $CoC_{14}H_{24}ClN_6O_7S$ where the ligand is sulfanilamide, are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions of $a$ = 10.591 (1), $b$ = 13.970 (2), and $c$ = 14.270 (3) Å. The complex II, $CoC_{14}H_{24}Cl_2N_5O_6$ where the ligand is 4-chloroaniline, is triclinic, space group $P\bar{1}$, with cell dimensions of $a$ = 7.494 (3), $b$ = 11.838 (4), and $c$ = 13.758 (6) Å, and $\alpha$ = 106.31 (3), $\beta$ = 91.25 (3), and $\gamma$ = 112.79 (3)°. Both structures were determined using the heavy-atom method and refined by least-squares methods to an $R$ of 0.056 for the 1696 reflections used in the analysis of I and $R$ of 0.047 for the 2000 reflections used in the case of II. The hydrogen atoms were located in both structures and were refined in the case of II. The most unusual feature in the two structures is the orientation of the benzene ring of both the sulfanilamide and 4-chloroaniline groups over the dianionic ligand. The various distances, orientation, etc., suggest a $\pi$-type interaction between the ligand and dmg rings. The coordination of the weakly basic ligands has apparently induced a shift of a proton from one Hdmg group to the other, thereby enhancing the stability of the complex. The concept of LIPS should have important implications in biological systems.

A number of sulfonamides, $R-SO_2-NH_2$, are known to inhibit the zinc metalloenzyme carbonic anhydrase.[1] The sulfonamide presumably bonds directly to the metal atom at the active site by replacement of a water molecule in the coordination sphere.[2] Although no stable zinc complexes of sulfonamides have been isolated, a bismuth trichloride complex with 3-sulfanilamide-6-methoxypyridazine in which the Bi atom is bonded to the O and N atoms of the sulfonamide group has been characterized.[3] Complexes of sulfanilamide with Co have been prepared and infrared studies suggested that the metal atom was coordinated to the amino rather than to the sulfonamide group.[4,5] Since cobalt can replace the zinc atom in carbonic anhydrase with only a 50% decrease in activity, the cobalt sulfanilamide complexes might be useful as model compounds. Therefore, in order to confirm the infrared studies, we undertook a study of the reported $ClCo(Hdmg)_2(sulfa)$ complex, where Hdmg is the monoprotonated form of the dimethylglyoxime dianion dmg, and sulfa is sulfanilamide. In addition at the start of our investigation, there was very little structural data on $Co(Hdmg)_2$ complexes in spite of the fact that cobaloximes had been proposed[6] as models for vitamin $B_{12}$. Our results, together with very recently reported structural data, provide an interesting comparison of the effect of axial groups on the $Co(Hdmg)_2$ skeleton. However, of more importance is the ligand-induced proton shift (LIPS) which has occurred in the complex, which should be formulated more exactly as $ClCo(H_2dmg)(dmg)(sulfa)$ (I).

The presence of both a dianionic and a neutral dimethylglyoxime group in I was unexpected. Therefore, we prepared the corresponding 4-chloroaniline derivative to eliminate possible hydrogen bonding effects of the $-SO_2NH_2$ group and to investigate the scope of LIPS. The results of our crystal structure study of the 4-chloroaniline complex indicate that the LIPS has also occurred in this complex and therefore that LIPS may be of general importance in cobaloxime complexes as well as other systems.

## Experimental Section

**Collection and Reduction of the X-Ray Data.** The method of Ablov and Shafranskii[4] was used to prepare I. Recrystallization of the crude product from hot ethanol gave small, well-formed, brown crystals. The complex $Co(H_2dmg)(dmg)$(4-chloroaniline) (II) was synthesized[7] and recrystallized from acetone.

Preliminary Weissenberg and precession photographs were taken from both compounds. The crystals of I were orthorhombic. The systematic absence of $h00$ if $h = 2n + 1$, $0k0$ if $k = 2n + 1$, and $00l$ if $l = 2n + 1$ uniquely determined the space group to be $P2_12_12_1$ ($D_2^4$). Crystals of II showed no systematic absences nor symmetry, and the space group was either $P1$ or $P\bar{1}$. The intensity statistics suggested $P\bar{1}$ as the correct space group, and the analysis was carried out on that basis.

A computer-controlled Syntex $P\bar{1}$ diffractometer and graphite monochromatized molybdenum radiation ($\lambda\alpha_1$ = 0.70926 and $\lambda\alpha_2$ = 0.71354 Å) were used for all subsequent measurements. The unit cell dimensions and orientation matrix were derived from a least-squares fit of the angular values of 15 reflections. The densities were measured by flotation. The pertinent crystal data are given in Table I.

The intensities of all the reflections in the appropriate $2\theta$ range were measured using a variable speed $\theta$-$2\theta$ scan technique. The slowest speed was 1°/min for reflections with $I$(intensity) < 75 Hz, and the fastest rate was 24°/min if $I$ > 750 Hz. A linear interpolation was used for values between these two limits. The scan was from 1° below the $\alpha_1$ peak to 1° above the $\alpha_2$ peak with background counts at the beginning and end of the scan. A set of four standard reflections was measured after every 96 reflections and showed a slight random variation (2% for I and 7% for II) over the period of data collection.

The total number of reflections measured in each case is given in Table I together with the total number considered to be reliable.

Table I. Crystal Data for $ClCo(H_2dmg)(dmg)(sulfa)\cdot H_2O$ [I] and $ClCo(H_2dmg)(dmg)(4\text{-chloroaniline})\cdot 2H_2O$ [II]

| | I | II |
|---|---|---|
| Molecular formula | $CoC_{14}H_{24}ClN_6O_7S$ | $CoC_{14}H_{24}Cl_2N_5O_6$ |
| Molecular weight | 514.83 | 488.22 |
| Crystal system | Orthorhombic | Triclinic |
| Space group | $P2_12_12_1$ | $P\bar{1}$ |
| a, Å | 10.591 (1) | 7.494 (3) |
| b, Å | 13.970 (2) | 11.838 (4) |
| c, Å | 14.270 (3) | 13.758 (6) |
| α, deg | | 106.31 (3) |
| β, deg | | 91.25 (3) |
| γ, deg | | 112.79 (3) |
| Volume, Å$^3$ | 2111.3 (6) | 1068.3 (7) |
| Z | 4 | 2 |
| ρ (calcd), g/cm$^3$ | 1.619 | 1.518 |
| ρ (meas), g/cm$^3$ | 1.61 | 1.52 |
| Crystal size, mm$^3$ | 0.19 × 0.16 × 0.09 | 0.24 × 0.18 × 0.07 |
| Method of data collection | Moving crystal<br>Moving counter | Moving crystal<br>Moving counter |
| Radiation used | Mo Kα | Mo Kα |
| μ, cm$^{-1}$ | 11.2 | 11.2 |
| 2θ range, deg | 0–50 | 0–45 |
| No. of unique reflections | 2105 | 2807 |
| No. of obsd reflections | 1696 | 2000 |

The criteria used were $I > 1.3\sigma(I)$ for I and $I > 2.0\sigma(I)$ for II. These data were reduced to a set of structure amplitudes on an arbitrary scale by the application of Lorentz-polarization factors. The monochromator was assumed to be a 50% mosaic and 50% perfect crystal. The linear absorption coefficients were only 11.2 cm$^{-1}$, and absorption corrections were considered negligible and not applied.

**Solution and Refinement.** In both complexes the position of the cobalt atom was determined from a sharpened three-dimensional Patterson function. The remaining atoms were located in successive Fourier syntheses. The R value ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0.18 for I and 0.27 for II after the location of all the nonhydrogen atoms. Three full-matrix least-squares cycles with individual isotropic thermal parameters reduced R for I to 0.083 and for II to 0.095. Further refinement with anisotropic thermal parameters reduced the R value to 0.066 for both compounds. The block approximation was used in the anisotropic refinement because our experience as well as that of others[8] has indicated that the full matrix and block approximation converge to identical results. At this point a difference Fourier synthesis was used to locate the hydrogen atoms in both compounds. After three least-squares cycles during which the hydrogen atom contributions were included in the structure factor calculations but their parameters were not varied R was reduced to 0.056 for I and to 0.052 for II. In the case of II the hydrogen atoms were refined using isotropic thermal parameters and the final R value was 0.047 with the "goodness-of-fit" equal to 1.15. The final positional and thermal parameters are given in Tables II-V. A list of observed and calculated structure factors for both complexes is available.[9]

The quantity minimized in the least-squares calculations was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme used was $\sqrt{w} = |F_o|/F(\text{low})$ if $|F_o| < F(\text{low})$, $\sqrt{w} = 1$ if $F(\text{low}) < |F_o| < F(\text{high})$, and $\sqrt{w} = F(\text{high})/|F_o|$ if $|F_o| > F(\text{high})$, where F(low) and F(high) are given in Table II. The scattering factors for the nonhydrogen atoms were from Hanson et al.,[10] with the hydrogen scattering factor from Stewart et al.[11] All calculations were carried out on an IBM 370/165 with programs written or modified by G.J.P.

## Results and Discussion

Both I and II crystallize with discrete molecules of the complex and water molecules linked in a three-dimensional hydrogen-bonded network. The atomic numbering and thermal ellipsoids of the $ClCo(H_2dmg)(dmg)(sulfa)$ molecules are shown in Figure 1 while those of the $ClCo(H_2dmg)(dmg)(4\text{-chloroaniline})$ complex are presented in Figure 2. The individual bond distances are tabulated in Table VI, and the corresponding bond angles are available.[9]

The two dmg groups in both I and II are approximately

Table II. Final Atomic Parameters of Nonhydrogen Atoms for $ClCo(H_2dmg)(dmg)(sulfa)\cdot H_2O$[a]

| Atom | x | y | z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 11 546 (12) | 13 968 (9) | 2 804 (8) | 354 (9) | 188 (5) | 164 (5) | −28 (14) | 14 (15) | 3 (11) |
| Cl | 3 190 (2) | 1 301 (2) | −123 (2) | 43 (2) | 39 (1) | 30 (1) | 1 (3) | 10 (3) | 4 (2) |
| S | −1 957 (3) | 819 (2) | 4 655 (2) | 69 (2) | 43 (1) | 23 (1) | 16 (3) | 19 (3) | 15 (2) |
| O(11) | 1 133 (8) | −577 (5) | 689 (6) | 92 (8) | 23 (3) | 57 (5) | −16 (10) | −2 (12) | 3 (7) |
| O(12) | 1 806 (8) | 2 949 (5) | 1 475 (5) | 103 (9) | 25 (4) | 41 (4) | −21 (10) | −4 (11) | −31 (7) |
| O(21) | 1 294 (7) | 3 368 (4) | −170 (6) | 71 (7) | 25 (4) | 56 (5) | −28 (8) | −16 (11) | 9 (7) |
| O(22) | 573 (8) | −142 (5) | −964 (5) | 95 (9) | 27 (4) | 41 (4) | −3 (9) | −22 (10) | −21 (7) |
| O(1) | −2 857 (7) | 67 (6) | 4 686 (6) | 80 (8) | 78 (6) | 42 (4) | −33 (12) | 0 (12) | 49 (10) |
| O(2) | −2 247 (11) | 1 721 (6) | 5 067 (6) | 222 (16) | 59 (5) | 28 (4) | 99 (16) | 69 (13) | 24 (8) |
| N(2) | −726 (9) | 418 (7) | 5 156 (6) | 74 (9) | 56 (6) | 33 (5) | −19 (12) | −37 (12) | 15 (9) |
| N(1) | −690 (8) | 1 484 (6) | 639 (5) | 61 (8) | 26 (4) | 24 (4) | −3 (10) | −5 (9) | −2 (7) |
| N(11) | 1 340 (8) | 296 (6) | 1 014 (6) | 46 (8) | 34 (4) | 34 (4) | −9 (10) | 10 (10) | −1 (8) |
| N(12) | 1 655 (8) | 1 997 (6) | 1 402 (6) | 45 (8) | 34 (5) | 22 (4) | −18 (10) | −9 (9) | −17 (7) |
| N(21) | 956 (7) | 2 509 (5) | −478 (5) | 30 (7) | 30 (4) | 34 (4) | −2 (9) | 17 (9) | 11 (7) |
| N(22) | 637 (8) | 808 (6) | −853 (6) | 57 (8) | 36 (4) | 21 (4) | −6 (10) | 11 (9) | −12 (7) |
| C(11) | 1 626 (9) | 428 (9) | 1 882 (8) | 32 (9) | 52 (7) | 32 (5) | −13 (13) | 15 (11) | 14 (11) |
| C(12) | 1 832 (9) | 1 457 (8) | 2 126 (7) | 48 (9) | 43 (6) | 26 (5) | 1 (14) | 41 (12) | 14 (10) |
| C(13) | 1 733 (14) | −365 (10) | 2 619 (9) | 129 (16) | 52 (7) | 47 (7) | 51 (19) | −59 (19) | 36 (13) |
| C(14) | 2 158 (14) | 1 824 (10) | 3 074 (8) | 120 (16) | 79 (9) | 21 (6) | 31 (21) | −12 (16) | −30 (12) |
| C(21) | 549 (9) | 2 371 (8) | −1 320 (7) | 36 (9) | 54 (7) | 19 (5) | 1 (13) | 18 (11) | 23 (10) |
| C(22) | 378 (9) | 1 369 (9) | −1 545 (7) | 42 (9) | 56 (6) | 23 (5) | −2 (15) | 4 (11) | −5 (11) |
| C(23) | 379 (12) | 3 192 (10) | −1 978 (9) | 77 (13) | 67 (8) | 43 (7) | 4 (18) | −9 (16) | 64 (13) |
| C(24) | −186 (13) | 1 024 (11) | −2 438 (9) | 79 (13) | 90 (10) | 27 (6) | 7 (19) | −11 (14) | −18 (13) |
| C(1) | −1 052 (9) | 1 320 (8) | 1 605 (6) | 25 (7) | 43 (5) | 26 (4) | −27 (14) | 14 (11) | 28 (9) |
| C(2) | −1 032 (12) | 2 086 (7) | 2 221 (7) | 107 (13) | 17 (4) | 33 (5) | 30 (15) | 21 (16) | 6 (8) |
| C(3) | −1 343 (11) | 1 940 (7) | 3 157 (7) | 78 (11) | 32 (5) | 20 (4) | −3 (14) | 19 (12) | −7 (8) |
| C(4) | −1 622 (10) | 1 040 (7) | 3 460 (7) | 53 (10) | 38 (6) | 18 (4) | 14 (12) | 17 (11) | −3 (8) |
| C(5) | −1 647 (10) | 268 (8) | 2 854 (7) | 50 (9) | 36 (6) | 31 (5) | −42 (13) | 20 (12) | 17 (9) |
| C(6) | −1 360 (11) | 424 (8) | 1 911 (7) | 74 (11) | 32 (5) | 29 (5) | −28 (14) | −5 (13) | −9 (9) |
| O(w) | 3 509 (8) | −1 542 (7) | 495 (7) | 78 (9) | 78 (7) | 77 (7) | −25 (13) | 29 (12) | −11 (12) |

[a] All values are ×$10^4$ except for Co which are ×$10^5$. The estimated standard deviations are given in parantheses. The temperature factor is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Final Parameters for the Hydrogen Atoms in ClCo$(H_2dmg)$(dmg)(sulfa)$\cdot H_2O$[a]

| Atom [bonded to] | Distance | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|---|
| H(2) [C(2)] | 0.95 | −123 | 270 | 197 | 3.5 |
| H(3) [C(3)] | 1.21 | −105 | 251 | 376 | 3.0 |
| H(5) [C(5)] | 1.15 | −179 | −036 | 337 | 4.0 |
| H(6) [C(6)] | 0.89 | −113 | −011 | 161 | 4.0 |
| H(7) [N(1)] | 0.78 | −088 | 107 | 030 | 3.5 |
| H(8) [N(1)] | 1.03 | −123 | 204 | 040 | 3.5 |
| H(9) [N(2)] | 0.85 | −060 | −009 | 484 | 4.5 |
| H(10) [N(2)] | 0.94 | −007 | 074 | 547 | 4.5 |
| H(11) [C(13)] | 0.90 | 178 | −090 | 227 | 5.0 |
| H(12) [C(13)] | 1.34 | 296 | −026 | 282 | 5.0 |
| H(13) [C(13)] | 1.24 | 213 | −017 | 341 | 5.0 |
| H(14) [C(14)] | 1.25 | 206 | 109 | 357 | 5.0 |
| H(15) [C(14)] | 1.26 | 318 | 174 | 352 | 5.0 |
| H(16) [C(14)] | 1.32 | 126 | 226 | 355 | 5.0 |
| H(21) [C(23)] | 0.89 | 089 | 366 | −179 | 5.0 |
| H(22) [C(23)] | 0.97 | −051 | 332 | −189 | 5.0 |
| H(23) [C(23)] | 1.30 | 120 | 307 | −264 | 5.0 |
| H(24) [C(24)] | 0.82 | −062 | 145 | −268 | 5.0 |
| H(25) [C(24)] | 1.08 | 069 | 082 | −277 | 5.0 |
| H(26) [C(24)] | 0.93 | −001 | 037 | −244 | 5.0 |
| H(w1) [O(w1)] | 1.03 | 293 | −210 | 029 | 6.0 |
| H(w2) [O(w2)] | 0.98 | 273 | −125 | 072 | 6.0 |
| H(B1) [O(22)] | 1.04 | 091 | −040 | −033 | 3.5 |
| H(B2) [O(21)] | 0.90 | 160 | 327 | 041 | 3.5 |

[a] The hydrogen atom is given followed by the atom to which it is bonded in brackets, the corresponding bond distance (in Å), the positional parameters ($\times 10^{+3}$), and the isotropic thermal parameter (in Å$^2$).

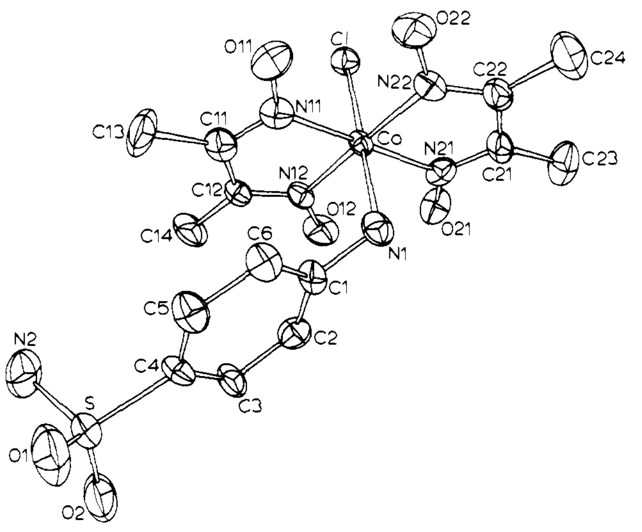

Figure 1. An ORTEP drawing of the chloro(dimethylglyoximato)(dimethylglyoxime)(sulfanilamide)cobalt(III) molecule showing the atomic numbering and thermal ellipsoids. The water molecule has not been included. The ligand N(11) to N(12) is the dianion while N(21) to N(22) is the neutral molecule.

planar[9] and are linked by two intramolecular hydrogen bonds (see Table VII). Although we initially anticipated that one hydrogen atom would be found on each dimethylglyoxime group, the difference Fourier synthesis in each case indicated that the hydrogen atoms were bonded to O(21) and O(22). The distances of O(21)-H(B2) of 0.90 and 1.13 Å and O(22)-H(B1) of 1.04 and 1.16 Å in I and II, respectively, are clearly in agreement with the formulation $H_2dmg$ and dmg for the ligands. These results are in sharp contrast to the results reported for various $Co(Hdmg)_2$ complexes,[12-16] as well as for $Fe(Hdmg)_2(imidazole)_2$,[17] $Ni(Hdmg)_2$,[18] and $Cu(Hdmg)_2$,[19] where the ligands are either monoprotonated or the hydrogens were *assumed* to be equidistant from the two oxygen atoms. Furthermore, the diprotonated ligand has larger deviations from planarity when compared to the dianionic group. A final point in support of the unusual formulation is the difference in the Co-N bond distances. The lengths of the Co-N bonds to the dmg side range from 1.870 to 1.884 Å with an average of 1.878 (8) Å compared to a range on the

Table IV. Final Atomic Parameters of Nonhydrogen Atoms for ClCo$(H_2dmg)$(dmg)(4-chloroaniline)$\cdot 2H_2O$[a]

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 19 148 (12) | 36 142 (8) | 21 611 (6) | 1287 (16) | 454 (7) | 276 (4) | 822 (17) | 219 (13) | 157 (9) |
| Cl(1) | −1353 (2) | 2 445 (1) | 1 882 (1) | 148 (3) | 65 (2) | 53 (1) | 78 (4) | 25 (3) | 14 (2) |
| Cl(2) | 8 142 (4) | 10 300 (2) | 3 785 (2) | 512 (9) | 67 (2) | 138 (2) | 65 (7) | 46 (7) | 46 (4) |
| O(11) | 1 633 (7) | 4 573 (4) | 534 (3) | 305 (13) | 95 (5) | 36 (3) | 168 (14) | 7 (9) | 44 (6) |
| O(12) | 1 742 (6) | 4 621 (4) | 4 260 (3) | 304 (13) | 89 (5) | 32 (3) | 167 (13) | 70 (9) | 33 (6) |
| O(21) | 2 285 (7) | 2 611 (4) | 3 796 (3) | 314 (13) | 104 (5) | 41 (3) | 199 (14) | 74 (10) | 70 (6) |
| O(22) | 1 944 (7) | 2 468 (4) | 17 (3) | 298 (13) | 114 (6) | 30 (3) | 199 (14) | 31 (9) | 25 (6) |
| N(1) | 4 821 (7) | 4 589 (5) | 2 375 (3) | 157 (12) | 93 (6) | 37 (3) | 123 (14) | 29 (10) | 50 (7) |
| N(11) | 1 600 (7) | 4 753 (5) | 1 536 (3) | 179 (12) | 75 (6) | 35 (3) | 108 (14) | 24 (10) | 26 (7) |
| N(12) | 1 693 (7) | 4 792 (4) | 3 347 (3) | 156 (12) | 58 (5) | 35 (3) | 71 (13) | 30 (9) | 19 (6) |
| N(21) | 2 289 (7) | 2 459 (5) | 2 788 (3) | 191 (13) | 72 (5) | 41 (3) | 123 (14) | 41 (10) | 39 (7) |
| N(22) | 2 144 (7) | 2 398 (5) | 980 (3) | 168 (12) | 74 (5) | 35 (3) | 99 (13) | 21 (10) | 12 (7) |
| C(11) | 1 403 (8) | 5 758 (6) | 2 145 (5) | 170 (15) | 67 (7) | 53 (4) | 101 (17) | 25 (13) | 41 (9) |
| C(12) | 1 443 (8) | 5 772 (6) | 3 208 (5) | 168 (15) | 59 (6) | 51 (4) | 73 (16) | 30 (13) | 14 (8) |
| C(13) | 1 247 (10) | 6 794 (6) | 1 785 (5) | 268 (19) | 85 (8) | 76 (5) | 190 (21) | −5 (16) | 55 (10) |
| C(14) | 1 310 (10) | 6 815 (7) | 4 067 (5) | 281 (20) | 100 (8) | 62 (5) | 214 (22) | 50 (16) | −6 (10) |
| C(21) | 2 584 (9) | 1 516 (6) | 2 201 (5) | 214 (17) | 66 (7) | 56 (4) | 134 (18) | 47 (14) | 44 (9) |
| C(22) | 2 509 (9) | 1 475 (6) | 1 124 (5) | 164 (15) | 65 (7) | 60 (5) | 110 (17) | 52 (13) | 24 (9) |
| C(23) | 3 010 (14) | 584 (8) | 2 593 (7) | 530 (32) | 112 (10) | 102 (7) | 347 (31) | 148 (24) | 106 (14) |
| C(24) | 2 779 (12) | 465 (7) | 277 (6) | 410 (27) | 121 (10) | 73 (6) | 301 (28) | 87 (20) | 11 (12) |
| C(1) | 5 676 (7) | 5 999 (5) | 2 722 (4) | 96 (13) | 70 (6) | 44 (4) | 72 (15) | 23 (11) | 44 (8) |
| C(2) | 6 105 (9) | 6 655 (6) | 3 753 (5) | 198 (16) | 71 (7) | 47 (4) | 89 (17) | 4 (13) | 28 (9) |
| C(3) | 6 866 (9) | 7 971 (6) | 4 082 (5) | 221 (17) | 91 (8) | 42 (4) | 95 (19) | 4 (14) | 8 (9) |
| C(4) | 7 201 (10) | 8 629 (6) | 3 382 (6) | 195 (17) | 73 (7) | 82 (6) | 61 (18) | 23 (16) | 39 (10) |
| C(5) | 6 809 (10) | 7 972 (7) | 2 340 (5) | 237 (19) | 99 (8) | 69 (5) | 99 (20) | 83 (16) | 95 (11) |
| C(6) | 6 047 (9) | 6 644 (6) | 2 005 (5) | 191 (16) | 82 (7) | 52 (4) | 104 (18) | 56 (13) | 52 (9) |
| O(w1) | 6 682 (7) | 3 785 (5) | 646 (4) | 264 (13) | 148 (7) | 80 (4) | 241 (16) | 102 (11) | 100 (8) |
| O(w2) | 6 802 (7) | 3 830 (5) | 3 690 (3) | 276 (13) | 166 (7) | 53 (3) | 295 (16) | 20 (10) | 22 (7) |

[a] All values are $\times 10^4$ except for Co which are $\times 10^5$. The estimated standard deviations are given in parentheses. The temperature factors are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

**Table V.** Final Parameters for the Hydrogen Atoms for ClCo(H$_2$dmg)(dmg)(4-chloroaniline)·2H$_2$O (The Estimated Standard Deviations are Given in Parentheses)[a]

| Atom [bonded to] | Distance | *x* | *y* | *z* | *B* |
|---|---|---|---|---|---|
| H(2) [C(2)] | 0.89 (5) | 591 (7) | 621 (5) | 420 (4) | 2.0 (1.1) |
| H(3) [C(3)] | 0.99 (7) | 726 (10) | 858 (7) | 478 (5) | 6.7 (1.9) |
| H(5) [C(5)] | 0.90 (7) | 709 (10) | 838 (7) | 187 (5) | 5.8 (1.7) |
| H(6) [C(6)] | 1.01 (5) | 568 (7) | 609 (5) | 127 (4) | 2.0 (1.1) |
| H(7) [N(1)] | 1.03 (7) | 522 (10) | 434 (6) | 166 (5) | 6.1 (1.7) |
| H(8) [N(1)] | 0.83 (6) | 518 (9) | 428 (6) | 278 (5) | 4.5 (1.5) |
| H(11) [C(13)] | 0.96 (8) | 243 (11) | 753 (7) | 212 (6) | 8.2 (2.1) |
| H(12) [C(13)] | 0.79 (9) | 37 (11) | 692 (7) | 203 (6) | 8.5 (2.2) |
| H(13) [C(13)] | 1.00 (1) | 102 (10) | 663 (7) | 103 (5) | 7.1 (1.9) |
| H(14) [C(14)] | 1.02 (7) | 46 (9) | 639 (6) | 453 (5) | 5.8 (1.7) |
| H(15) [C(14)] | 0.78 (7) | 62 (9) | 708 (6) | 388 (5) | 4.9 (1.5) |
| H(16) [C(14)] | 0.87 (8) | 228 (11) | 734 (8) | 456 (6) | 8.6 (2.2) |
| H(21) [C(23)] | 0.86 (10) | 414 (12) | 59 (8) | 248 (6) | 9.6 (2.4) |
| H(22) [C(23)] | 0.92 (9) | 239 (12) | −21 (8) | 211 (6) | 9.3 (2.4) |
| H(23) [C(23)] | 0.97 (9) | 266 (12) | 52 (8) | 326 (7) | 9.8 (2.5) |
| H(24) [C(24)] | 1.03 (9) | 242 (12) | 44 (8) | −46 (7) | 9.4 (2.4) |
| H(25) [C(24)] | 0.84 (10) | 396 (12) | 58 (8) | 29 (6) | 9.1 (2.3) |
| H(26) [C(24)] | 1.00 (7) | 210 (10) | −38 (7) | 40 (5) | 5.9 (1.7) |
| H(w1) [O(w1)] | 0.70 (8) | 659 (11) | 319 (7) | 69 (6) | 7.2 (2.0) |
| H(w1′) [O(w1)] | 0.80 (13) | 771 (16) | 438 (11) | 72 (9) | 15.2 (3.7) |
| H(w2) [O(w2)] | 0.79 (7) | 736 (10) | 420 (7) | 425 (5) | 6.6 (1.8) |
| H(w2′) [O(w2)] | 0.71 (7) | 747 (10) | 371 (6) | 337 (5) | 6.0 (1.8) |
| H(B1) [O(22)] | 1.16 (8) | 153 (10) | 335 (7) | 17 (5) | 6.3 (1.8) |
| H(B2) [O(21)] | 1.13 (8) | 184 (10) | 345 (7) | 402 (5) | 6.7 (1.8) |

[a] The hydrogen atom is given followed by the atom to which it is bonded in brackets, the corresponding bond distance (in Å), the positional parameters with estimated standard deviations ($\times 10^{+3}$), and the isotropic thermal parameter (in Å$^2$).

**Table VI.** Bond Distances in ClCo(H$_2$dmg)(dmg)(sulfa)·H$_2$O [1] and ClCo(H$_2$dmg)(dmg)(4-chloroaniline)·2H$_2$O [II] with Their Estimated Standard Deviations

| | Distances, Å | | | Distances, Å | |
|---|---|---|---|---|---|
| Bond | I | II | Bond | I | II |
| Co–Cl(1) | 2.235 (3) | 2.257 (2) | Co–N(1) | 2.023 (8) | 1.999 (6) |
| Co–N(11) | 1.870 (8) | 1.872 (5) | Co–N(21) | 1.905 (8) | 1.908 (5) |
| Co–N(12) | 1.884 (8) | 1.884 (5) | Co–N (22) | 1.896 (8) | 1.906 (5) |
| N(11)–O(11) | 1.323 (11) | 1.337 (6) | N(21)–O(21) | 1.326 (10) | 1.348 (6) |
| N(12)–O(12) | 1.344 (11) | 1.329 (6) | N(22)–O(22) | 1.338 (11) | 1.359 (6) |
| N(11)–C(11) | 1.289 (14) | 1.311 (8) | N(21–C(21) | 1.292 (12) | 1.280 (8) |
| N(12)–C(12) | 1.293 (13) | 1.308 (8) | N(22)–C(22) | 1.290 (14) | 1.288 (8) |
| C(11)–C(12) | 1.494 (16) | 1.457 (9) | C(21)–C(22) | 1.447 (17) | 1.468 (9) |
| C(11)–C(13) | 1.532 (17) | 1.488 (10) | C(21)–C(23) | 1.494 (17) | 1.486 (11) |
| C(12)–C(14) | 1.488 (16) | 1.487 (10) | C(22)–C(24) | 1.488 (16) | 1.498 (11) |
| O(11)···O(22) | 2.507 (11) | 2.497 (7) | O(12)···O(21) | 2.479 (11) | 2.479 (7) |
| C(1)–C(2) | 1.386 (14) | 1.374 (8) | C(1)–N (1) | 1.449 (12) | 1.461 (8) |
| C(2)–C(3) | 1.392 (14) | 1.364 (10) | C(4)–Cl (2) | | 1.734 (8) |
| C(3)–C(4) | 1.362 (14) | 1.370 (10) | C(4)–S | 1.769 (10) | |
| C(4)–C(5) | 1.383 (15) | 1.388 (10) | S–N (2) | 1.588 (10) | |
| C(5)–C(6) | 1.397 (15) | 1.378 (10) | S–O (1) | 1.419 (9) | |
| C(6)–C(1) | 1.365 (15) | 1.379 (9) | S–O (2) | 1.424 (9) | |

**Table VII.** Hydrogen Bonds in ClCo(H$_2$dmg)(dmg)(sulfa)·H$_2$O [I] and ClCo(H$_2$dmg)(dmg)(4-chloroaniline)·2H$_2$O [II] (The Estimated Standard Deviations are Given in Parentheses)

| | Bond | | Distances, Å | | | Angles, deg |
|---|---|---|---|---|---|---|
| | D–H···A[a] | Position of A | D–H | H···A | D···A | D–H···A |
| I | O(21)–H(B2)···O(12) | *x, y, z* | 0.90 | 1.60 | 2.479 | 164 |
| | O(22)–H(B1)···O(11) | *x, y, z* | 1.02 | 1.50 | 2.507 | 165 |
| | N(1)–H(7)···O(1) | −½ − *x*, −*y*, −½ + *z* | 0.78 | 2.25 | 2.985 | 156 |
| | N(1)–H(8)···Cl | −½ + *x*, ½ − *y*, −*z* | 1.03 | 2.43 | 3.395 | 157 |
| | N(2)–H(9)···O(21) | −*x*, −½ + *y*, ½ − *z* | 0.85 | 2.32 | 2.927 | 128 |
| | N(2)–H(10)···O(w) | ½ − *x*, −*y*, ½ + *z* | 0.94 | 2.00 | 2.865 | 153 |
| | O(w)–H(w1)···O(2) | −*x*, −½ − *y*, ½ − *z* | 1.03 | 1.87 | 2.884 | 166 |
| | O(w)–H(w2)···O(11) | *x, y, z* | 0.98 | 1.94 | 2.869 | 160 |
| II | O(21)–H(B2)···O(12) | *x, y, z* | 1.13 (8) | 1.36 (8) | 2.479 (7) | 166 (7) |
| | O(22)–H(B1)···O(11) | *x, y, z* | 1.16 (8) | 1.37 (8) | 2.497 (7) | 161 (6) |
| | N(1)–H(7)···O(w1) | *x, y, z* | 1.03 (7) | 1.92 (7) | 2.900 (7) | 157 (6) |
| | N(1)–H(8)···O(w2) | *x, y, z* | 0.83 (6) | 2.04 (7) | 2.849 (7) | 164 (6) |
| | O(w1)–H(w1)···Cl(1) | 1 + *x*, *y*, *z* | 0.70 (8) | 2.76 (8) | 2.284 (6) | 134 (8) |
| | O(w1)–H(w1′)···O(11) | 1 − *x*, 1 − *y*, −*z* | 0.80 (13) | 2.34 (12) | 2.823 (7) | 120 (11) |
| | O(w2)–H(w2)···O(12) | 1 − *x*, 1 − *y*, 1 − *z* | 0.79 (7) | 2.05 (7) | 2.813 (6) | 164 (8) |
| | O(w2)–H(w2′)···Cl(1) | 1 + *x*, *y*, *z* | 0.71 (7) | 2.56 (7) | 3.226 (5) | 157 (7) |

[a] Donor–hydrogen···acceptor. D–H at *x, y, z*.

Table VIII. A Summary of the Average Bond Distances (in Å) in XY $Co(Hdmg)_2$ Complexes (The Ligands X and Y are Normal to the Plane of the Two dmg Groups)

| X[a] | Y[a] | Co–X | Co–Y | Co–N | N–O | C–N | C–C | C–$CH_3$ | O···O | Ref |
|---|---|---|---|---|---|---|---|---|---|---|
| Cl | sulfa | 2.235 (3) | 2.023 (8) | 1.889 (15) | 1.333 (9) | 1.291 (13) | 1.471 (16) | 1.492 (35) | 2.493(11) | This work |
| Cl | clan | 2.257 (2) | 1.999 (6) | 1.893 (5) | 1.343 (6) | 1.297 (8) | 1.463 (9) | 1.490 (11) | 2.488 (7) | |
| Cl | $NH_3$ | 2.251 (1) | 1.965 (4) | 1.890 (5) | 1.346 (10) | 1;282 (4) | 1.483 (6) | 1.50 (2) | 2.486 (7) | 12 |
| Cl | $PPh_3$ | 2.277 (4) | 2.327 (4) | 1.89 (1) | 1.343 (9) | 1.300 (14) | 1.485 (15) | 1.501 (8) | 2.50 (1) | 12 |
| C-py | $P(But)_3$ | 1.979 (1) | 2.339 (1) | 1.876 (3) | 1.339 (7) | 1.295 (7) | 1.443 (3) | 1.499 (3) | 2.474 (2) | 13 |
| $CH_3$ | $H_2O$ | 1.990 (5) | 2.058 (3) | 1.890 (3) | 1.352 (5) | 1.302 (5) | 1.463 (7) | 1.494 (7) | 2.486 (4) | 14 |
| $CH_2COOCH_3$ | py | 2.04 | 2.04 | 1.88 | 1.37 | 1.28 | 1.46 | 1.50 | 2.50 | 15 |
| an | an | 2.001 (5) | | 1.887 (6) | 1.343 (6) | 1.294 (6) | 1.463 (7) | 1.479 (12) | 2.491 (8) | 16 |

[a] The abbreviations used are: sulfa is sulfanilamide, C-py is a carbon-bonded pyridine, py is pyridine, an is aniline, and clan is 4-chloroaniline.

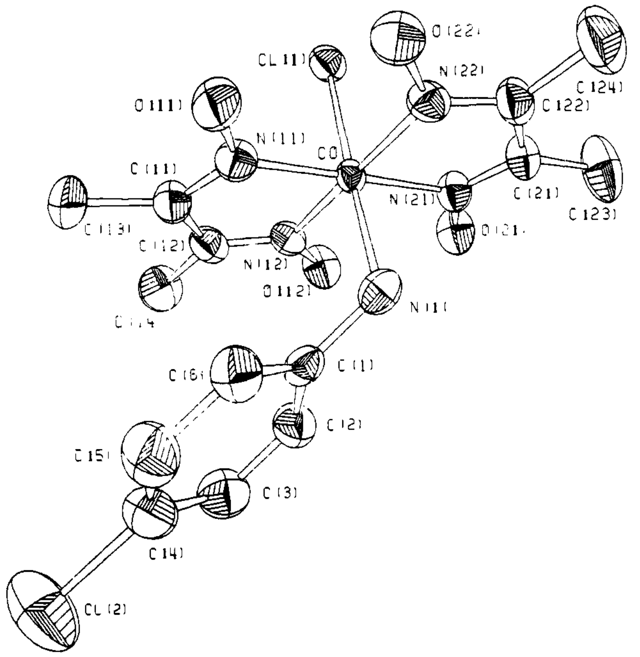

Figure 2. An ORTEP drawing of the chloro(dimethylglyoximato)(dimethylglyoxime)(4-chloroaniline)cobalt(III) molecule showing the atomic numbering and thermal ellipsoids. The water molecules have not been included. The ligand N(11) to N(12) is the dianion while N(21) to N(22) is the neutral molecule.

$H_2dmg$ side from 1.896 to 1.908 Å with an average of 1.904 (5) Å. The difference in the Co–N bond lengths is significant. In addition the orientation of the sulfa and 4-chloroaniline groups relative to the plane of the Co and dimethylglyoxime groups is most intriguing. Although Figures 1 and 2 illustrate that both the sulfa and 4-chloroaniline groups have almost the same relative orientation, a view down the Co–N(1) bond as given in Figure 3 is more revealing. We see that in the sulfa and 4-chloroaniline complexes the aromatic ring is oriented over the dianionic dmg ligand while in the $Co(Hdmg)_2(aniline)_2{}^+Cl^-$ complex the two rings are skewed relative to the ligands. The benzene rings in the present study are tipped slightly (25.2° for I and 29.7° for II) from being parallel to the anionic dmg ligand. The distances between the two planes vary from 2.8 Å at C(1) to 4.0 Å at C(4) and suggest a $\pi$-type interaction between the anionic dmg group and the benzene ring. Furthermore, in both complexes N(1) is displaced from the plane of the benzene ring (by 0.061 Å in I and 0.041 Å in II) toward the cobalt atom, again suggesting a slight distortion to enhance the $\pi$ interaction. All of the above observations can be rationalized in terms of the relative $K_b$'s for sulfanilamide ($2.3 \times 10^{-12}$),[20] 4-chloroaniline ($9.6 \times 10^{-11}$),[21] and aniline ($4.0 \times 10^{-10}$).[21] A proton transfer occurs from one Hdmg ligand to the other Hdmg ligand producing a dianion which would favor a $\pi$-type interaction and enhancing the basicity of the sulfa or 4-chloroaniline ligands. The net result is the formation of a stronger complex than might be expected in terms of the $K_b$ values alone. We believe our results represent the first example of a ligand-induced proton shift (LIPS) in a molecular complex. Since proton transfers in biological systems are relatively common, our results pro-

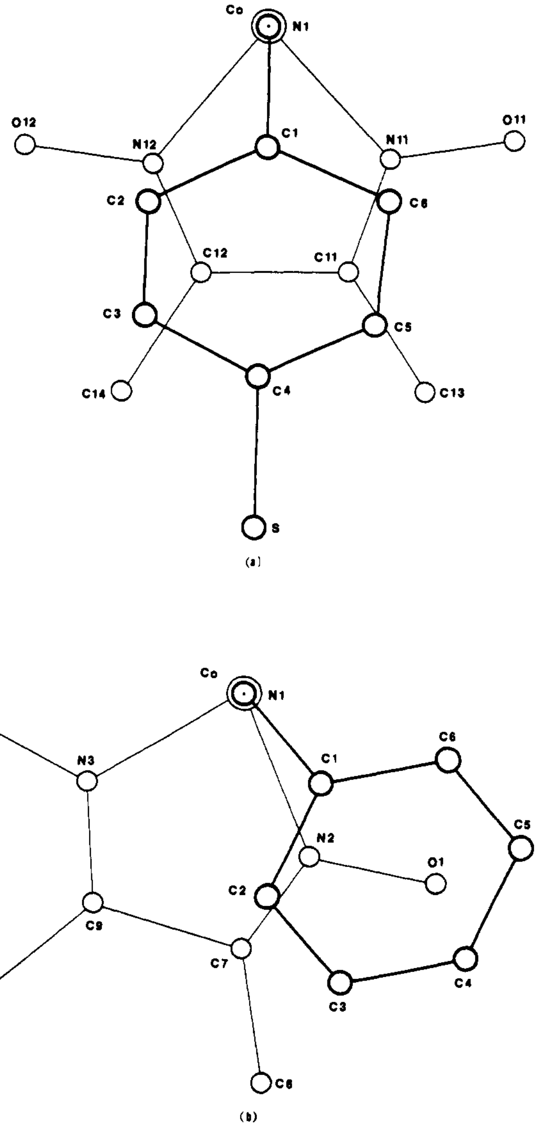

Figure 3. A view down the N(1)–Co bond in three cobaloxime complexes. (a) The view in the $Co(H_2dmg)(dmg)(sulfa)$ complex. The corresponding view in the 4-chloroaniline is virtually identical and is not shown. (b) The view in the bis(aniline)bis(dimethylglyoximato)cobalt(III) cation. Note the differences in the orientation of the phenyl ring relative to the dimethylglyoxime moiety.

vide an important example of the orientation effects and enhanced stabilities which can be achieved by an apparently small shift of one hydrogen atom. Studies are in progress to extend these observations to other systems.

A comparison of our results with data reported for related cobalt-dimethylglyoxime complexes is tabulated in Table VIII. There appears to be very little variation in the average Co-N or dimethylglyoxime dimensions as a function of the axial ligands. However, there is a definite variation of the Co-Cl bond length with the nature of the trans group. The longest Co-Cl distance is found when $PPh_3$ is the trans ligand. This result is not too surprising since phosphines are known to have a very large trans influence.[22]

The N-O distances in both I and II are not significantly different regardless of whether or not the oxygen atom is protonated. In the other cobalt-dimethylglyoxime complexes reported to date[12-16] the N-O distances are also equivalent; however, that is not the case in $Cu(Hdmg)_2$[19] nor in $Fe(Hdmg)_2(imidazole)_2$.[17] The longer Cu-N bonds presumably weaken the O-H···O interaction, making the two N-O bonds unequal. However, this argument cannot be used in the iron case, since the Fe-N bond lengths of 1.893 and 1.918 Å are comparable to the Co-N distances. In the closely related dimethyl[3,3′-trimethylenedinitrilo]bis(butan-2-one oximato)cobalt(III) complex the two N-O distances are also equal even though the difference Fourier clearly shows an asymmetric hydrogen bridge.[23] Although a difference in the N-O bond lengths as a function of protonation is reasonable, no definitive conclusions can be reached without additional data on other iron complexes.

The benzene ring in both I and II is planar with an average C-C bond distance of 1.381 Å in I and 1.378 Å in II (the individual values are in Table VI). The S-N(2) distance of 1.588 (10) Å is one of the shortest found in a variety of sulfonamides[24] although there is excellent agreement with the more accurate structure determinations. Similarly, the S-O bond distances (1.419 (9) and 1.424 (9) Å) are on the short side of the reported values which range from 1.415 (7) to 1.47 (1) Å although, again, the more precise determinations are in better agreement.

There is extensive hydrogen bonding in both compounds. The dimensions of the various hydrogen bonds are given in Table VII. While the majority of the hydrogen atoms capable of forming hydrogen bonds do so, there are three short contacts in Table VII where the angles are unusually small. In the case of N(2)-H(9)···O(21), O(w1)-H(w1)···Cl(1), and O(w1)-H(w2)···O(11) the small angles make hydrogen bonding questionable. The remaining distances of the hydrogen bonds in Table VII are not unusual.

All the intermolecular distances less than 3.6 Å were calculated and scrutinized. No unusually short intermolecular distances were found.

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**Supplementary Material Available:** tables of the interatomic angles and least-squares planes, together with the observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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