crystalline compound, $Cp_2Cr_2(O\text{-}t\text{-}Bu)_2(CF_3C{\equiv}CCF_3)$. This compound is formulated as a 1:1 adduct on the basis of (1) analytical data, (2) a cryoscopic molecular weight determination, and (3) its mass spectrum. The last shows a molecular ion $Cp_2Cr_2(O\text{-}t\text{-}Bu)_2(C_4F_6)^+$ followed by loss of C_4F_6 to give the peak $Cp_2Cr_2(O\text{-}t\text{-}Bu)_2^+$. From this we conclude that hexafluoro-2-butyne has not irreversibly attacked the Cp ring or reacted with the *tert*-butoxy ligand. However, there is no band in the infrared spectrum readily assignable to $\nu(C{\equiv}C)$, and since the compound is paramagnetic and does not yield to NMR investigations, the nature of the coordination of the acetylene is unknown. Crystals suitable for X-ray studies have not yet been obtained. Full spectroscopic data of this interesting 1:1 acetylene adduct are given in the Experimental Section.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. $(C_5H_5)_2Cr_2(\mu\text{-}O\text{-}t\text{-}Bu)_2$, 68108-73-6; $Cr_2(O_2CO\text{-}t\text{-}Bu)_4(THF)_2$, 68108-74-7; $(C_5H_5)_2Cr_2(O\text{-}t\text{-}Bu)_2(NO)_2$, 68108-75-8; hexafluoro-2-butyne, 692-50-2; $C_5H_5Cr(O\text{-}t\text{-}Bu)(CO)_2$, 68108-76-9; chromocene, 1271-24-5.

Supplementary Material Available: Tables of structure factors (15 pages). See any current masthead page for ordering information.

References and Notes

(1) (a) Princeton University. (b) Texas A&M University.
(2) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 335 (1972).
(3) J. K. Kochi, *Acc. Chem. Res.*, **7**, 351 (1974).
(4) F. J. Karol, G. L. Karapinka, C. Wu, A. W. Dow, R. N. Johnson, and W. L. Carrick, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 2621 (1972).
(5) M. H. Chisholm, F. A. Cotton, M. W. Extine, and D. C. Rideout, *Inorg. Chem.*, **17**, 3536 (1978).
(6) D. F. Evans, *J. Chem. Soc.*, 2203 (1959).
(7) G. Hoch, H. Sasse, and M. L. Ziegler, *Z. Naturforsch., B*, **30**, 704 (1975).
(8) "Gmellin Chrom-Organisch Verbindungen", Vol. 3, pp 335–336, and references therein.
(9) F. A. Cotton, M. W. Extine, and G. W. Rice, *Inorg. Chem.*, **17**, 176 (1978).
(10) F. A. Cotton and G. W. Rice, *Inorg. Chem.*, **17**, 2004 (1978).

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Oxygen-Carrying Cobalt Complexes. 9. Preparation and Crystal Structure of the Dioxygen Adduct of Aquo[*N*,*N*′-(1,1,2,2-tetramethylethylene)bis(3-methoxysalicylideniminato)]cobalt(II)[1]

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The dioxygen adduct of aquo[*N*,*N*′-(1,1,2,2-tetramethylethylene)bis(3-methoxysalicylideniminato)]cobalt(II) ((H_2O)-Co(3-OMe-Saltmen)) has been prepared and crystallized as a dimethoxyethane solvate. The material crystallizes in a monoclinic cell, space group $P2_1/c$, with $a = 10.918$ (1) Å, $b = 20.035$ (1) Å, $c = 13.442$ (1) Å and $\beta = 110.21$ (1)°. There are four formula units of $Co_2O_2N_2C_{22}H_{26}{\cdot}O_2{\cdot}H_2O{\cdot}C_4H_{10}O_2$ in the cell. Intensity measurements were made on an automatic diffractometer using a θ–2θ scan technique; 3750 independent reflections were used in a least-squares refinement which led to a final R index of 0.095. The Co(3-OMe-Saltman) portion of the molecule has normal geometry. The dioxygen molecule is disordered between two positions, with an average Co–O distance of 1.88 (1) Å and an average O–O distance of 1.25 (2) Å. The axial base trans to the dioxygen group is a water molecule 2.048 (4) Å from the cobalt atom.

In recent years, many studies of metal complexes with dioxygen as one ligand have been reported. The impetus behind these studies is, of course, understanding the binding between oxygen and transition metals in the proteins involved in oxygen transport in living beings. One of the first questions, that of the geometry of the dioxygen group and the iron atom in oxyhemoglobin, has been settled by X-ray studies of the iron picket fence porphyrin[2] and of several cobalt–dioxygen complexes.[3] The consistent picture is the one predicted by Pauling in 1949,[4] with a "bent" metal–O–O geometry. What is not yet clear or understood is the detailed description of the metal–oxygen binding. From a simple molecular orbital view, the metal–dioxygen bond is the result of the transfer of some electron density from the metal to antibonding orbitals on the oxygen. If this is the case, then the O–O bond length should depend on the availability of electrons at the metal atom, which in turn should depend on the other ligands attached to the metal. By studying the influence of other ligands on the O–O distance or the M–O–O geometry, it should be possible to explain in detail the electronic state of the bound dioxygen.

Some recent theoretical studies[5] have suggested, on the other hand, that the bonding of O_2 to Fe in oxyhemoglobin and oxymyoglobin is essentially similar to the bonding of O_2 to O in ozone. This description implies that the O–O bond is a combination of a normal σ bond and a three-center, four-electron π bond. Such a description is said to explain many of the experimental observations regarding oxyhemoglobin; it also accounts for the ~1.3 Å O–O bond distance observed in model compounds. The π bond is formed from electrons in the d_{xz} orbital of the metal atom; the electron density in this orbital can be influenced by groups on the in-plane ligands or by axial groups. Thus, in order to obtain experimental evidence which can support or refute this hypothesis, or the others which can be tested, it is necessary to obtain experimental information regarding the molecular geometries of oxygen adducts of metal ions with various ligand systems and axial bases. This paper reports the crystal and molecular structure of a dioxygen adduct of [*N*,*N*′-(1,1,2,2-tetramethylethylene)bis(3-methoxysalicylideniminato)]cobalt(II) (Co(3-OMe-Saltmen); Saltmen = Salen with *t*etra*m*ethyl substitution on the en bridge), a reversibly oxygenated complex with a ring substituent on the in-plane ligand (3-methoxy) which has not been studied before and with a previously unknown axial base, a water molecule.

Experimental Section

Materials. 2,3-Dimethyl-2,3-dinitrobutane was purchased from Aldrich Chemical Co., 1,2-dimethoxyethane from MCB, pyridine from Mallinckrodt, and 2-hydroxy-3-methoxybenzaldehyde from California Corporation for Biochemical Research.

Preparation of the Schiff Base (3-OMe-Saltmen). 2,3-Diamino-2,3-dimethylbutane was prepared according to published procedure.[6] A 3.438-g sample of 2-hydroxy-3-methoxybenzaldehyde

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Table I. Crystal Data for Co(3-OMe-Saltmen)$\cdot O_2 \cdot H_2O \cdot CH_3OCH_2CH_2OCH_3$ ($CoO_7N_2C_{26}H_{38}$)

$a = 10.918$ (1) Å	space group = $P2_1/c$
$b = 20.035$ (1) Å	$Z = 4$
$c = 13.442$ (1) Å	fw = 581.53
$\beta = 110.21$ (1)°	$D_x = 1.40$ g/cm^3
$V = 2759$ Å^3	$F_{000} = 1228$ electrons

was dissolved in 15 mL of hot ethanol and the 2,3-diamino-2,3-dimethylbutane was added dropwise with agitation. The product crystallized as a yellow solid mass; it was washed with ethanol and dried overnight.

Preparation of Co(3-OMe-Saltmen). 3-OMe-Saltmen (1.58 g) was dissolved in 20 mL of ethanol. Cobalt(II) acetate (1.0 g) in 10 mL of H_2O was added under N_2. After 0.5 h of stirring at 70 °C, the solution was allowed to cool, yielding dark burgundy crystals. Addition of water to the filtrate produced additional bright red solid. The product was collected by filtration and air-dried; yield about 90%.

Preparation of Co(3-OMe-Saltmen)(H_2O)(O_2)$\cdot C_4H_{10}O_2$. Co(3-OMe-Saltmen) (23 mg) was dissolved in 4 drops of pyridine and diluted to 25 mL with 1,2-dimethoxyethane. The resulting solution was cooled to 0 °C for 1 h in a flask covered with a serum cap. The cap was then punctured with a short hypodermic needle, allowing air to diffuse into the flask. The flask was kept at −5 °C; dark red crystals formed overnight. After several days they were collected by quickly filtering the cold solution. Treating the crystals with polar organic solvents caused vigorus evolution of oxygen gas. The crystals were not stable for more than a few days at room temperature but could be preserved longer by coating them with epoxy cement.

X-ray Data Collection. A crystal of appoximate dimensions of 0.34 × 0.48 × 0.38 mm was placed on a Datex-automated General Electric quarter-circle diffractometer. The orientation angles of 17 manually centered reflections were used to obtain the lattice parameters given in Table I. Iron-filtered Co Kα radiation (λ 1.790 21 Å) was used for the data collection with a θ–2θ scan at a scan speed of 2°/min and 30-s background counts were taken at each end of the scan. Data were collected between 2θ values of 4 and 155°. A total of 3750 reflections were surveyed; of these, 3492 were measured above zero. All 3750 reflections were used in the final refinement. The estimated variances in the intensities (used to derive the weights for the least-squares refinement) were obtained from counting statistics plus an additional term, (0.02 × scan counts)^2, to account for errors dependent upon intensity.

Three check reflections (24$\bar{2}$, 40$\bar{8}$, and 170) at different 2θ values (29.65, 67.33, and 37.90°, respectively) were measured every 100 reflections to monitor crystal decay; these reflections decayed 14, 23, and 22% (based on F), respectively, through the course of data collection. A decay correction linear in both time and in $(\sin \theta)/\lambda$ (to account for the apparent anisotropy of the decay) was applied to the entire data set. Because the data were collected in shells, the weaker, high-angle data suffered most from crystal decay and the corrections to them were the largest. Following the correction, residual variations in the standards were less than 4% (based on F). In addition, another dozen or so reflections well distributed in reciprocal space which had been collected twice showed an average variation of only 5%; the overall "R factor" for averaging all multiply measured reflections is a satisfying 0.012.

The data were corrected for the effects of absorption by Gaussian integration[7] using a transmission factor $\mu = 22.51$ cm^{-1} (transmission coefficients range from 0.42 to 0.51) and they were put on an absolute scale using a Wilson plot. The final data set is not the best, but it probably is as good as can be obtained for this complex at room temperature. When a crystal is subject to decay, one always faces the choice of correcting for decay or of trying to scale together multiple data sets from several crystals. We chose the former alternative and our final results justify the choice. We have obtained a chemically reasonable structure with meaningful distances and angles; if our corrections had not been adequate, the final results would not have been satisfactory.

Solution and Refinement of the Structure. Initial coordinates for all the nonhydrogen atoms in the Co(3-OMe-Saltmen) plane, as well as the other two atoms bonded to cobalt, were obtained from an E map produced by the program MULTAN.[8] The remaining ordered nonhydrogen atoms were easily found in Fourier maps; these also revealed a molecule of solvent (glyme) and showed that one of the methoxy carbon atoms had been incorrectly positioned initially. The hydrogen atoms which could be located geometrically were placed 0.95 Å from their respective carbon atoms; hydrogen atoms on methyl groups and on the water molecule were found from Fourier difference syntheses. The hydrogen atoms were assigned isotropic thermal parameters 1 Å^2 greater than that of the atom to which each is attached. Eventually the parameters of the hydrogen atoms of the water molecule were refined; all the others were held fixed.

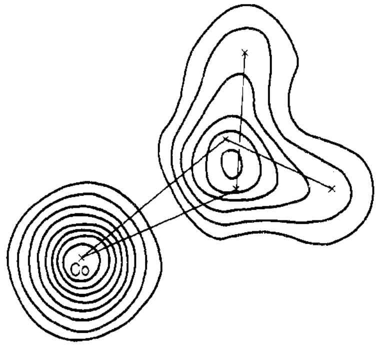

Figure 1. Section of the electron density map through the mean plane of the cobalt atom and the disordered O_2 groups. Contours are drawn at 1 e/Å^3 for oxygen beginning at 1 e/Å and at 1, 5, 10, 15, ... e/Å^3 for cobalt.

The cobalt atom and the atoms bonded to it (except the oxygen atom of the O_2 group) were refined anisotropically. The remaining atoms were refined isotropically for reasons of economy. In similar structures where we have refined the entire CoSalen nucleus as anisotropic atoms we have not gained any additional chemical information. The final isotropic thermal parameters are reasonable, with the atoms at the ends of the molecule [C(6) and C(13)] having the highest B's. The CH_3-group carbon atoms also have large B's; that of C(20) is especially high, probably because C(20) is involved in the O_2 disorder and may be slightly disordered itself.

The major complication in the refinement resulted from the disordered O_2 group. Positions for four half-oxygen atoms were determined from Fourier syntheses (Figure 1); the "outer" half-oxygen atoms which are well-separated were allowed to refine along with the rest of the structure while the "inner" pair, separated by less than 0.5 Å, had to be refined by difference Fourier techniques because their parameters are very strongly coupled. These two half-atoms were allowed to refine after the rest of the structure had converged, a technique we have used successfully before. The positional and isotropic thermal parameters of the solvent molecules were refined by least squares but the resulting atomic positions are not entirely satisfactory. The atoms display high apparent thermal motion and the central C–C bond is very short. Since we were not interested in this portion of the structure and since the refinement converged adequately, we did not attempt to improve the description of the glyme molecule. The final refinement converged with $R_1 = 0.095$ and $R_2 = 0.028$ for 3750 reflections measured greater than zero. The goodness-of-fit is 3.36 and the secondary extinction factor[9] is 1.1 (2) × 10^{-6}. A final difference Fourier showed 17 peaks (listed in the supplementary material) with $|\rho| \geq 0.5$ e/Å^3; the largest of these was 0.7 e/Å^3, about the height of an average hydrogen atom. Most of the larger of these are associated with the solvent, the remainder with the 3-OMe-Saltmen group. Final parameters are given in Table II; observed and calculated structure factors are available.[10]

Description of the Structure

The Co(3-OMe-Saltmen) Group. The numbering scheme for the Co(3-OMe-Saltmen) group, along with averaged distances and angles, is shown in Figure 2. The complex shows noncrystallographic mirror symmetry with the two halves having almost identical bond lengths and angles (Tables III and IV); as a result, these have been averaged for this discussion. The individual bond distances are given in Table III. These values are in good agreement with those found in similar structures.[3] The ligand is nearly planar; slight deviations from planarity can be described in terms of the angles α, β, and γ, where α and β are the angles which the salicylaldimine residues make with the cobalt coordination plane and γ is the angle between the residue planes. For a "stepped" conformation,

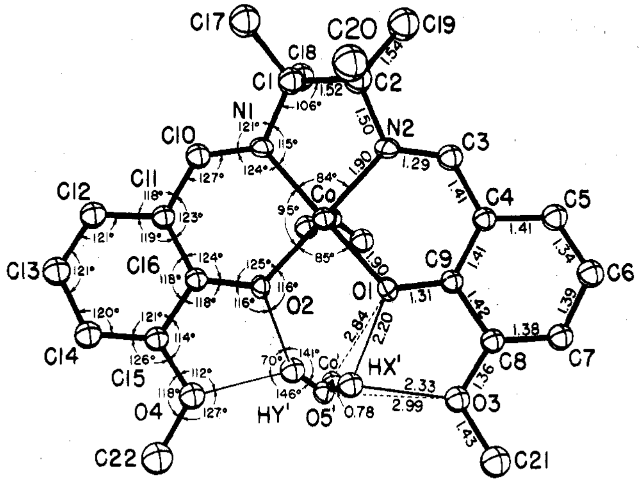

Figure 2. Average bond distances and angles of the Co(3-OMe-Saltmen) portion of the molecule. The hydrogen bonding from a second molecule is shown.

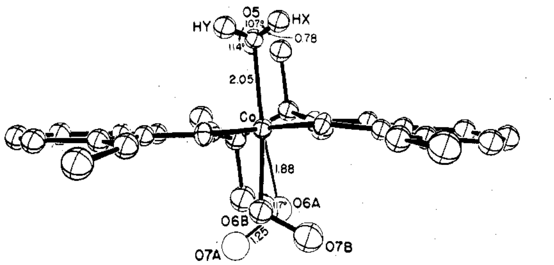

Figure 3. Average bond distances and angles for the axial ligands. The alternate positions of the dioxygen are shown as O6A–O7A and O6B–O7B.

$\beta \simeq \alpha + \gamma$; in this complex $\alpha = 4.6°$, $\beta = 9.5°$, and $\gamma = 5.0°$.

The methoxy oxygen atoms show nearly trigonal geometry and a somewhat short phenyl C–O distance (1.36 Å). This is similar to the geometry observed in 1,4-dimethoxybenzene, where some double-bond character was ascribed to the C–O bond.[11]

The Dioxygen Group. Figure 3 shows a side view of the complex along with the numbering system and distances and angles for the axial ligands. The oxygen molecule is disordered with the two orientations related by an approximate twofold axis. The O–O distance has a high standard deviation because the oxygen atom sites are only half-occupied and because the parameters of these atoms are strongly coupled; the two values, which differ by only 3.1σ, are 1.282 (19) and 1.223 (19) Å. The average value, 1.25 (2) Å, although shorter than those found previously in dioxygen complexes of cobalt, is not significantly less than some (1.273 (10) Å,[3a] 1.277 (3) Å,[3b] 1.302 (3) Å[3c]). On the other hand, it might not even be significantly greater than the O–O distance in oxygen gas, 1.21 Å. Such a short distance is difficult to equate with a superoxide ion formulation, but it may be compatible with an ozone model description of the Co–O–O bonding.[4] The Co–O–O angle is 117 (1)°, essentially the same as found in other dioxygen adducts.

The disordered dioxygen ligand lies in a hydrophobic "pocket", surrounded by hydrogen atoms. Thus the dioxygen has three short contacts (≤2.6 Å) with hydrogen atoms in either of its two conformations (Table VI). In this structure the two positions have appoximately equal nonbonding contacts, leading to about equal energies for the two conformations and thus the observed disorder. This is in marked contrast to three structures[3] in which intermolecular contacts led to ordered structures. In those complexes, the dioxygen ligand showed freedom in choosing between the two possible conformations with respect to the tetramethylethylenediamine bridge; in this structure both sites are occupied. In all cases, however, relative to the cobalt coordination plane, the dioxygen ligand occupies a site over an O–Co–N angle, never over O–Co–O or N–Co–N. This geometry can be described in terms of two torsion angles: O(Salen)–Co–O–O (ϕ) and N(Salen)–Co–O–O (ξ). For this complex O6A–O7A has $\phi = 42\ (1)°$ and $\xi = 53\ (1)°$; O6B–O7B had $\phi = 46\ (1)°$ and $\xi = 49\ (1)°$.

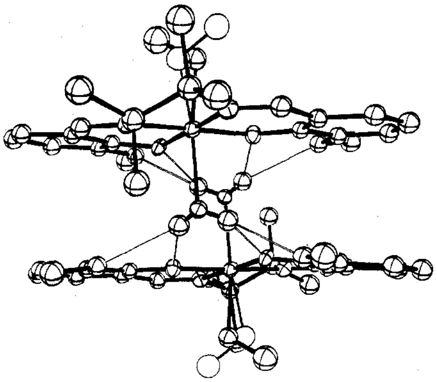

Figure 4. Perspective view of a hydrogen-bonded "dimer" showing the symmetric, bifurcated hydrogen bonds joining the two molecules across the center of symmetry.

Coordinated H_2O; H Bonding. The Co–O distance of 2.048 (5) Å is typical of those found in Co(III) aquo complexes. It is shorter than those found in two acetonylcobalt complexes, 2.128 (3) and 2.20 Å, respectively, for water and methanol trans to acetonyl.[12] The water molecule participates in hydrogen bonding to the phenolic and methoxy O atoms of another molecule of Co(3-OMe-Saltmen) across a center of symmetry to form a dimer. The distances and angles associated with the interaction are shown in Figure 2 and the overall "dimerization" is shown in Figure 4. Each hydrogen atom forms a bifurcated hydrogen bond with both a methoxy and phenolic O atom and completes trigonal geometry about those atoms. This "dimerization" is similar to that observed in the acetonyl adduct of aquo(*N*,*N'*-ethylene)bis(3-fluorosalicylideniminato)cobalt(II).[12a]

Solvent. Except for one interaction with the dioxygen, the glyme molecule has no significant contacts with the rest of the structure. The thermal motion of the atoms in the solvent molecule is quite large, leading to the apparently short bond lengths observed (C–C = 1.34 (1) Å, C–O = 1.39 Å (average), uncorrected for thermal motion).

Discussion

Although disorder is seldom considered valuable in a crystal, at times we can learn something about the relative energies of the various conformations found in a disordered crystal. Such is the case here; the twofold disorder of the dioxygen ligand, with each position occupied half the time, shows that the inter- and intramolecular steric and electronic effects are similar for the two orientations. In previous complexes we have studied, the dioxygen ligand was always ordered. The orientation of the O_2 group—its location relative to the oxygen and nitrogen atoms of the ligand and relative to the methyl groups on the tetramethylethylene bridge—was variable from compound to compound, although in every case the Co–O–O plane roughly bisected a N–Co–O in-plane angle. The O_2 group pointed toward the axial methyl group in one structure.[3a] The fact that in this complex it adopts both orientations confirms that the two are of comparable energies.

It was most surprising to us to discover a water molecule as the axial ligand trans to the dioxygen group. The crystals were grown from a solution containing pyridine; our experience

Table II. Atomic Parameters[a]

Atom	X	Y	Z	U_{11} or B	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	4332(1)	8824(.4)	9688(1)	527(6)	388(6)	452(6)	-31(5)	146(4)	-10(5)
O(1)	6067(3)	9105(2)	10480(3)	532(24)	476(24)	420(22)	-16(19)	116(19)	95(19)
O(2)	4442(3)	9431(2)	8634(3)	543(24)	460(24)	318(19)	-64(20)	113(17)	-27(19)
O(5)	3679(5)	9603(2)	10357(4)	536(29)	384(27)	449(27)	-9(25)	133(23)	27(25)
N(1)	2595(5)	8554(2)	8923(4)	609(32)	373(27)	535(30)	-125(25)	211(25)	7(25)
N(2)	4198(5)	8216(2)	10725(4)	552(32)	365(28)	628(32)	-100(25)	183(26)	19(26)
O(3)	8401(4)	9585(2)	11275(3)	4.7(1)					
O(4)	5170(4)	10150(2)	7349(3)	4.9(1)					
O(6A)	4816(13)	8153(8)	8913(13)	6.5(4)					
O(6B)	5193(15)	8162(8)	9204(11)	5.6(4)					
O(7A)	5790(11)	7785(6)	9428(9)	7.8(3)					
O(7B)	4830(11)	8066(6)	8247(10)	8.8(3)					
O(8)	8156(5)	8988(3)	7826(4)	7.9(1)					
O(9)	8851(5)	8190(3)	6275(4)	6.7(1)					
C(1)	1949(6)	8162(3)	9548(5)	5.2(2)					
C(2)	3024(7)	7770(4)	10362(5)	5.7(2)					
C(3)	5077(6)	8134(3)	11636(5)	4.6(1)					
C(4)	6286(5)	8462(3)	12049(4)	3.9(1)					
C(5)	7096(6)	8306(3)	13096(5)	4.9(1)					
C(6)	8289(6)	8575(3)	13522(5)	5.3(2)					
C(7)	8768(6)	9011(3)	12944(5)	4.8(1)					
C(8)	8019(6)	9174(3)	11924(4)	4.1(1)					
C(9)	6738(5)	8915(3)	11445(4)	3.7(1)					
C(10)	1950(6)	8735(3)	7950(5)	4.5(1)					
C(11)	2400(5)	9142(3)	7295(4)	4.0(1)					
C(12)	1564(6)	9235(3)	6234(5)	4.9(1)					
C(13)	1938(6)	9606(3)	5564(5)	5.6(2)					
C(14)	3149(6)	9919(3)	5894(5)	5.2(2)					
C(15)	3990(6)	9855(3)	6926(5)	4.1(1)					
C(16)	3628(5)	9461(3)	7653(4)	3.7(1)					
C(17)	837(7)	7724(4)	8858(6)	7.1(2)					
C(18)	1339(7)	8671(4)	10105(5)	6.3(2)					
C(19)	2642(8)	7524(4)	11294(6)	7.5(2)					
C(20)	3393(8)	7149(4)	9838(6)	8.1(2)					
C(21)	9749(7)	9778(4)	11641(6)	6.7(2)					
C(22)	5628(7)	10559(4)	6688(6)	7.2(2)					
C(23)	7681(9)	8975(5)	8678(7)	9.6(3)					
C(24)	7270(11)	8663(6)	6930(10)	12.0(3)					
C(25)	7726(11)	8533(5)	6146(9)	11.2(3)					
C(26)	8694(8)	7522(5)	6091(7)	8.5(2)					
H(X)	3338(55)	9863(29)	10026(45)	1.7(19)					
H(Y)	4304(66)	9777(33)	10855(54)	8.4(22)					

Non-refined Hydrogen Atoms

Atom	X	Y	Z	B
H(3)	4891	7815	12088	5.6
H(5)	6789	8004	13504	5.9
H(6)	8815	8465	14229	6.3
H(7)	9614	9198	13254	5.8
H(10)	1081	8575	7650	5.5
H(12)	725	9034	5995	5.9
H(13)	1368	9655	4852	6.6
H(14)	3398	10180	5406	6.2
H(17A)	1028	7549	8305	8.1
H(17B)	57	7965	8606	8.1
H(17C)	688	7367	9257	8.1
H(18A)	865	8991	9608	7.3
H(18B)	2006	8892	10632	7.3
H(18C)	805	8454	10388	7.3
H(19A)	2596	7883	11741	8.5
H(19B)	1820	7323	11059	8.5
H(19C)	3245	7219	11708	8.5
H(20A)	3449	7256	9173	9.1
H(20B)	2776	6800	9736	9.1
H(20C)	4216	6974	10258	9.1
H(21A)	10301	9416	11856	7.7
H(21B)	9959	10003	11095	7.7
H(21C)	9932	10086	12212	7.7
H(22A)	5787	10295	6140	8.3
H(22B)	4975	10874	6316	8.3
H(22C)	6373	10786	7060	8.3
H(23A)	8291	9169	9303	10.6
H(23B)	7534	8540	8863	10.6
H(23C)	6901	9217	8539	10.6
H(24A)	6510	8930	6655	13.0
H(24B)	7010	8254	7155	13.0
H(25A)	7819	8952	5851	12.2
H(25B)	7053	8298	5620	12.2
H(26A)	9393	7318	5987	9.5
H(26B)	7943	7428	5502	9.5
H(26C)	8566	7293	6676	9.5

[a] Coordinates have been multiplied by 10^4 and anisotropic thermal parameters by 10^3. The form of the thermal ellipsoids is $\exp[-2\pi^2 \cdot (U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$. Estimated standard deviations in the final digit are given in parentheses.

had been that some nitrogen base is necessary to promote the oxygenation of CoSalen complexes in solution. It is clear that a pyridine complex of cobalt is more stable in solution than an aquo complex, but in the crystal there are two good hydrogen bonds formed per mole of complex; these bonds must provide enough energy to overcome the intrinsic advantage of the pyridine as a ligand. Moreover, there was probably much more water than pyridine present in the oxygenation solution; the concentration of pyridine was less than 15 mM, whereas the glyme surely had a greater concentration of water than that. Even though the presence of the water molecule as an axial base is surprising, there are no obvious structural effects resulting from its presence. The in-plane atoms adopt the same geometry as in complexes containing imidazole bases and the O_2 group does not appear changed, within our limits of error, from such other complexes.

It is frustrating that the O–O distance in this complex is so imprecise. In order to make any reasonable tests of the various theories regarding the electronic state of the cobalt atom and the dioxygen ligand in the adduct, we need to have accurate data for a variety of complexes. The variations we have noted in O–O distance as we have changed substituents have been, at most, a few standard deviations.[3] This determination, therefore, does not add to our understanding of the nature of the dioxygen binding, but it does allow us to say with considerable confidence that, if we observe any systematic changes in O–O bond lengths in this series of complexes, the changes will almost surely be related to electronic effects and not to "packing force" or steric interactions. We hope to obtain such accurate data for several other of these complexes shortly

Table III. Bond Distances[a]

Co–O5	2.048 (5)		
O6A–O6B	0.460 (21)		
C1–C2	1.517 (9)		
Co–O1	1.909 (3)	Co–O2	1.901 (3)
Co–N2	1.896 (4)	Co–N1	1.898 (4)
Co–O6A	1.885 (15)	Co–O6B	1.868 (15)
O1–C9	1.308 (6)	O2–C16	1.307 (6)
O5–HX	0.703 (59)	O5–HY	0.848 (70)
N2–C2	1.499 (8)	N1–C1	1.494 (8)
N2–C3	1.279 (7)	N1–C10	1.304 (7)
O3–C8	1.365 (7)	O4–C15	1.351 (7)
O3–C21	1.434 (8)	O4–C22	1.421 (8)
O6A–O7A	1.282 (19)	O6B–O7B	1.223 (19)
C2–C19	1.532 (10)	C1–C17	1.525 (10)
C2–C20	1.551 (11)	C1–C18	1.545 (9)
C3–C4	1.406 (8)	C10–C11	1.407 (8)
C4–C5	1.415 (8)	C11–C12	1.415 (8)
C4–C9	1.415 (8)	C11–C16	1.412 (8)
C5–C6	1.341 (9)	C12–C13	1.334 (9)
C6–C7	1.386 (9)	C13–C14	1.391 (9)
C7–C8	1.372 (8)	C14–C15	1.379 (8)
C8–C9	1.421 (8)	C15–C16	1.421 (8)
C24–C25	1.337 (16)		
O8–C23	1.410 (10)	O9–C25	1.364 (12)
O8–C24	1.416 (13)	O9–C26	1.361 (10)

[a] Distances which were averaged for the discussion are shown side by side.

so as to test this prediction.

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Registry No. Co(3-OMe-Saltmen)$(H_2O)(O_2)\cdot C_4H_{10}O_2$, 68108-70-3; Co(3-OMe-Saltmen), 68108-72-5.

Supplementary Material Available: Table 4 (bond angles), Table 5 (distance and angles in the hydrogen bonding), Table 6 (close nonbonded contacts), Table 7 (residuals in the final difference fourier), and a listing of observed structure factors, their estimated standard deviations, and the calculated structure factors (23 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Previous papers in this series: (1) W. P. Schaefer and R. E. Marsh, *Acta Crystallogr., Sect. B*, **25**, 1675 (1969); (2) B.-C. Wang and W. P. Schaefer, *Science*, **166**, 1404 (1969); (3) L. A. Lindblom, W. P. Schaefer, and R. E. Marsh, *Acta Crystallogr.*, **27**, 1461 (1971); (4) A. Avdeef and W. P. Schaefer, *Inorg. Chem.*, **15**, 1432 (1976); (5) ref 3a; (6) ref 3c; (7) ref 3b; (8) ref 12a.

(2) J. P. Collman, R. R. Gagné, C. A. Reed, W. T. Robinson, and G. S. Rodley, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 1326–1329 (1974).

(3) (a) R. S. Gall, J. F. Rogers, W. P. Schaefer, and G. G. Christoph, *J. Am. Chem. Soc.*, **98**, 5135–5144 (1976); (b) R. S. Gall and W. P. Schaefer, *Inorg. Chem.*, **15**, 2758–2763 (1976); (c) A. Avdeef and W. P. Schaefer, *J. Am. Chem. Soc.*, **98**, 5153–5159 (1976).

(4) L. Pauling in "Haemoglobin", Butterworths, London, 1949, pp 57–65.

(5) W. A. Goddard, III, and B. D. Olafson, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2335–2339 (1975).

(6) R. Sayre, *J. Am. Chem. Soc.*, **78**, 6890 (1956).

(7) W. Busing and H. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

(8) P. Main, M. M. Woolfson, L. Lessinger, G. Germain, and J.-P. Delclercq, "Multan 74", University of York, York, England, and Laboratoire de Chimie Physique et de Cristallographie, Louvain, Belguim, 1974.

(9) $R_1 = \sum|F_o - |F_c||/\sum F_o$; $R_2 = [\sum w^2(F_o^2 - F_c^2)^2]/\sum w^2F_o^4$. The secondary extinction factor is defined in A. Larson, *Acta Crystallogr.*, **23**, 664 (1967). The goodness of fit = $[\sum w^2(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$; n = the number of data, p = the number of parameters.

(10) Supplementary material.

(11) T. H. Goodwin, M. Przybylska, and J. M. Robertson, *Acta Crystallogr.*, **3**, 279 (1950).

(12) (a) W. P. Schaefer, R. Waltzman, and B. T. Huie, *J. Am. Chem. Soc.*, **100**, 5063 (1978); (b) A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Gaugher, *Inorg. Chim. Acta, Rev.*, **4**, 41 (1970).

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$[Rh_9P(CO)_{21}]^{2-}$. Example of Encapsulation of Phosphorus by Transition-Metal–Carbonyl Clusters

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The reaction of $Rh(CO)_2acac$ with triphenylphosphine in the presence of cesium benzoate in tetraethylene glycol dimethyl ether solution resulted in the selective formation of $[Rh_9P(CO)_{21}]^{2-}$ (80% yield) after 4 h of contact time under ~400 atm of carbon monoxide and hydrogen ($CO/H_2 = 1$) at 140–160 °C. The cluster has been isolated as the cesium and benzyltriethylammonium salts, both of which are sensitive to moisture and oxygen. The salts are soluble in acetone, acetonitrile, tetrahydrofuran, and sulfolane but insoluble in organic solvents of lower polarity. The $[C_6H_5CH_2N(C_2H_5)_3]_2[Rh_9P(CO)_{21}]\cdot CH_3C(O)CH_3$ complex has been characterized via a complete three-dimensional X-ray diffraction study. The complex crystallizes in the space group $P\bar{1}$ with $a = 11.705$ (4) Å, $b = 12.866$ (11) Å, $c = 22.747$ (12) Å, $\alpha = 101.40$ (6)°, $\beta = 92.72$ (4)°, $\gamma = 108.29$ (5)°, $V = 3.171$ Å^3, and ρ (calcd) = 2.04 g cm^{-3} for mol wt 1952.04 and $Z = 2$. Diffraction data were collected with an Enraf-Nonius CAD4 automated diffractometer using graphite-monochromatized Mo Kα radiation. The structure was solved by direct methods and refined by difference-Fourier and least-squares techniques. All nonhydrogen atoms have been located and refined: final discrepancy indices are $R_F = 4.5\%$ and $R_{wF} = 4.7\%$ for 5007 reflections in the range of $0.5° < 2\theta < 45°$. The anion's structure shows eight rhodium atoms in the corners of a cubic antiprism and the ninth rhodium atom capping one of the square faces, and it also contains a naked phosphorus atom placed near the center of the cluster. Average bonding distances for the anion are in the ranges Rh–Rh = 2.880–3.008 Å, Rh–P = 2.401–3.057 Å, Rh–C = 1.847–2.169 Å, and C–O = 1.153–1.188 Å. ^{13}C and ^{31}P NMR results are interpreted as indicative of the fluxionality of the carbon monoxides and rhodium atom core, respectively. A mechanism is proposed to explain the scrambling of the rhodium atoms.

Introduction

The extreme versatility noted for sulfur ligands has resulted in a large variety of different organometallic species in which the sulfur center is sharing from two to four valence electrons[1] and in complexes in which atomic sulfur acting as a ligand is able to give rise to a large variety of organometallic species, e.g., $S_2Fe_3(CO)_9$,[2] $Co_3(CO)_9S$,[3] and $[Fe_2(CO)_6(\mu\text{-}SCH_3)_2]_2S$.[4] As has been already noted,[1] it might be expected that this