References and Notes

(1) (a) Preliminary results presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 30, 1973. (b) Abstracted in part from the Ph.D. thesis of M. P. Li, University of Illinois, Urbana, Ill. (c) National Defense Education Act Predoctoral Fellow, 1971–1974.
(2) G. Dolcetti and N. W. Hoffman, *Inorg. Chim. Acta*, **9**, 269 (1974).
(3) J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.*, 7, 53 (1968).
(4) J. P. Collman, *Acc. Chem. Res.*, **1**, 136 (1968).
(5) R. Cramer and R. V. Lindsey, *J. Am. Chem. Soc.*, **88**, 3534 (1966).
(6) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
(7) C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 2762 (1974).
(8) W. Partenheimer and E. F. Hoy, *J. Am. Chem. Soc.*, **95**, 2840 (1973).
(9) (a) L. M. Haines, *Inorg. Nucl. Chem. Lett.*, **5**, 399 (1969); (b) L. M. Haines, *Inorg. Chem.*, **9**, 1517 (1970).
(10) J. Chatt and L. M. Venanzi, *Nature (London)*, **177**, 852 (1956).
(11) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
(12) R. Cramer, *Inorg. Chem.*, **1**, 723 (1962).
(13) L. M. Haines, *Inorg. Chem.*, **10**, 1685 (1971).
(14) P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, 17, 913 (1961).
(15) E. Merkel, *Z. Elektrochem.*, **63**, 373 (1959).
(16) G. Pannetier et al. *J. Organomet. Chem.*, **60**, 375 (1973).
(17) A. Maisonnat, P. Kalck, and R. Poilblanc, *Inorg. Chem.*, **13**, 661 (1974).
(18) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).
(19) R. Cramer, *J. Am. Chem. Soc.*, **89**, 4621 (1967).
(20) K. Vrieze, H. C. Volger, and A. P. Pratt, *J. Organomet. Chem.*, **14**, 135 (1968).
(21) J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **88**, 3491 (1966).
(22) R. S. Drago, M. S. Nozari, and G. C. Vogel, *J. Am. Chem. Soc.*, **94**, 90 (1972).
(23) M. S. Nozari and R. S. Drago, *Inorg. Chem.*, **11**, 280 (1972).
(24) R. M. Guidry and R. S. Drago, *J. Am. Chem. Soc.*, **95**, 759 (1973).
(25) R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).
(26) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Am. Chem. Soc.*, **93**, 6014 (1971).
(27) R. S. Drago, *Struct. Bonding (Berlin)*, **15**, 73 (1973); L. Parr, R. S. Drago, and C. Chamberlain submitted for publication.
(28) W. Partenheimer and R. S. Drago, *Inorg. Chem.*, **9**, 47 (1970).
(29) R. L. Courtright, R. S. Drago, J. A. Nusz, and M. S. Nozari, *Inorg. Chem.*, **12**, 2809 (1973).
(30) (a) J. J. Eisch and R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, N.Y., 1965, p 132; (b) J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, **8**, 211 (1966).
(31) N. K. Kildahl and R. S. Drago, *J. Am. Chem. Soc.*, **95**, 6245 (1973).
(32) T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 5015 (1965); **88**, 3921 (1966).
(33) F. L. Slejko and R. S. Drago, *Inorg. Chem.*, **12**, 176 (1973).
(34) M. S. Nozari and R. S. Drago, *J. Am. Chem. Soc.*, **92**, 7086 (1970).
(35) D. Brodzki and G. Pannetier, *J. Organomet. Chem.*, **63**, 431 (1973).
(36) P. Uguagliati, G. Deganello, and U. Belluco, *Inorg. Chim. Acta*, **9**, 203 (1974).
(37) A. J. Pribula and R. S. Drago, *J. Am. Chem. Soc.*, **98**, 2784 (1976).
(38) N. Rösch, R. P. Messmer, and K. H. Johnson, *J. Am. Chem. Soc.*, **96**, 3855 (1974).
(39) D. A. McMillin, R. S. Drago, and J. A. Nusz, *J. Am. Chem. Soc.*, **98**, 3120 (1976).
(40) R. S. Drago and D. W. Meek, *J. Phys. Chem.*, **65**, 1446 (1961).
(41) D. W. Meek, D. K. Straub, and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 6013 (1960).
(42) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, N.Y., 1970, p 210–212.
(43) A. D. Sherry and K. F. Purcell, *J. Phys. Chem.*, **74**, 3535 (1970).
(44) A. D. Sherry and K. F. Purcell, *J. Am. Chem. Soc.*, **94**, 1853 (1972).
(45) R. S. Drago, T. F. Bolles, and R. J. Niedzielski, *J. Am. Chem. Soc.*, **88**, 2717 (1966).
(46) L. Parr and R. S. Drago, to be submitted for publication.
(47) M. S. Nozari and R. S. Drago, *J. Am. Chem. Soc.*, **94**, 6877 (1972).
(48) R. S. Drago, J. A. Nusz, and R. C. Courtright, *J. Am. Chem. Soc.*, **96**, 2082 (1974).
(49) M. F. Rettig and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 2966 (1966).
(50) W. Partenheimer and E. F. Hoy, *Inorg. Chem.*, **12**, 2805 (1973).

The Structure of a Monomeric Oxygen Carrying Cobalt Complex: Dioxygen-*N,N′*-(1,1,2,2-tetramethyl)ethylenebis(3-*tert*-butylsalicylideniminato)-(1-benzylimidazole)cobalt(II)

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Abstract: The synthesis and structural characterization of a new oxygen-carrying cobalt complex, *N,N′*-{1,1,2,2-tetramethyl}ethylenebis(3-*tert*-butylsalicylideniminato)cobalt(II), abbreviated Co(*t*-Bsalten), and its monomeric σ-bonded dioxygen complex with 1-benzylimidazole as the axial base, Co(*t*-Bsalten)(bzImid)(O_2) are reported. The M–O_2 structural parameters for Co(*t*-Bsalten)(bzImid)(O_2) have been determined to a greater precision than previously attained. Co(*t*-Bsalten) crystallizes in the monoclinic space group $P2_1/c$ with a = 12.728 (1) Å, b = 10.642 (2) Å, c = 19.643 (3) Å, β = 95.22 (2)°, and Z = 4. Anisotropic least-squares refinement gave R = 0.085 for 4349 independent diffractometry data. Data were collected at both room temperature and −152 °C for Co(*t*-Bsalten)(bzImid)(O_2). It crystallizes as an acetone solvate in the monoclinic space group $P2_1/c$ with a = 11.918 (1) Å, b = 21.331 (5) Å, c = 17.267 (2) Å, β = 108.89 (1)°, and Z = 4 at room temperature and a = 11.933 (4) Å, b = 21.238 (11) Å, c = 17.004 (2) Å, and β = 109.86 (3)° at −152 °C. Anisotropic least-squares refinement R = 0.062 for 1395 independent diffractometry data with $I > 3\sigma(I)$ and R = 0.077 for 1437 reflections with $I > 3\sigma(I)$ at room temperature and −152 °C, respectively. Co(*t*-Bsalten) is a planar molecule. The cobalt atom in Co(*t*-Bsalten)(bzImid)(O_2) is octahedrally coordinated with a Co–N(bzImid) distance of 1.974 (8) Å and a Co–O_2 distance of 1.873 (7) Å. The O–O bond length is 1.273 (10) Å and the Co–O–O bond angle is 117.5 (6)°. The x-ray results for Co(*t*-Bsalten)(bzImid)(O_2) are consistent with a superoxide ion, O_2^-, bonded to Co(III).

In 1938, Tsumaki[2a] described the preparation of *N,N′*-ethylenebis(salicylideniminato)cobalt(II), Co(salen), a compound which reversibly absorbed molecular oxygen from the atmosphere. This compound and many others closely related to it were studied extensively by Calvin and his collaborators in 1944–1945.[2b] Calvin determined that Co(salen) absorbed one molecule of oxygen per two cobalt atoms. No single-crystal x-ray work was undertaken by Calvin's group.

In subsequent years x-ray structural determinations have been carried out on a number of compounds which bind oxygen with a 2:1 metal-to-oxygen ratio. Only recently have 1:1 complexes with various metals been characterized by single-crystal x-ray crystallography. Some of these have heavy-metal centers which bind oxygen symmetrically by a π-bond. Such a π-bonded structure has been proposed by Griffith[3] as the mode of O_2 binding in oxyhemoglobin and oxymyoglobin. The weight of current evidence, however, favors a σ-bonded dioxygen in these proteins in accord with Pauling's model.[4] This evidence consists of structural work on a number of cobalt compounds[5] which bind oxygen in this manner and, most convincingly, the "picket-fence" iron porphyrin synthetic model of Collman and co-workers.[6] All these structures with σ-bonded dioxygen have, however, suffered from solid-state disorder or excessively high thermal motion of the dioxygen ligand. This has reduced the precision (and perhaps also the accuracy) of the structural parameters for dioxygen coordinated in this manner.

N,N'-{1,1,2,2-tetramethyl}ethylenebis(3-*tert* - butylsalicylideniminato)cobalt(II) is a new derivative of Co(salen) not among those studied by Calvin. Substitution into the Co(salen) framework has been found to prevent the formation of peroxo-bridged dimers. Most importantly, the σ-bonded dioxygen adduct of this compound with 1-benzylimidazole as the axial base exhibits neither solid-state disorder nor unusually large anisotropic thermal vibration. This leads to a precision in the determination of the geometry of the Co-O-O grouping much higher than any previously attained. We have also undertaken a low-temperature study (−152 °C) of this adduct to determine experimentally whether any serious error was present due to thermal motion of the dioxygen ligand at room temperature where the molecule is only marginally stable without safeguards to protect the crystals. The structural parameters of the Co-O-O grouping at the two temperatures are found to agree within experimental error.

Experimental Section

Materials. 1-Benzylimidazole, 2,3-dimethyl-2,3-dinitrobutane, and 2-*tert*-butylphenol were purchased from Aldrich Chemical Co. 1-Benzylimidazole was purified by sublimation prior to use. Oxygen gas was dried by passage through concentrated H_2SO_4, KOH (solid), and 3A Linde molecular sieves. All other reagents and solvents were purchased from J. T. Baker Chemical Co., and used without further purification.

Preparation of the Ligand. 2,3 Diamino-2,3-dimethylbutane was prepared from 2,3 dimethyl-2,3-dinitrobutane by acidic reduction with metallic tin,[7] and isolated and refrigerated as the free base until use. 3-*tert*-Butylsalicylaldehyde was prepared from 2-*tert*-butylphenol by the method of Duff.[8] In 20 ml of absolute methanol 2.5 ml (ca. 0.02 mol) of 2,3-diamino-2,3-dimethylbutane was added to 3.2 ml (ca. 0.02 mol) of 3-*tert*-butylsalicylaldehyde. The solution was gently refluxed for 10 min and then allowed to evaporate to about one-third of its original volume, yielding on cooling a thick mass of fine, pale yellow-orange crystals. These were collected, air-dried, and recrystallized from ethanol. Anal. Calcd for $C_{28}H_{40}N_2O_2$: C, 77.02; H, 9.23; N, 6.42. Found: C, 76.15; H, 9.02; N, 6.23.

Preparation of Co(*t*-Bsalten).[9] To 0.709 g of ligand in 10 ml of absolute methanol was added a solution of 0.406 g of cobalt(II) acetate in 25 ml of methanol, followed by ca. 15 ml of methanol containing 0.13 g of NaOH. The solution was gently heated with stirring for about 1 h and allowed to cool and the bright red product filtered out. On further standing a second crop of bright red crystals was obtained. The product was recrystallized from *n*-hexane. Anal. Calcd for $Co(C_{28}H_{38}N_2O_2)$: C, 68.14; H, 7.76; N, 5.68. Found: C, 68.07; H, 7.67; N, 5.83.

Preparation of Co(*t*-Bsalten)(py)(O_2)·2(C_3H_6O). $Co(C_{28}H_{38}N_2O_2)$ (0.060 g) was dissolved in 6 ml of acetone to which 0.5 ml of pyridine had been added. The flask was immersed in a −15 °C cold bath and pure O_2 was blown over the surface through a glass pipet. After 10 days the solution had evaporated nearly to dryness leaving dark black-brown crystals of the presumed monooxygenated complex. On warming to 25 °C these slowly decomposed (24 h) to yield the red starting material. On immersion of the crystals in room-temperature solvents (e.g., CCl_4, acetone, cyclohexane, pyridine) they dissolved amid a froth of oxygen bubbles, leaving a red solution of the parent complex. Thermogravimetric analysis of the black crystals gave a weight loss of 32 ± 1% on heating to 80 °C, and gave as product only the red parent complex. If the crystals were formulated as $Co(C_{28}H_{38}N_2O_2)(py)(O_2)\cdot 2((CH_3)_2CO)$, loss of O_2, py, and acetone of crystallization gives a calculated weight loss of 31.5%.

Preparation of Co(*t*-Bsalten)(bzImid)(O_2)·1.5(C_3H_6O). Co-*t*-Bsalten readily adds dioxygen at −15 °C in the presence of an equimolar amount of 1-benzylimidazole. Complete evaporation of the acetone solvent (2 ml/25 mg of Co-*t*-Bsalten) gave dark-red crystals of the oxygen adduct. A tendency to form supersaturated solutions can be minimized by seeding the solutions with previously isolated crystals. The crystals are stable for varying lengths of time depending on their size and habit. Well-formed crystals of dimensions as large as 0.5 cm were grown, but were not stable for longer than a few days. Small crystals of the type used in the room-temperature data collection could be preserved by coating them with epoxy cement.

Magnetic Measurements. The magnetic moment of the Co(*t*-Bsalten) was determined by the Evans method[10] using the modified equations of Live and Chan[11] for the condition of coaxial magnetic field. The effective magnetic moment, using acetone solutions 0.02 M in Co-*t*-Bsalten (external Me_4Si standard), was 1.89 ± 0.03 μ_B over the range 220–290 K, indicative of one unpaired spin. Similar experiments on the same system in which 3% by weight pyridine and an undetermined amount of atmospheric oxygen were present were frustrated by the equilibria between the uncomplexed and complexed forms of the molecule. The μ_{eff} determined from the bulk susceptibility in this way was found to vary from 2.8 β at 220 K to 3.1 β at 290 K.

Crystal Structure Determinations. A. Unoxygenated Co(*t*-Bsalten). Data Collection. Large red prismatic crystals were obtained by slow evaporation of acetone or pyridine-containing acetone solutions at room temperature. The space group was uniquely determined as monoclinic, $P2_1/c$ (No. 14), by systematic absences found on Weissenberg photographs ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). The cell constants were obtained by least-squares fit of the 2θ angles of 40 high-angle reflections measured on Weissenberg photographs prepared on a special camera that holds the film in the asymmetric position. The values of the wavelengths used were: Cu $K\bar{\alpha}$, 1.541 78 Å; Cu $K\alpha_1$, 1.540 51 Å; Cu $K\alpha_2$, 1.544 33 Å; Co $K\bar{\alpha}$, 1.790 21 Å; Co $K\alpha_1$, 1.788 92 Å; and Co $K\alpha_2$, 1.792 78 Å. The resulting values of the cell constants (and their estimated standard deviations) are given in Table I. The density measured by flotation in aqueous $ZnBr_2$ solution, 1.239 (2) g cm^{-3}, agrees well with that calculated for four molecules per unit cell, 1.2376 (5) g cm^{-3}. Three-dimensional intensity data were collected on a Datex-automated G.E. XRD-5 diffractometer using graphite monochromatized Mo $K\alpha$ radiation. Data were taken using two crystals. The first crystal, a parallelepiped with approximate dimensions 0.15 × 0.15 × 0.18 mm was used for data having $2\theta \leq 40.00°$. A second, larger crystal (0.11 × 0.33 × 0.37 mm) was used to collect data between $2\theta = 35.00°$ and $2\theta = 48.00°$ because data in this range from the first crystal were too weak to measure with reasonable counting times. The θ–2θ scan method was used, with a scan rate of 1°/min and scan widths which varied from 1.75° at $2\theta = 4.00°$ to 2.50° at $2\theta = 55.00°$ Sixty-second background counts were made at each end of each scan. Six check reflections were monitored throughout the data collection; these served as a check on the crystal condition and were also later used to scale the data from the two crystals together. A plot of the intensities of the check reflections as a function of exposure time revealed an average decay of 2.2% in the intensities, linear with exposure time. No measureable decay was observed for the second crystal. Because of the low value of μr, no absorption corrections were made. After correction for crystal decay and Lorentz and polarization effects, the two sets of data were scaled together using as the scale factor the average of the intensity ratios of the check reflection intensities from the two sets. The R factor[12] for scaling was about 5%. The standard deviations in the intensities were estimated using $\sigma^2(I) = S + (B1 + B2)T^2 + (dS)^2$, where S, $B1$, and $B2$ are respectively the scan counts and the two background counts, T is a conversion factor to correct for the difference between the time spent on the scan and the backgrounds, and d is a factor,[13] taken to be 0.02, which reflects that part of the error attributable to fluctuations proportional to the diffracted intensity. The final data set consisted of 4257 independent reflections of which 1073 had $I > 3\sigma(I)$.

B. Co(*t*-Bsalten)(bzImid)(O_2) (Room Temperature). A small wedge-shaped crystal with poorly defined faces cut from a cluster of crystals was used for intensity data collection; its dimensions were 0.26 × 0.15 × 0.09 mm with the [100] axis along the longest dimension. This axis was nearly coincident with the Φ axis of a Datex-automated General Electric quarter-circle diffractometer equipped with a scintillation counter. The crystal was completely coated with epoxy cement to enhance stability. The lattice constants given in Table I were obtained from the 2θ values of nine carefully centered reflections measured with graphite monochromatized Mo Kα radiation.

Intensity data were collected with θ–2θ scans for the independent reciprocal-lattice octants hkl and $\bar{h}kl$. The x-ray beam was collimated to 0.5 mm and the takeoff angle was 3°. The scan speed (0.5° min^{-1}) was constant and the scan widths varied linearly from 1.50° ($2\theta = 5°$) to 1.70° ($2\theta = 40°$). Background was counted for 30 s at each side of each peak. Three standard reflections measured every 75 reflections to monitor system stability showed an approximately linear decay of 9% during the course of data collection and the data were corrected for this decay and for Lorentz and polarization effects. The intensities of 3884 independent reflections were measured, of which 676 measured less than zero. There were 1385 reflections with $I > 3\sigma(I)$. No corrections for absorption or extinction were made. Standard deviations of the intensities were obtained as before.

C. Co(*t*-Bsalten)(bzImid)(O$_2$), (−152 °C). Low-temperature intensity data were collected on an automated Syntex P$\bar{1}$ diffractometer equipped with a scintillation counter, pulse height analyzer, and a low-temperature cooling device. The crystal was mounted on a glass fiber and enclosed within a borosilicate capillary. The crystal was cooled to −152 ± 5 °C. The dimensions of the crystal were 0.28, 0.08, and 0.16 mm (maximum) perpendicular to the {100}, {010}, and {10$\bar{3}$} faces, respectively. The other crystal faces were {$\bar{1}$00}, {$\bar{1}$02}, {001}, {010}, and {0$\bar{1}$0}. Lattice parameters obtained from the 2θ values of 15 reflections are also given in Table I (primed quantities). A shrinkage of 2.5% in the unit-cell volume is found at the lower temperature.

Intensity data were collected in the θ–2θ scan mode to $2\theta = 45°$ with graphite-crystal monochromatized Mo Kα radiation. The takeoff angle was 4°. The incident beam was collimated to 1 mm. Reflections were scanned at a rate of 2° min^{-1} from 1° below the Kα_1 peak to 1° above the Kα_2 peak. The ratio of the total background time to scan time was unity.

Four standard reflections were measured every 100 reflections to monitor system stability. These reflections showed no significant deviations during one-half of the course of data collection. After 2900 reflections had been collected, a gradual decline in the intensities of these four standard reflections of about 8% was observed. The intensities remained at this level for about 1000 reflections after which the intensities returned suddenly to their original values. The cause of these variations was later found to be a malfunction in the high-voltage power supply to the counter. To correct for these systematic variations in the intensities of the affected reflections, a sufficient number of reflections was re-collected, especially those which had been measured during the sudden readjustment of the standard reflections.

The reflections were corrected for Lorentz and polarization effects. The intensity of a reflection and its standard deviation were calculated from the equations $I = (\mathrm{CT}) - (t_\mathrm{c}/t_\mathrm{b})(B_1 + B_2)/2$ and $\sigma(I) = [\sigma_\mathrm{s}^2 + (0.04I)^2]^{1/2}$ where I is the net integrated intensity, CT is the total integrated count, t_c and t_b are the scan and background counting times, B_1 and B_2 are the two background counts, and σ_s is the standard deviation in the intensity due to counting statistics. The intensities of 5835 independent reflections were measured. Even at −152 °C, a large number of reflections (4321) had intensities less than three times their standard deviation. Only those reflections with $I < 0$ were excluded from further calculations. 1514 reflections had $I > 3\sigma(I)$.

Solution and Refinement of the Structures. For all three structures calculations were carried out using the CRYM crystallographic computing system on IBM 370/158 (CIT) and IBM 370/165 (OSU) computers. The scattering factors for cobalt, oxygen, nitrogen, and carbon atoms were taken from the usual tabulation,[14] while the scattering factor for hydrogen is that given by Stewart, Davidson, and Simpson.[15] For Co(*t*-Bsalten) the values for the real part of the anomalous dispersion for cobalt were taken from the tabulation by Cromer[16] and from ref 14 for the oxygenated complexes.

A. Co(*t*-Bsalten). The position of the cobalt atom was determined from a three-dimensional Patterson map. A Fourier map calculated with phases based on the cobalt atom position revealed most of the non-hydrogen atoms, and a second Fourier calculation using these atoms gave the positions of the remaining non-hydrogen atoms. The structure-factor calculation based on these coordinates gave an R factor[17] of 0.30. Two cycles of least-squares refinement of the scale factor, atomic coordinates, and isotropic thermal parameters reduced R to 0.17. Approximate coordinates for all of the hydrogen atoms were then found on a difference map. The coordinates of the methyl hydrogens were "improved" by assuming a tetrahedral configuration and C–H distances of 0.92 Å and performing a least-squares fit of the idealized methyl group to the observed hydrogen positions. The positional and anisotropic thermal parameters were refined by the usual full-matrix least-squares techniques, the hydrogen positions being recalculated at idealized geometry after each cycle and held constant, as were the hydrogen isotropic thermal parameters, during each refinement cycle. The R factor at convergence (all shifts less than 0.1 esd) was 0.085. A difference map calculated at this point possessed several positive and negative regions of approximately 0.7–0.9 eÅ^{-3} in magnitude in the vicinity of the geminal methyl groups on the ethylenediamine bridge and also near the cobalt atom. The general noise level in the map was about 0.3 eÅ^{-3}. The C–C bond distances in the ethylenediamine bridge, and the features in the difference map, suggest the presence of an alternate gauche conformation of the ethylenediamine linkage, with the methyl groups merely exchanging positions, from axial to equatorial. That this conformer is a minor component of the crystal (<10%) is supported by our being able to locate on difference maps the methyl hydrogens for the major conformer, and also a population factor of about 0.10 when we attempted to refine a disordered model of the bridge grouping. Although it improved the C–C bond distances in the major conformer, refinement of a disordered model was unsuccessful in that it resulted in an increase in the R factor and in the goodness of fit and produced unacceptable bond distances for the minor conformer. The bond distances and angles for the rest of the molecule were unaffected by inclusion of the minor conformer in the refinement.

Table I. Crystal Data

Parent Complex	
Formula $Co(C_{28}H_{38}N_2O_2)$	Fw = 493.54
Space group: $P2_1/c$ (No. 14)	$Z = 4$
$a = 12.728$ (1) Å	
$b = 10.642$ (2) Å	$V = 2650$ (1) Å^3
$c = 19.643$ (3) Å	
$\beta = 95.22$ (2)°	
$\rho_\mathrm{exptl} = 1.239$ (2) g cm^{-3}	$\rho_\mathrm{calcd} = 1.237$ (5) g cm^{-3}
λ (Mo K$\bar{\alpha}$) = 0.710 69 Å	
μ (MoKα) = 7.01 cm^{-1}	
$F(000) = 1052$ electrons	
Wilson[a] B = 3.2 Å^2	
Oxygen Adduct	
Formula	
$Co(C_{28}H_{38}N_2O_2)(O_2)(C_{10}H_{10}N_2)\cdot 1.5(C_3H_6O)$	
Fw = 770.94	
μ(Mo Kα) = 4.82 cm^{-1}	
$F(000) = 1632$ electrons	
Space group: $P2_1/c$	$Z = 4$
Room temperature	Low temperature
$a = 11.918$ (1) Å	$a' = 11.933$ (4) Å
$b = 21.331$ (5) Å	$b' = 21.238$ (11) Å
$c = 17.267$ (2) Å	$c' = 17.004$ (8) Å
$\beta = 108.89$ (1)°	$\beta' = 109.86$ (3)°
$V = 4153$ Å^3	$V' = 4053$ Å^3
$\rho_\mathrm{calcd} = 1.233$ g cm^{-3}	$\rho'_\mathrm{calcd} = 1.263$ g cm^{-3}
Wilson[a] B = 2.9 Å^2	Wilson[a] B = 0.5 Å^2

[a] A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).

We consequently report here the structure as found at the conclusion of our refinement of the ordered model. The final R factor is 0.085 for 4257 independent reflections. The goodness of fit[18] is 1.98, which primarily reflects the small amount of disorder we were unable to resolve.

The standard deviations in the bond distances estimated from the diagonal elements of the inverse matrix from the final least-squares cycle are 0.004 Å for distances involving the cobalt atom and 0.007 Å for distances involving the other non-hydrogen atoms. The agreement between chemically equivalent bond distances is quite good, with the exception of the bond distances of the terminal-methyl groups, which are undergoing moderate thermal motion for which correction has not been made.

B. Co(*t*-Bsalten)(bzImid)(O$_2$). The position of the cobalt atom was readily found from the Patterson map. Successive Fourier and structure-factor calculations revealed the positions of all atoms in the molecule. Least-squares cycles with isotropic temperature factors for all atoms reduced the R index to 0.22. A difference Fourier at this

Table II. Atomic Parameter[a] Co(*t*-Bsalten)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	6864(4)[b]	7917(6)	22559(3)	349(3)	400(3)	428(3)	-4(3)	83(2)	40(3)
O(1)	1959(2)	663(3)	2789(1)	38(1)	49(2)	45(2)	2(2)	9(1)	6(2)
O(2)	1465(2)	1006(3)	1512(2)	40(1)	64(2)	43(2)	1(2)	5(1)	5(2)
N(1)	-106(2)	345(4)	2966(2)	37(2)	54(2)	59(2)	-2(2)	13(2)	6(2)
N(2)	-596(3)	1156(4)	1768(2)	46(2)	51(2)	55(2)	2(2)	12(2)	6(2)
C(1)	2151(3)	359(4)	3434(2)	50(2)	49(3)	45(3)	2(2)	10(2)	2(2)
C(2)	3216(3)	326(5)	3746(2)	45(2)	61(3)	48(3)	10(2)	4(2)	5(2)
C(3)	3386(4)	-66(7)	4413(3)	54(3)	104(5)	58(3)	10(3)	3(2)	16(4)
C(4)	2576(4)	-411(7)	4799(3)	80(3)	116(6)	54(3)	2(4)	2(3)	29(4)
C(5)	1570(4)	-371(6)	4521(2)	67(3)	105(4)	44(3)	-8(3)	13(2)	13(3)
C(6)	1332(3)	13(5)	3843(2)	54(2)	63(3)	46(3)	2(3)	12(2)	9(3)
C(7)	259(3)	19(6)	3574(2)	47(2)	71(4)	54(3)	-1(3)	17(2)	6(3)
C(8)	4142(3)	734(6)	3341(2)	39(2)	79(4)	58(3)	12(3)	8(2)	5(3)
C(9)	3984(4)	2052(6)	3074(3)	45(2)	77(4)	72(3)	-8(3)	8(2)	7(3)
C(10)	4241(4)	-178(6)	2759(3)	68(3)	96(4)	77(4)	18(4)	25(3)	6(4)
C(11)	5194(4)	749(8)	3787(3)	49(3)	145(6)	74(4)	19(4)	0(3)	11(5)
C(12)	-1266(3)	220(6)	2749(3)	38(2)	69(4)	90(4)	-2(2)	13(3)	13(3)
C(13)	1147(3)	1292(5)	874(2)	63(3)	44(2)	42(3)	-3(2)	3(2)	-1(2)
C(14)	1899(3)	1387(5)	379(2)	67(3)	54(3)	46(3)	-2(3)	17(2)	3(2)
C(15)	1540(4)	1712(6)	-274(3)	77(4)	81(4)	52(3)	4(3)	18(3)	11(3)
C(16)	484(5)	1916(6)	-487(3)	100(4)	86(4)	44(3)	9(4)	6(3)	12(3)
C(17)	-239(4)	1805(6)	-26(3)	64(3)	72(4)	50(3)	11(3)	-8(3)	10(3)
C(18)	73(3)	1509(5)	638(2)	55(3)	57(3)	48(3)	0(3)	4(2)	1(3)
C(19)	-728(3)	1449(5)	1126(2)	48(2)	64(3)	58(3)	2(3)	-4(2)	5(3)
C(20)	3072(4)	1122(6)	586(2)	61(3)	74(4)	54(3)	-2(3)	20(2)	2(3)
C(21)	3470(4)	2038(7)	1138(3)	50(3)	107(5)	89(4)	-14(3)	13(3)	4(4)
C(22)	3200(4)	-228(7)	820(3)	56(3)	101(5)	87(4)	23(3)	21(3)	-2(4)
C(23)	3740(4)	1332(8)	-28(3)	66(3)	155(7)	79(4)	2(4)	36(3)	10(5)
C(24)	-1498(3)	1228(5)	2213(3)	35(2)	66(4)	83(4)	7(2)	14(2)	9(3)
C(25)	-1912(3)	298(8)	3359(3)	32(2)	140(6)	103(5)	13(3)	32(3)	40(5)
C(26)	-1452(4)	2530(5)	2579(3)	60(3)	59(4)	95(4)	10(3)	26(3)	-4(3)
C(27)	-2577(4)	1080(7)	1794(3)	46(3)	111(6)	88(4)	-3(3)	4(3)	7(4)
C(28)	-1427(4)	-1086(5)	2380(4)	47(3)	48(4)	206(8)	-18(3)	14(4)	-8(4)

Atom		x	y	z	B(Å²)	Atom		x	y	z	B(Å²)
H(1)	C(9)	456	228	285	4.5	H(20)	C(26)	-204	262	281	4.5
H(2)	C(9)	338	208	278	4.5	H(21)	C(26)	-143	316	226	4.5
H(3)	C(9)	392	259	343	4.5	H(22)	C(25)	-226	106	335	4.5
H(4)	C(10)	371	-76	275	4.5	H(23)	C(25)	-239	-35	334	4.5
H(5)	C(10)	488	-58	282	4.5	H(24)	C(25)	-147	25	376	4.5
H(6)	C(10)	419	26	235	4.5	H(25)	C(27)	-270	178	152	4.5
H(7)	C(11)	524	4	406	4.5	H(26)	C(27)	-257	37	153	4.5
H(8)	C(11)	522	146	406	4.5	H(27)	C(27)	-310	101	209	4.5
H(9)	C(11)	574	76	351	4.5	H(28)	C(28)	-202	-105	208	4.5
H(10)	C(21)	397	164	144	4.5	H(29)	C(28)	-85	-126	214	4.5
H(11)	C(21)	292	230	137	4.5	H(30)	C(28)	-151	-170	270	4.5
H(12)	C(21)	377	272	94	4.5	H(31)	C(19)	-140	164	95	4.5
H(13)	C(22)	262	-46	104	4.5	H(32)	C(7)	-23	-23	386	4.5
H(14)	C(22)	380	-30	111	4.5	H(33)	C(3)	407	-10	461	4.5
H(15)	C(22)	325	-74	45	4.5	H(34)	C(4)	272	-67	524	4.5
H(16)	C(23)	430	78	0	4.5	H(35)	C(5)	103	-60	478	4.5
H(17)	C(23)	399	215	-2	4.5	H(36)	C(17)	-94	192	-16	4.5
H(18)	C(23)	333	120	-43	4.5	H(37)	C(16)	28	212	-93	4.5
H(19)	C(26)	-86	256	288	4.5	H(38)	C(15)	203	180	-59	4.5

[a] The *x*, *y*, *z* fractional coordinates are multiplied by 10^5 for the cobalt atom, 10^4 in the case of the non-hydrogen atoms, and by 10^3 otherwise. The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$. The U_{ij} elements are multiplied by 10^4 for the cobalt atom and by 10^3 otherwise. The carbon atom to which the hydrogen atoms are bound are designated after the hydrogen atom label. [b] In this and the following tables the estimated standard deviation of the last significant figure is given in parentheses.

Table III. Atomic Parameters[a] Co(*t*-Bsalten)(bzImid)(O_2)·1.5C_3H_6O (−152 °C)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	1836(2)	2992(1)	4147(1)	13(1)	21(1)	15(1)	0(1)	4(1)	2(1)
O(1)	316(7)	3300(4)	3525(4)	10(5)	24(6)	17(5)	-7(4)	1(4)	2(4)
O(2)	1020(6)	2290(3)	4405(4)	9(5)	14(5)	24(5)	-5(4)	4(4)	12(4)
O(3)	1737(7)	3368(4)	5118(5)	22(6)	28(6)	18(5)	6(5)	10(4)	-5(5)
O(4)	1207(8)	3896(4)	5041(5)	46(7)	36(7)	32(6)	17(6)	7(5)	0(5)
O(5)	-2763(8)	4393(4)	5758(6)	17(6)	42(6)	85(8)	6(5)	22(6)	8(6)
N(2)	3378(8)	2680(4)	4785(5)	12(6)	20(6)	12(6)	5(5)	-5(5)	-5(5)
N(1)	2657(8)	3697(4)	3949(5)	15(6)	25(7)	9(6)	4(6)	2(5)	-2(5)
N(3)	1827(8)	2537(4)	3133(6)	5(6)	24(7)	15(6)	-2(5)	-2(5)	-6(5)
N(4)	1910(9)	1747(4)	2327(6)	35(7)	16(7)	15(6)	-3(6)	7(6)	2(5)

Atom	x	y	z	B(Å²)	Atom	x	y	z	B(Å²)
C(1)	45(11)	3820(6)	3051(7)	1.8(0.3)	C(23)	-1335(13)	909(6)	4905(8)	3.2(0.3)
C(2)	-1205(11)	3905(6)	2530(7)	1.6(0.3)	C(24)	4402(10)	3047(6)	4661(7)	1.5(0.2)
C(3)	-1428(11)	4446(6)	2055(7)	2.1(0.3)	C(25)	4697(12)	4077(6)	4033(7)	2.4(0.3)
C(4)	-566(11)	4881(6)	2026(7)	1.5(0.3)	C(26)	4075(11)	4099(6)	5262(7)	2.2(0.3)
C(5)	591(11)	4779(5)	2520(7)	1.3(0.2)	C(27)	5547(11)	2996(6)	5405(7)	2.4(0.3)
C(6)	912(11)	4244(6)	3018(7)	1.4(0.3)	C(28)	4622(12)	2731(6)	3901(8)	3.3(0.3)
C(7)	2170(11)	4183(6)	3500(7)	1.6(0.3)	C(29)	1588(10)	2753(5)	2309(7)	1.4(0.3)
C(8)	-2144(12)	3433(6)	2546(7)	2.2(0.3)	C(30)	1643(11)	2263(6)	1830(7)	2.0(0.3)
C(9)	-2249(12)	3409(6)	3425(8)	3.1(0.3)	C(31)	2011(10)	1921(6)	3111(7)	1.3(0.2)
C(10)	-1832(11)	2774(6)	2288(7)	2.4(0.3)	C(32)	2151(12)	1117(6)	2073(8)	2.4(0.3)
C(11)	-3371(12)	3609(6)	1908(8)	2.9(0.3)	C(33)	3471(11)	976(6)	2275(7)	1.9(0.3)
C(12)	3572(10)	3737(5)	4473(7)	0.9(0.2)	C(34)	4297(12)	1458(6)	2418(8)	2.6(0.3)
C(13)	1459(11)	1854(6)	4970(7)	1.6(0.3)	C(35)	5510(13)	1312(6)	2591(8)	3.1(0.3)
C(14)	658(11)	1412(6)	5128(7)	1.8(0.3)	C(36)	5859(13)	689(7)	2617(8)	3.3(0.3)
C(15)	1140(11)	949(6)	5712(7)	1.9(0.3)	C(37)	5055(13)	205(6)	2489(9)	2.7(0.3)
C(16)	2366(12)	896(6)	6151(8)	2.4(0.3)	C(38)	3852(12)	359(6)	2319(8)	2.2(0.3)
C(17)	3143(12)	1318(6)	6021(7)	2.4(0.3)	C(39)	-1796(14)	4242(6)	5765(9)	2.9(0.3)
C(18)	2718(10)	1801(5)	5414(7)	1.2(0.2)	C(40)	-1169(18)	3682(10)	6240(12)	5.1(0.5)
C(19)	3381(11)	2215(6)	5292(7)	1.9(0.3)	C(41)	-1136(16)	4612(18)	5327(11)	4.2(0.4)
C(20)	-696(11)	1457(6)	4641(7)	2.0(0.3)	OA	3262(20)	602(10)	4166(12)	5.2(0.5)
C(21)	-1155(10)	2067(6)	4845(7)	2.2(0.3)	CA(1)	4288(30)	389(15)	4637(19)	3.6(0.8)
C(22)	-925(12)	1394(6)	3712(8)	2.6(0.3)	CA(2)	5227(32)	728(16)	4614(20)	5.4(0.8)
					CA(3)	4237(28)	-205(16)	5085(19)	4.4(0.8)

Atom		x	y	z	Atom		x	y	z
H(1)	C(40)	-164(10)	355(6)	651(7)	H(28)	C(22)	-64	99	360
H(2)	C(40)	-95(10)	339(5)	579(6)	H(29)	C(22)	-52	172	353
H(3)	C(41)	-56(10)	382(5)	660(7)	H(30)	C(23)	-218	94	460
H(4)	C(41)	-61(10)	439(5)	511(6)	H(31)	C(23)	-119	93	549
H(5)	C(41)	-160(10)	493(5)	489(7)	H(32)	C(23)	-104	52	478
H(6)	C(41)	-40(10)	487(5)	575(6)	H(33)	C(25)	442	450	392
H(7)	C(3)	-224	453	172	H(34)	C(25)	461	387	352
H(8)	C(4)	-78	524	167	H(35)	C(25)	552	406	438
H(9)	C(5)	119	508	255	H(36)	C(26)	431	407	586
H(10)	C(7)	271	452	350	H(37)	C(26)	325	421	504
H(11)	C(9)	-285	311	343	H(38)	C(26)	454	442	512
H(12)	C(9)	-247	382	357	H(39)	C(27)	578	256	550
H(13)	C(9)	-150	329	385	H(40)	C(27)	542	316	589
H(14)	C(10)	-243	248	230	H(41)	C(27)	619	323	530
H(15)	C(10)	-108	264	267	H(42)	C(28)	439	280	334
H(16)	C(10)	-180	279	173	H(43)	C(28)	410	239	391
H(17)	C(11)	-395	330	193	H(44)	C(28)	542	252	424
H(18)	C(11)	-332	362	136	H(45)	C(29)	142	318	212
H(19)	C(11)	-360	402	204	H(46)	C(30)	152	228	124
H(20)	C(15)	61	65	582	H(47)	C(31)	219	164	358
H(21)	C(16)	266	56	655	H(48)	C(32)	176	108	148
H(22)	C(17)	398	129	634	H(49)	C(32)	183	81	236
H(23)	C(19)	441	212	555	H(50)	C(34)	405	189	240
H(24)	C(21)	-200	210	454	H(51)	C(35)	609	164	269
H(25)	C(21)	-75	241	469	H(52)	C(36)	668	59	273
H(26)	C(21)	-102	209	344	H(53)	C(37)	531	-23	252
H(27)	C(22)	-177	142	341	H(54)	C(38)	328	3	223

[a] The *x*, *y*, *z* fractional coordinates are multiplied by 10^4 for non-hydrogen atoms and by 10^3 for H atoms. The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$. The U_{ij} elements are multiplied by 10^3. B = 3.0 Å² for all hydrogen atoms. The carbon atoms to which the hydrogen atoms are bonded are designated after the hydrogen atom label.

point clearly showed a molecule of acetone. Additional least-squares refinement with reflections having ($\sin^2\theta/\lambda^2$) less than 0.13 gave an *R* index of 0.17.

Further difference Fourier syntheses showed a region of diffuse electron density around the center of symmetry located at (½, 0, ½). Using all the data, it was possible to resolve eight independent peaks, the largest having a peak maximum of 1.90 eÅ^{-3}. We assumed that this volume was occupied by one disordered acetone molecule and represented the disorder by four quarter-weighted, idealized acetone molecules adjusted to fit the peaks as best we could.[19] Attempts to refine the positional parameters were unsuccessful in producing any consistent or geometrically reasonable model. We therefore abandoned any attempt to refine the disordered atoms. Instead, idealized acetone molecules were fitted to the electron density and adjusted after each least-squares cycle. This approach gave a substantial reduction of the residual electron density and improvement in the *R* factor and goodness of fit. Most convincingly, the low-temperature data (see below) gave a model which refined to reasonable positional and thermal parameters for one independent half-acetone molecule near (½, 0, ½). The difference at the two temperatures may be accounted for by partial ordering of the disordered acetone at the lower temperature.

Once the disorder was satisfactorily explained, the least-squares refinement of the structure was completed normally. Two matrices, one containing the positional parameters and one containing the scale factor and anisotropic thermal parameters were used in the refinements. All the hydrogen atoms in the Co(*t*-Bsalten)(bzImid)(O_2) portion of the asymmetric unit were placed at idealized locations with isotropic thermal parameters of 6.0 Å². It was possible to find reasonable locations for two of the methyl-hydrogen atoms on each of the ordered acetone-methyl carbons. The two missing hydrogen atoms were then placed in idealized positions 0.96 Å from the carbon atom, with *B* = 11.0 Å². The hydrogen atoms were repositioned after every least-squares cycle.

In the last least-squares cycle, no parameter shifted more than three-quarters of its esd. The final value of the *R* index is 0.062 for 1385 reflections with $I > 3\sigma(I)$ and 0.15 for 3208 reflections with $I > 0$. The goodness of fit is 1.20 for 3881 measurements and 460 parameters. The esd's for the bond lengths given in Table IV are based on all the data with no observations excluded from least-squares refinements. A final Fourier synthesis showed two residual peaks of 1.0 eÅ^{-3} in the vicinity of the methyl-carbon atoms of the ethylenediamine bridge. However, in this case the peaks were not reasonable locations for an alternate configuration of the carbon atoms in the bridge.

C. Co(*t*-Bsalten)(bzImid)(O_2) at −152 °C. The room-temperature coordinates for all the atoms except those in the disordered region were used directly for least-squares refinement. One cycle of least squares with data having $\sin^2\theta/\lambda^2$ less 0.133 gave an *R* index of 0.23. A Fourier difference synthesis at this point showed four peaks in the disordered region which gave a reasonable initial geometry for an acetone molecule. Inclusion of these atoms lowered the *R* index to 0.16 for the same data. Refinement from this point proceeded as described previously, except that it was possible to locate the hydrogen atoms on the ordered acetone molecule and to refine their positional parameters. Near the end of the refinement a number of carbon atoms in both the oxygen adduct and the ordered acetone molecule showed nonpositive definite anisotropic thermal parameters. This was due to the off-diagonal terms of the thermal tensor being slightly negative, but zero within the esd calculated. Specifically, this may be attributed to some errors within the data; however, at −152 °C the thermal motions of most of the atoms are nearly isotropic. All the carbon atoms were therefore given isotropic thermal parameters. We retained anisotropic temperature factors for the heavier atoms because the cor-

Table IV. Bond Lengths (Å)[a]

N(1)–C(12)	1.505 (6)	C(12)–C(26)	1.573 (8)	O(3)–O(4)	1.27 (1)
	1.52 (1)		1.52 (1)		1.26 (1)
	1.52 (1)		1.48 (1)	N(3)–C(29)	1.41 (1)
N(2)–C(24)	1.509 (6)	C(13)–C(14)	1.429 (6)		1.40 (1)
	1.52 (1)		1.43 (2)	N(3)–C(31)	1.33 (1)
	1.49 (1)		1.42 (1)		1.32 (1)
C(1)–C(2)	1.437 (6)	C(13)–C(18)	1.413 (6)	N(4)–C(30)	1.36 (1)
	1.47 (2)		1.44 (1)		1.32 (1)
	1.47 (1)		1.43 (1)		
C(1)–C(6)	1.423 (6)	C(14)–C(15)	1.367 (7)	N(4)–C(31)	1.35 (1)
	1.40 (2)		1.38 (2)		1.33 (1)
	1.43 (1)		1.35 (2)	N(4)–C(32)	1.46 (1)
C(2)–C(3)	1.374 (7)	C(14)–C(20)	1.536 (6)		1.44 (1)
	1.38 (2)		1.55 (2)	C(29)–C(30)	1.34 (1)
	1.34 (1)		1.54 (1)		1.34 (1)
C(2)–C(8)	1.542 (6)	C(15)–C(16)	1.388 (7)	C(32)–C(33)	1.52 (2)
	1.51 (2)		1.40 (2)		1.50 (1)
	1.50 (1)		1.44 (2)	C(33)–C(34)	1.38 (2)
C(3)–C(4)	1.384 (8)	C(16)–C(17)	1.354 (7)		1.36 (2)
	1.39 (2)		1.36 (2)	C(33)–C(38)	1.38 (2)
	1.37 (2)		1.36 (2)		1.32 (2)
C(4)–C(5)	1.346 (7)	C(17)–C(18)	1.401 (7)	C(34)–C(35)	1.41 (2)
	1.37 (1)		1.42 (1)		1.39 (2)
	1.38 (2)		1.36 (1)	C(35)–C(36)	1.38 (2)
C(5)–C(6)	1.396 (7)	C(18)–C(19)	1.435 (6)		1.33 (2)
	1.39 (1)		1.42 (1)	C(36)–C(37)	1.37 (2)
	1.39 (1)		1.40 (1)		1.37 (2)
C(6)–C(7)	1.420 (6)	C(20)–C(21)	1.512 (7)	C(37)–C(38)	1.40 (2)
	1.45 (1)		1.49 (2)		1.40 (2)
	1.45 (1)		1.49 (2)	C(39)–C(40)	1.49 (2)
C(8)–C(9)	1.505 (7)	C(20)–C(22)	1.513 (7)		1.46 (2)
	1.54 (2)		1.51 (2)		
	1.51 (2)		1.49 (2)	C(39)–C(41)	1.46 (2)
C(8)–C(10)	1.514 (7)	C(20)–C(23)	1.554 (8)		1.48 (2)
	1.55 (2)		1.54 (2)	O(5)–C(39)	1.19 (2)
	1.55 (2)		1.54 (2)		1.19 (2)
C(8)–C(11)	1.529 (7)	C(24)–C(27)	1.543 (7)	OA–CA (1)	1.30 (3)
	1.54 (2)		1.52 (2)	CA(2)–CA(1)	1.34 (4)
	1.54 (2)		1.55 (1)	CA(3)–CA(1)	1.49 (4)
C(12)–C(24)	1.514 (7)	C(24)–C(28)	1.559 (7)	C(40)–H(1)	0.9 (1)
	1.55 (1)		1.56 (2)	C(40)–H(2)	1.1 (1)
	1.57 (1)		1.53 (1)	C(40)–H(3)	0.8 (1)
C(12)–C(25)	1.515 (8)	Co–O(3)	1.873 (7)	C(41)–H(4)	1.0 (1)
	1.51 (1)		1.882 (6)	C(41)–H(5)	1.0 (1)
	1.51 (1)		1.974 (8)	C(41)–H(6)	1.1 (1)
		Co–N(3)	1.966 (7)		

[a] Bond lengths are given in the order Co(*t*-Bsalten), Co(*t*-Bsalten)(bzImid)$(O_2)\cdot 1.5(C_3H_6O)$ at −152 °C and at room temperature.

rections are more important for them. At convergence the R index for 1437 reflections with $I > 3\sigma(I)$ was 0.077 and the R index for 4215 reflections with $I_0 > 0$ was 0.21. The goodness of fit was 1.07. A final difference Fourier synthesis showed one peak of 1.7 eÅ^{-3} in the vicinity of the cobalt atom, and a number of peaks of approximately 1.0 eÅ^{-3} mostly near the atoms bonded directly to the cobalt atom. A typical carbon atom had a peak maximum of 8 eÅ^{-3}.

Tables II and III give the final values of the positional and thermal parameters for Co(*t*-Bsalten) and Co(*t*-Bsalten)(bzImid)(O_2) (at −152 °C), respectively. Bond lengths and selected bond angles are given in Tables IV and V. Tables of observed and calculated structure factors are available for all three refinements.[20]

General Description of the Molecular and Crystal Structures

As shown in Figure 2, the molecules of Co(*t*-Bsalten) are stacked along the [010] direction. The most important feature of this arrangement is that the bulky substituents of the ligand separate the cobalt atoms from one another and completely prevent the formation of inactive dimers; the Co–Co distances are also too long to allow an oxygen molecule to form a peroxo bridge. The closest intermolecular approaches are all van der Waals contacts between the peripheral bulky groups of the ligands. The crystal structure of the reversible oxygen adduct with 1-benzylimidazole as the axial base reveals a 1:1 monomeric structure as expected from these considerations (Figure 3). There is also one ordered acetone molecule and one acetone molecule disordered about a center of symmetry per monomer (Figure 4). The closest contact to the terminal oxygen atom is intermolecular to the assumed position of a methylene hydrogen atom of a benzylimidazole base (2.3 Å). Slightly longer intermolecular distances are from the terminal oxygen atom to a methyl hydrogen atom of an acetone molecule (2.4 Å) and from the other oxygen atom of the dioxygen ligand to an im-

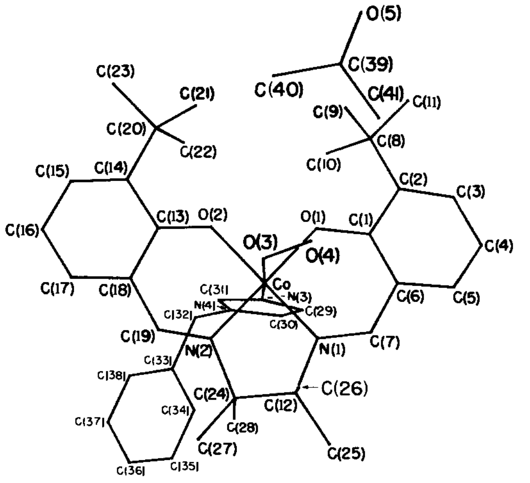

Figure 1. The labeling scheme for all three refinements.

Table V. Selected Bond Angles (deg)[a]

Co–O(1)–C(1)	129.9 (3)	N(2)–C(24)–C(12)	104.9 (4)	C(21)–C(20)–C(23)	107.0 (4)
	128.2 (6)		106.6 (8)		109.3 (9)
	127.4 (6)		104.6 (7)		108.9 (9)
Co–O(2)–C(13)	129.7 (3)	N(1)–C(12)–C(25)	111.1 (4)	C(22)–C(20)–C(23)	108.8 (4)
	127.8 (6)		112.9 (8)		107.8 (9)
	127.2 (6)		111.8 (8)		106.5 (9)
Co–N(1)–C(7)	126.2 (3)	N(1)–C(12)–C(26)	107.0 (4)	C(12)–C(24)–C(27)	114.0 (4)
	125.6 (7)		107.7 (8)		112.4 (9)
	125.0 (7)		110.3 (8)		111.5 (8)
Co–N(2)–C(19)	125.8 (3)	N(2)–C(24)–C(28)	108.3 (4)	C(12)–C(24)–C(28)	108.1 (4)
	125.2 (7)		105.4 (8)		111.9 (9)
	122.8 (6)		106.8 (8)		113.5 (8)
Co–N(1)–C(12)	113.4 (3)	N(2)–C(24)–C(27)	112.0 (4)	C(24)–C(12)–C(25)	115.2 (5)
	115.8 (6)		112.6 (8)		110.5 (8)
	115.0 (6)		111.4 (8)		110.2 (8)
Co–N(2)–C(24)	113.0 (3)	C(2)–C(8)–C(9)	111.0 (4)	C(24)–C(12)–C(26)	107.2 (4)
	114.1 (6)		110.1 (9)		112.0 (8)
	115.8 (6)		110.6 (9)		110.8 (8)
O(1)–C(1)–C(2)	120.3 (4)	C(2)–C(8)–C(10)	109.2 (4)	C(25)–C(12)–C(26)	110.9 (5)
	118.0 (9)		110.1 (9)		107.9 (9)
	120.6 (8)		110.4 (9)		108.6 (9)
O(1)–C(1)–C(6)	122.1 (4)	C(2)–C(8)–C(11)	112.1 (4)	C(27)–C(24)–C(28)	109.3 (4)
	122.1 (10)		111.1 (9)		107.7 (9)
	123.8 (9)		113.4 (9)		108.9 (8)
O(2)–C(13)–C(14)	119.8 (4)	C(9)–C(8)–C(10)	110.6 (4)	Co–N(3)–C(29)	130.5 (7)
	118.5 (9)		110.5 (9)		130.1 (6)
	117.8 (8)		108.6 (10)	Co–N(3)–C(31)	123.7 (7)
O(2)–C(13)–C(18)	121.9 (4)	C(9)–C(8)–C(11)	105.8 (4)		126.0 (7)
	121.8 (9)		108.6 (9)	O(2)–Co–O(3)	86.6 (3)
	123.1 (8)		107.3 (10)		86.2 (3)
N(1)–C(7)–C(6)	127.0 (4)	C(10)–C(8)–C(11)	108.1 (4)	O(3)–Co–N(1)	90.6 (3)
	125.0 (10)		106.4 (9)		91.7 (3)
	127.4 (9)		106.5 (9)	O(3)–Co–N(2)	89.1 (3)
N(2)–C(19)–C(18)	126.6 (4)	C(14)–C(20)–C(21)	109.0 (4)		88.5 (3)
	126.6 (10)		109.2 (9)	O(1)–Co–N(3)	87.7 (3)
	129.1 (9)		109.1 (9)		86.6 (3)
C(7)–N(1)–C(12)	120.0 (4)	C(14)–C(20)–C(22)	109.3 (4)	O(2)–Co–N(3)	88.0 (3)
	117.9 (8)		109.7 (9)		87.5 (3)
	118.9 (8)		109.7 (9)	O(3)–Co–N(3)	174.5 (3)
C(19)–N(2)–C(24)	120.9 (4)	C(14)–C(20)–C(23)	110.8 (4)		173.5 (3)
	120.8 (8)		109.2 (9)		
	121.3 (8)		111.5 (9)		
N(1)–C(12)–C(24)	105.0 (4)	C(21)–C(20)–C(22)	111.9 (4)	N(2)–Co–N(3)	92.6 (3)
	105.8 (8)		111.6 (9)		93.7 (3)
	105.0 (8)		111.3 (9)	Co–O(3)–O(4)	117.5 (6)
					118.5 (6)
				O(1)–Co–O(3)	90.6 (3)
					91.3 (3)
				N(1)–Co–N(3)	94.7 (4)
					94.6 (3)

[a] See footnote to Table IV for the order of parameters.

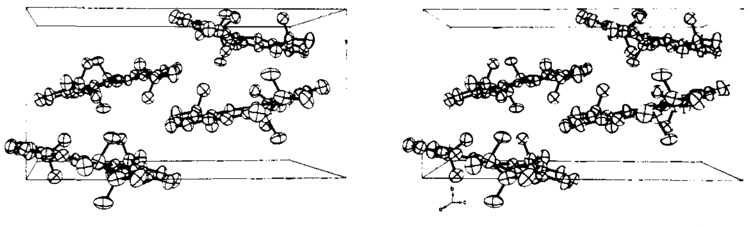

Figure 2. An ORTEP stereopair drawing of the crystal packing of Co(*t*-Bsalten) molecules in the unit cell viewed parallel to *a**.

idazole hydrogen atom (2.4 Å). These contacts are only slightly shorter than the sum of the van der Waals radii.

Specific Results and Discussion

(a) Co(*t*-Bsalten). This new compound was designed with sufficient steric hindrance in the Co(salen) framework to prevent the formation of either inactive dimers[21] or the familiar peroxo-bridged complexes[22] in its reactions with oxygen. The Co···Co separation is 5.64 Å. In the oxygen-inactive Co(salen) dimer, the cobalt-cobalt distance is about 2.85 Å and it is about 4.50 Å in a planar peroxo-bridged dimer[22c] in which the cobalt-cobalt separation is expected to be maximal.

In the Co(*t*-Bsalten) molecule the coordination about the cobalt is essentially square planar, with but a slight tetrahedral distortion (one set of trans nitrogen and oxygen atoms is 0.13 Å above the least-squares plane of the cobalt atom and its four coordinated atoms, and the other set is 0.13 Å below the plane). The cobalt-oxygen and cobalt-nitrogen bond distances (Figure 5) are in good agreement with those found for other square planar cobalt(II) salen complexes.[23] The molecule as a whole has a slight propeller-like twist, with the axis of the propeller passing through the cobalt atom and the midpoint of the C–C bond of the ethylenediamine linkage.

The bond distances within the ligand itself are not unusual

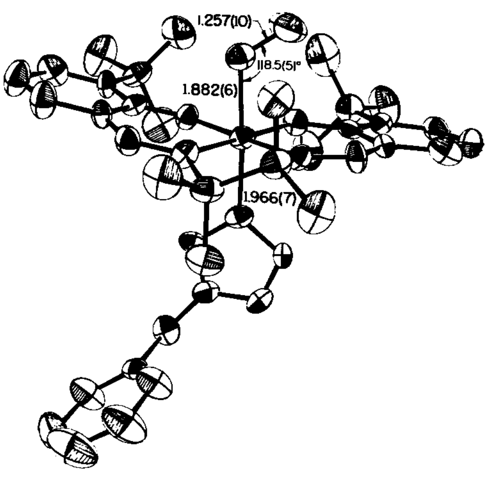

Figure 3. An ORTEP drawing of the Co(t-Bsalten)(bzImid)(O_2) molecule showing the thermal ellipsoids (40% probability level) for the room-temperature refinement.

in comparison with those found for salen derivatives.[24] Even the slight disorder in the ethylenediamine linkage is a common feature in metal-salen complexes, and the C-N and C-C distances, although not highly precise, are in reasonable agreement with the published values for other Co(salen) structures. Two of the geminal-methyl groups are axial relative to the general plane of the molecule, and the *tert*-butyl substituents on the salicylalidene rings similarly project above and below the plane of the molecule, without significantly crowding the empty trans coordination sites of the cobalt atoms. Axial groups extend further out from the molecular plane and are primarily responsible for the intermolecular separations in the solid state. However, unlike Co(salen) and its derivatives studied by Calvin,[2b] solid Co(t-Bsalten) does not appear to absorb oxygen.

The thermal motion in the molecule is reasonable, the atoms with the largest root mean square excursions (ca. 0.4 Å) being the terminal carbon atoms of the *tert*-butyl groups. The thermal motions of the geminal-methyl groups on the ethylenediamine bridge are certainly artifactual consequences of the disorder which the least-squares process has attempted to compensate for by adjustment of the thermal parameters of these atoms.

(b) Co(t-Bsalten)(bzImid)(O_2). The coordination of two additional ligands to the cobalt atom produces octahedral coordination with concomitant increases (Figure 4) in the in-plane metal-ligand distances which are more characteristic of Co(III) salen complexes (although it has been emphasized that correlation of these distances with different formal oxidation states of the same metal is not possible[24]). Also these longer Co-N distances cause the five-membered bridge ring to become more nearly planar. Consequently the axial substituents do not extend out as far from the equatorial plane. Coordination about the cobalt atom is more nearly planar in the oxygen adduct (the root mean square deviation of the ligand atoms is 0.020 Å from the coordination plane); however, the substituted salicylaldimine residues make a somewhat larger angle with the cobalt coordination plane. No unusual differences are noted among the other bond lengths.

We had hoped that the low-temperature data would yield more accurate results than the room-temperature data, but unfortunately there was only a small gain in the number of reflections with $I > 3\sigma(I)$ and a large increase in the number of weak reflections because $2\theta_{max}$ was increased. The low-temperature bond lengths are more reasonable, the value of the O-O distance is longer and closer to the value for a superoxide ion and bond lengths which should be equivalent are more nearly so. The disordered solvent region is less disordered; the model is in basic agreement with our room-temperature model. For these reasons, we will use the structural results at −152 °C in the following discussion.

Table VI compares the structural parameters of Co(t-Bsalten)(bzImid)(O_2) relevant to the bound dioxygen with those of previously reported σ-bonded dioxygen adducts. With the single exception of Co(t-Bsalten)(bzImid)(O_2) all the structures tabulated have dioxygen ligands which are disordered or undergo excessive anisotropic thermal motion.[25] This has caused considerable uncertainty in the important structural features for dioxygen bound in this manner. Not only is the dioxygen ligand completely ordered in the solid state in Co(t-Bsalten)(bzImid)(O_2), but it also has normal anisotropic thermal parameters. The O-O distance of 1.257 (10) Å found at room temperature is the same within experimental error as that of 1.273 (10) Å at −152 °C. This distance is shorter than any found in dimeric Co(III) superoxide complexes (1.31-1.36 Å), but more importantly, it is very close to the O-O separation of 1.28 (2) Å in ionic superoxide and longer than the O-O bond length of 1.21 Å in uncoordinated oxygen. Our results are therefore consistent with the usual formulation of the dioxygen ligand as a superoxide ion, O_2^-, bound to Co(III); this characterization has recently been challenged,[26] and subsequently defended.[27,28] The Co-O-O angle of 117.5 (6)° is smaller than the M-O-O angles found previously, but very close to that expected for an sp² hybridized central oxygen atom.

All the structural results in Table VI lend considerable support to the postulate that dioxygen is σ-bonded to iron in the heme respiratory proteins. The "picket fence" porphyrin synthetic model[5c] is especially important for its similarity to these proteins. The preparation of Co(II) analogues of these proteins, viz., coboglobin,[29] with similar oxygenation properties, indicates that the cobalt-dioxygen complexes in Table VI

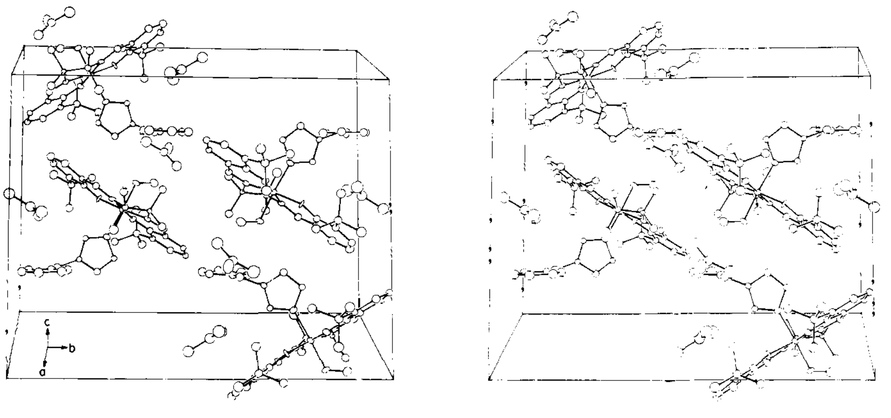

Figure 4. An ORTEP stereopair drawing of the crystal packing of Co(t-Bsalten)(bzImid)(O_2)·1.5(C_3H_6O) viewed parallel to a^*. The thermal ellipsoids of the low-temperature refinement are drawn at the 40% probability level.

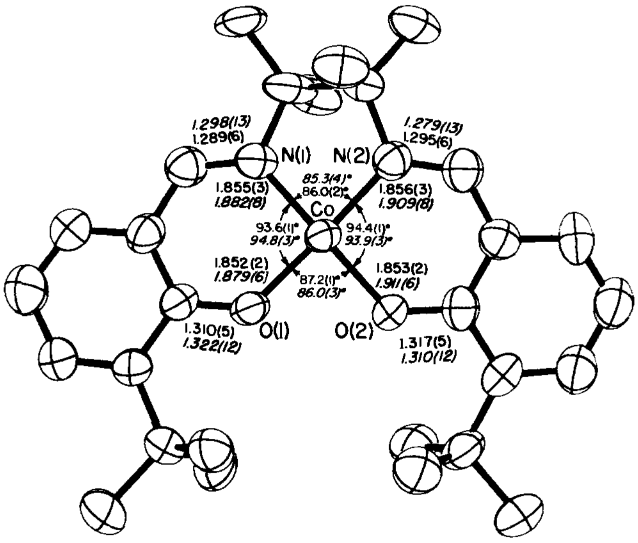

Figure 5. View of the Co(*t*-Bsalten) molecule showing in-plane bond distances for it and the oxygenated form (in italics). Thermal ellipsoids are drawn at the 50% probability level.

are also reasonable models for the naturally occurring oxygen carriers.

The stability of the oxygen adduct of Co(*t*-Bsalten) with 1-benzylimidazole as the axial base contrasts markedly with that of the complex with pyridine trans to the dioxygen ligand. This result is in basic agreement with more quantitative electrochemical experiments[30] which showed that the electron density on the cobalt ion available for transfer to the π^*-orbitals of oxygen is an important factor in the stability of the oxygen adduct. Imidazoles were found to stabilize oxygen adducts better than pyridines due to their ability to act as π donors and to donate electron density into the cobalt π orbitals. No Co(salen) ligands were included in that work, but their oxygen-carrying ability is expected to lie between the acacen chelates of cobalt, which are stabilized well by pyridine, and cobalt-porphyrin derivatives which are stable only at low temperatures even with imidazole bases.

Also of interest in this regard are studies[31] which show that Co(salen)B reacts by a different mechanism with an organic halide when B is an imidazole molecule than when B is a pyridine molecule. The imidazole complexes were found to have higher magnetic moments than the pyridine compounds which should favor electron transfer reactions especially with oxygen. Studies in progress in our laboratory with other substituted Co(salen) derivatives show imidazoles to be ideally suited for the stabilization of 1:1 oxygen adducts of these ligands.

The plane of the Co-O-O grouping in Co(*t*-Bsalten)(bzImid)(O_2) is approximately parallel to the imidazole plane; the dihedral angle is 18.5°. This slight deviation from coplanarity is likely due to both intermolecular packing forces and steric interactions with the bridge substituents. (The imidazole plane makes an angle of 96° with respect to the cobalt coordination plane and is tipped away from the bridge atoms.) Examination of molecular space-filling models shows that the methyl substituents on the ethylenediamine bridge impose considerable steric constraints on the orientation of the dioxygen ligand and the benzylimidazole base. The oxygen molecule is prohibited from assuming the same orientation as observed in Co(bzacan)(py)(O_2),[5a] where the terminal oxygen atom points toward the ethylenediamine bridge, although it is not sterically forbidden from other orientations by the *tert*-butyl substituents. The imidazole base is even more severely constrained, although its orientation is much the same as that in other cobalt-dioxygen complexes (i.e., approximately along the bisector of an O-Co-N in-plane angle). In the structure of the "picket-fence" iron porphyrin dioxygen complex, one set of disordered oxygen atoms is perpendicular, and the other set approximately parallel to the plane of the base with no apparent structural differences between the two sets. Hence, we conclude that steric effects are more important than electronic effects in determining the relative orientation of the Co-O-O grouping and the axial base plane.

The bond lengths in the imidazole base are all normal; the imidazole ring and the benzyl substituent are almost exactly planar. The Co-N(bzImid) distance is 1.974 (8) Å. Ibers[32] has considered both M-N(sp^2) and M-N(sp^3) distances and concluded that the former should be 0.05-0.06 Å less than the latter. For cobalt-imidazole bond lengths in porphyrin complexes, a value of 1.90 Å is expected from the sum of covalent radii, but steric interactions of the imidazole hydrogen atoms with the porphyrin plane make 1.93 Å a more reasonable estimate for Co(III)-N(Imid) distances. This distance varies with the orientation of the imidazole plane relative to the Co-N in-plane bonds with a minimum value along the bisector of these bonds. This is approximately the orientation of the imidazole plane in Co(*t*-Bsalten)(bzImid)(O_2), but the bulky substituents on the substituted ethylenediamine bridge provide more severe steric interaction with the base than a porphyrin ligand even in this orientation. A value of 1.97 Å for the Co-N(bzImid) distance is not unreasonable solely for steric reasons, but we cannot completely eliminate electronic effects. Such effects have been noted for ligands trans to coordinated

Table VI. Crystal Structure Analyses of σ-Bound Dioxygen Complexes

Complex	O–O distance (Å)	M–O distance (Å)	M–O–O angle (deg)	No. of data	*R* factor	Comment	Ref
Co(bzacen)(py)(O_2)	1.26 (8)	1.86	126 (4)	415, $I > 3\sigma(I)$	0.063	Possible space group ambiguity; high thermal motion of O_2[a]	5a
Co(salenC_2H_4py)(O_2)	1.1 (1)	NA	136	NA[b]	0.10	Disorder; high thermal motion of O_2	(5c, 5e)
Fe(*N*-MeImid)($\alpha,\alpha,\alpha,\alpha$TpivPP)($O_2$) (Picket fence porphyrin)	1.23 (8) 1.26 (8)	1.75 (2)	135 (4)	841, $F^2 > 3\sigma(F^2)$	0.15	Twinned crystals; disorder of O_2	5e
$Co(CN)_5(O_2)^{3-}$	1.24 (2)	1.91 (1)	153 (2)	2315, $F^2 > 3\sigma(F^2)$	0.069	Disordered O_2 group	5d
Co(acacen)(py)(O_2)	NA	1.95 (5)	NA	587, Visual data	0.19	Disorder of O_2	5b
Co(*t*-Bsalten)(bzImid)(O_2)	1.27 (1)	1.873 (7)	117.5 (6)	1437 $I > 3\sigma(I)$	0.077		(This work)

[a] Comparison of the lengths of chemically equivalent bonds in this structure (G. A. Rodley, personal communication) suggests that the estimated standard deviations should be at least double their published values. [b] NA = Not Available.

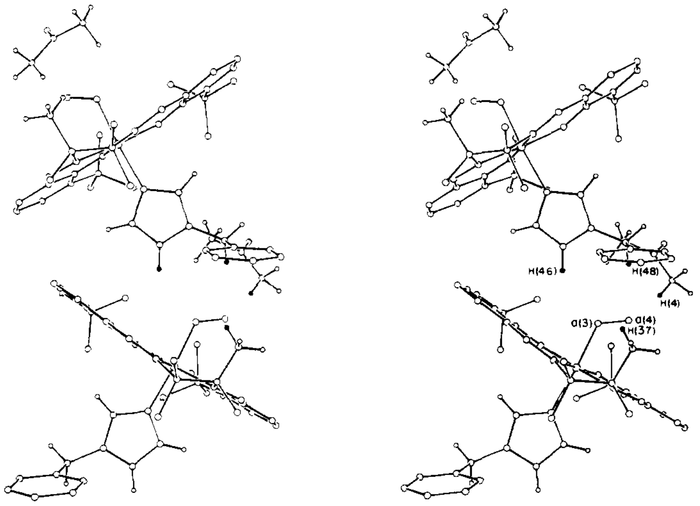

Figure 6. The interactions of the dioxygen ligand less than 2.6 Å.

dioxygen in μ-peroxo dimers.[33] In the $Co(CN)_5O_2^{3-}$ complex, however, no difference in the Co–CN distance trans to the dioxygen ligand is found.[5d,e]

Differences in rate and extent of oxygenation have been reported[34] for a series of ethylene-bridge substituted derivatives of Co(salen). These differences depend not only on the nature of the substituents, but also, in some cases, on the conformation of the bridge. The optically active form of *N*,*N*′-{1,2-dimethyl}ethylenebis(salicylideneiminato)cobalt(II), Co[salbn(+)], has a bridge conformation similar to that of Co(*t*-Bsalten) with one methyl group above and one below the equatorial plane, while the meso form has one substituent above and one in the plane.[35] The meso form has a larger equilibrium constant for the formation of the 1:1 oxygen adduct with pyridine as the axial base. Only the 2:1 oxygen adducts were isolated, however, these being the least soluble component of the solutions. In the case of Co(*t*-Bsalten), the 1:1 adduct is the least soluble species in polar solvents. The extent of formation of the 2:1 adduct in solution is unknown, but it should be destabilized relative to the 1:1 adduct for steric reasons.

In addition to its steric effect, the *tert*-butyl group should exert an electronic effect. Oxygenation of Co(salen) and its 3-substituted derivatives in solution showed the rate and extent of oxygenation to be dependent on the nature of the substituent.[36] Similar effects occur among the acacen chelates of cobalt. The *tert*-butyl group in the 3-position of Co(*t*-Bsalten) donates electron density to the cobalt atom through the equatorial π ligands and should enhance its oxygen-carrying ability and stability relative to an electron withdrawing group in the same position. Indeed, the 1:1 oxygen adduct with a 3-fluoro group[25] is less stable.

Finally, we consider why the dioxygen ligand of this compound is more well behaved in the solid state than in any of the previously reported crystal-structure determinations. We conclude that crystal packing forces determine the single orientation of the terminal oxygen in the solid state. The short intermolecular interactions of the dioxygen ligand with hydrogen atoms of a neighboring benzylimidazole base (2.3 Å) and of the ordered acetone molecule (2.4 Å) preferentially orient it in a hydrophobic pocket[37] (Figure 6). These separations are shorter than the sum of the van der Waals radii of oxygen (1.40 Å) and hydrogen (1.2 Å).[38] Although the uncertainties in these distances are admittedly high, we feel that these interactions are real and they are sufficiently strong to order the terminal oxygen atom and reduce its thermal motion.

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Supplementary Material Available: A complete list of observed and calculated structure factors (66 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) California Institute of Technology; (b) The Ohio State University.
(2) (a) T. Tsumaki, *Bull. Chem. Soc. Jpn.*, **13**, 252 (1938); (b) see A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, Englewood-Cliffs, N.J., 1952, pp 337–359, for a discussion of this work and original references.
(3) J. S. Griffith, *Proc. R. Soc. London, Ser. A*, **235**, 23 (1956).
(4) (a) L. Pauling, *Nature (London)*, **202**, 182 (1964); (b) L. Pauling, *Stanford Med. Bull.*, **6**, 215 (1948).
(5) (a) G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972); (b) G. Nardin, L. Randaccio, and G. Tauzher, *Inorg. Nucl. Chem. Lett.*, **9**, 419 (1973); (c) J. P. Collman, H. Takaya, B. Winkler, L. Libit, S. K. Seah, G. A. Rodley, and W. Robinson, *J. Am. Chem. Soc.*, **95**, 1656 (1973); (d) L. D. Brown and K. N. Raymond, *J. Chem. Soc., Chem. Commun.*, 470 (1974); (e) L. D. Brown and K. N. Raymond, *Inorg. Chem.*, **14**, 2595 (1975).
(6) J. P. Collman, R. E. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Natl. Acad. Sci. U.S.A.*, 71, 1326 (1974).
(7) R. Sayre, *J. Am. Chem. Soc.*, 77, 6690 (1955).
(8) J. C. Duff, *J. Chem. Soc.*, 547 (1941).
(9) Abbreviations in this paper are: Co(salen), *N*,*N*′-ethylenebis(salicylideniminato)cobalt(II); Co(*t*-Bsalten), *N*,*N*′-{1,1,2,2tetramethyl}ethylenebis(3-*tert*-butylsalicylideniminato)cobalt(II); Co(bzacen), *N*,*N*′-ethylenebis(benzoylacetoniminato)cobalt(II); Co(salenC_2H_4py); α,α′-{2-(2′-pyridyl)ethyl}ethylenebis(salicylideniminato)cobalt(II); Co(acacen), *N*,*N*′-ethylenebis(acetylacetoniminato)cobalt(II); Fe(α,α,α,α-TpivPP), *meso*-tetra(α,α,α,α-*o*-pivalamidephenyl)porphinatoiron(II); py, pyridine; *N*-MeImid, *N*-methylimidazole; bzImid, 1-benzylimidazole.
(10) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(11) D. H. Live and S. I. Chan, *Anal. Chem.*, **42**, 791 (1970).
(12) $R = (\Sigma|F_{\text{cryst}_1} - F_{\text{cryst}_2}|)/\Sigma|F_{\text{cryst}_1}|$.
(13) W. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(14) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, 1962, pp 202–205, 215.
(15) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(16) D. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(17) The R index is $\Sigma|F_o - F_c|/\Sigma|F_o|$. The function minimized in the least-squares calculations was $\Sigma w|F_o^2 - F_c^2|^2$ where $w = 1/\sigma^2(F_o^2)$.
(18) The goodness-of-fit is $\Sigma_w(F_o^2 - F_c^2)^2/(n - p)$ where n is the number of observations and p is the number of parameters.
(19) The mass spectrum of Co(*t*-Bsalten)(bzImid)(O_2)·1.5C_3H_8O showed no peaks which could not be assigned to Co(*t*-Bsalten), benzylimidazole, and acetone ions.
(20) See paragraph at end of paper regarding supplementary material.
(21) R. Delasi, S. L. Holt, and B. Post, *Inorg. Chem.*, **10**, 1498 (1971).
(22) (a) W. P. Schaefer, *Inorg. Chem.*, 7, 275 (1968); (b) L. A. Lindblom, W.

P. Schaefer, and R. E. Marsh, *Acta Crystallogr., Sect. B*, **27**, 1461 (1971); (c) J. R. Fritch, G. G. Christoph, and W. P. Schaefer, *Inorg. Chem.*, **12**, 2170 (1973).
(23) W. P. Schaefer and R. E. Marsh, *Acta Crystallogr., Sect. B*, **25**, 1675 (1969); C. L. Freinkel, J. S. Sherfinski, W. P. Schaefer, and G. G. Christoph, in preparation.
(24) M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, 7, 385 (1972).
(25) The structure of the monomeric dioxygen adduct of *N,N'*-{1,1,2,2-tetramethyl}ethylenebis(3-fluorosalicylideniminato)cobalt(II) with 1-methylimidazole as the axial base has been determined (A. Avdeef and W. P. Schaefer, *J. Am. Chem. Soc.*, in press. At −171 °C the crystal structure is completely ordered including two molecules of acetone solvent. The O-O bond length is 1.302 (3) Å and the Co-O-O angle is 117.3 (2)°.
(26) B. S. Tovrog and R. S. Drago, *J. Am. Chem. Soc.*, **96**, 6765 (1974).
(27) B. M. Hoffman, T. Syzmanski, and F. Basolo, *J. Am. Chem. Soc.*, **97**, 673 (1975).
(28) D. Getz, F. Melamud, B. L. Silver, and Z. Dori, *J. Am. Chem. Soc.*, **97**, 3846 (1975).
(29) B. M. Hoffman and D. H. Petering, *Proc. Natl. Acad. Sci. U.S.A.*, **67**, 637 (1970); G. S. Hsu, C. A. Spilburg, C. Bull, and B. M. Hoffman, *ibid.*, **69**, 2122 (1972).
(30) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).
(31) L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.*, **11**, 457 (1972), and references therein.
(32) R. G. Little and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4440 (1974); J. W. Lauher and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4447 (1974).
(33) F. R. Fronczek and W. P. Schaefer, *Inorg. Chim. Acta*, **9**, 143 (1974), and references therein.
(34) C. Busetto, F. Cariati, A. Fasi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J. Chem. Soc., Dalton Trans.*, 754 (1973).
(35) M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 419 (1973).
(36) O. L. Harle and M. Calvin, *J. Am. Chem. Soc.*, **68**, 2612 (1946).
(37) Strikingly similar intermolecular interactions of the dioxygen ligand with acetone solvent molecules and the *N*-methylimidazole base are found in the crystal structure of Co(3-Fsaltmen)(MeImid)(O_2).[25]
(38) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.

Nature of the Bound O_2 in a Series of Cobalt Dioxygen Adducts

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Abstract: A new series of dioxygen adducts of cobalt(II) complexes is reported whose EPR parameters span a considerably larger range than those reported earlier. The EPR spectra of these and other reported complexes are analyzed in detail, leading to a qualitative molecular orbital description of the adducts. The model shows that the unpaired electron resides on dioxygen regardless of the amount of electron transfer from cobalt(II) to oxygen. It is shown that the only source of electron transfer information lies in the spin polarization of a filled cobalt-oxygen σ bond by the unpaired electron residing in an essentially dioxygen π^* molecular orbital. The interpretation of these results indicates that there is a wide variation in the amount of electron transfer to O_2 in a series of adducts which depends on the ligands coordinated to the cobalt. Electron transfer into O_2 ranging from 0.1 to 0.8 of an electron is found in different adducts. The bonding interaction involves essentially a spin pairing of an unpaired electron in an antibonding orbital of O_2 with an unpaired electron in a d_{z^2} orbital of cobalt(II). This model is consistent with the observed magnetic properties of reported iron-dioxygen and manganese-dioxygen adducts. A previously unrecognized source of spin polarization is proposed and found to make a significant contribution to the observed coupling constants.

The ability of transition metal ions to reversibly coordinate O_2 has been known for a long time. Some of the first synthetic systems reported to bind O_2 were cobalt(II) complexes.[1] However, only recently has it been demonstrated that a wide variety of ligand environments about cobalt(II) result in reversible systems.[2-8] Neutral complexes in which the ligands contain N_2O_2 and N_4 donor atoms that are bound in a planar array and which also contain a fifth axial donor that is a σ donor,[3] π-acceptor,[7] sterically hindered base, or aromatic solvent molecule[8] have been reported. The complexes $Co(CN)_5{}^{3-}$,[9] $Co(pfp)_2$[10] (pfp = perfluoropinacol), and several derived from pentadentate ligands[11,12] have also been recently described. The reversible coordination of O_2 to iron(II) has also been an area in which significant recent advances have been made.[13]

Much of the recent activity in this area has been motivated by a desire to elucidate the factors which lead to reversible O_2 binding, to enhance the kinetic reactivity of O_2 by coordination, and to understand the transport of O_2 and oxidations by it in biological systems. Systematic approaches to these problems will require an understanding of the electronic nature of the coordinated O_2 fragment. The cobalt(II) complexes are particularly well suited for an investigation of the electronic structure because they contain at least one unpaired electron, making them ideal for electron spin resonance studies. Accordingly, we have directed our initial efforts toward a study of these complexes.

An EPR study[2] of Co(acacen)pyO_2 and other similar O_2 adducts has shown greatly reduced anisotropy ($A_\parallel - A_{iso}$) in the cobalt hyperfine coupling constants when compared to the parent five-coordinate cobalt(II) complex. These results along with some structural[14] and infrared data to be discussed shortly led to the formulation of the cobalt-O_2 adducts as Co(III)-$O_2{}^-$ with "nearly complete electron transfer from cobalt(II) to oxygen". In a subsequent EPR study of an enriched $^{17}O_2$ adduct,[14] the *isotropic* ^{17}O hyperfine coupling constant was reported and also interpreted in terms of an $O_2{}^-$ formulation.

The EPR spectra of the O_2 adduct of the pentadentate Schiff base complex CoSMDPT (SMDPT = bis(salicylidene-γ-iminopropyl)methylamine) and that of an isocyanide adduct have been reported.[11] The existence of this adduct was subsequently confirmed by Hoffman et al., who also agreed that, in both the O_2 and CH_3NC adducts, the cobalt hyperfine coupling constant in the parallel direction was reduced considerably below that of typical five-coordinate adducts.[15] The small observed proton contact shifts in the NMR of the six-coordinate isocyanide adduct enabled us to conclude that the observed reduction in the hyperfine coupling constant of the adduct occurred without "oxidation of cobalt" and formation of Co(III) $CNCH_3{}^-$. An interpretation of the isotropic ^{17}O hyperfine coupling constant in terms of a coordinated singlet O_2 formulation was presented.

The experimental result needed to resolve the question of