

(1) Silver-halogen distances increase systematically with increasing mass of the halogen atom. Thus, Ag-Cl = 2.6475 Å, Ag-Br = 2.7385 Å, and Ag-I = 2.9187 Å. The successive increments of 0.0910 and 0.1802 Å closely resemble those found within the analogous copper(I) species, [PEt₃CuX]₄ (increments are 0.1053 and 0.1401 Å).⁵

(2) Intramolecular halogen...halogen distances increase smoothly within the [PEt₃AgX]₄ (X = Cl, Br, I) series, with Cl...Cl in [PEt₃AgCl]₄ being 3.9263 Å, Br...Br in [PEt₃AgBr]₄ being 4.2009 Å, and I...I in [PEt₃AgI]₄ being 4.7527 Å. The incremental changes of 0.2746 and 0.5518 Å are fairly close to those found in the [PEt₃CuX]₄ series (0.2757 and 0.4476 Å). However, it must be emphasized strongly that the halogen...halogen distances within the [PEt₃CuX]₄ molecules are all at approximately the distance dictated by the van der Waals repulsive forces and therefore are important in dictating the molecular geometry—at least insofar as they determine the minimum size that the Cu₄X₄ cluster can have. The X...X distances within the [PEt₃AgX]₄ molecules are all significantly greater than the sum of the van der Waals radii.²⁰ [Cl...Cl(obsd) = 3.9263 Å vs. Cl...Cl(van der Waals) = 3.6 Å; Br...Br(obsd) = 4.2009 Å vs. 3.9 Å; I...I(obsd) = 4.7527 Å vs. 4.3 Å].

(3) Silver...silver distances within the [PEt₃AgX]₄ molecules decrease with increasing size of halogen atom, individual values being 3.5407 Å in [PEt₃AgCl]₄, 3.4751 Å in [PEt₃AgBr]₄, and 3.2083 Å in [PEt₃AgI]₄. The successive decrements of 0.0656 and 0.2668 Å again closely resemble those in the [PEt₃CuX]₄ series (0.0275 and 0.2564 Å, respectively).

(4) Silver-phosphorus distances increase systematically with values of 2.3895 (20) Å in [PEt₃AgCl]₄, 2.4018 (48) Å in [PEt₃AgBr]₄, and 2.4379 (19) Å in [PEt₃AgI]₄. Similar trends are found in both the [PEt₃CuX]₄ and the [PPh₃AgX]₄

series and are believed to result from decreased Cu → P back-donation as the electronegativity of X decreases.⁵

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Registry No. [PEt₃AgCl]₄, 60349-53-3; [PEt₃AgBr]₄, 60349-54-4.

Supplementary Material Available: Listing of structure factor amplitudes (1 page). Ordering information is given on any current masthead page.

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Preparation and Structural Characterization of a Monomeric Dioxygen Adduct of (*N,N'*-(1,1,2,2-Tetramethylethylene)bis(salicylideneiminato))(1-benzylimidazole)cobalt(II)

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The synthesis and structural characterization of a monomeric σ -bonded dioxygen adduct of (*N,N'*-(1,1,2,2-tetramethylethylene)bis(salicylideneiminato))cobalt(II) with 1-benzylimidazole as the axial base, Co(saltmen)(BzImid)(O₂), are reported. The dioxygen adduct crystallizes as a tetrahydrofuran solvate at -18 °C. The crystals are monoclinic (space group *P*2₁/*c*) with *a* = 11.485 (1) Å, *b* = 14.566 (1) Å, *c* = 19.102 (1) Å, β = 93.596 (5)°, and *Z* = 4. The calculated density is 1.340 g cm⁻³. Anisotropic least-squares refinement gave *R* = 0.069 for 3680 data with *F*_o² > 0. The O-O separation of 1.277 (3) Å and the Co-O-O angle of 120.0 (2)° are consistent with the formal representation of dioxygen coordinated to Co(III) as a superoxide ligand. The axial Co-N(imidazole) and Co-O₂ bond lengths are 2.011 (2) and 1.889 (2) Å, respectively. The imidazole plane and the plane of the Co-O-O grouping are approximately parallel. A comparison of some of the structural parameters of Co(saltmen)(BzImid)(O₂) with those of two other closely related monomeric dioxygen adducts is given.

Introduction

A wide variety of transition metal complexes which bind one dioxygen ligand per metal atom are now known.¹ The π or symmetrical mode dioxygen bonding is primarily found in complexes of some of the second and third transition series elements; in contrast, σ -bonded dioxygen adducts occur only among some first-row transition metals, primarily iron and cobalt.

The cobalt complex of the Schiff-base ligand 3-MeOsalen was oxygenated in pyridine solution² to give the first complex with σ -bonded dioxygen,³ although it was not definitely characterized because of its low solubility. Other cobalt

Schiff-base ligands⁴⁻⁶ in the presence of a nitrogenous base and the [Co(CN)₅]³⁻ anion in DMF solution⁷ have since been shown by x-ray crystallography to bind dioxygen in this manner. The synthesis and the structure determination of a sterically hindered "picket fence" porphyrin⁸ have demonstrated the likelihood that this is the mode of dioxygen binding in oxyhemoglobin and oxymyoglobin. Simpler porphyrins of cobalt^{9,10} and iron¹¹ also form 1:1 dioxygen-metal complexes at low temperatures. The evidence for σ -bonded dioxygen in these cases comes primarily from spectral studies.

Our approach to the isolation of σ -bonded dioxygen adducts has been to modify the framework of (*N,N'*-ethylene-

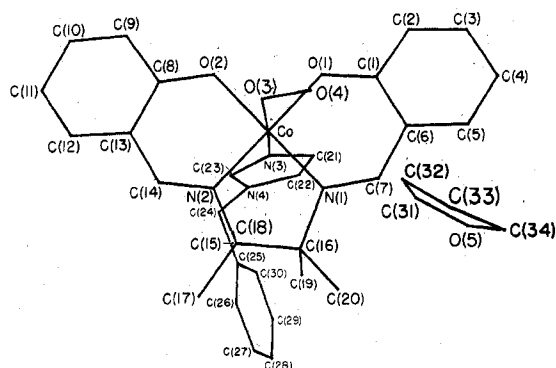
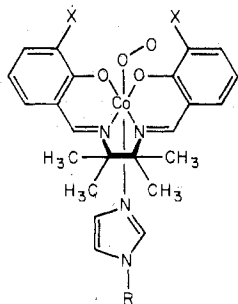


Figure 1. Labeling scheme for Co(saltmen)(BzImid)(O₂)·THF.

bis(salicylideneiminato)cobalt(II) (Co(salen)) by incorporating bulky groups to prevent the formation of peroxo-bridged dimers. (An added bonus of this approach is that the new compounds have greatly increased solubilities compared to the unsubstituted compounds which are efficient oxygen carriers.¹²) We have synthesized, isolated (at -15 to -18 °C), and determined the structures of several closely related 1:1 monomeric σ -bonded dioxygen adducts of the type



The prototype compound of this series (X = *tert*-butyl, R = benzyl) is sufficiently stable to allow a structural determination at room temperature, although we have also carried out a low-temperature structural study.¹³ A second compound¹⁴ (X = F, R = methyl) is significantly less stable so that its structure could be determined only at -171 °C. We report here the structure of the most stable dioxygen adduct (X = H, R = benzyl) we have found in this series. Our objective in this study has been to examine the structural consequences of the variation of the steric and electronic properties of the X substituent especially as it might affect the structural parameters of the coordinated dioxygen. Our results are of such a precision that these effects are detectable, particularly for the latter two compounds.

Experimental Section

Materials. Salicylaldehyde was purchased from Matheson Coleman and Bell. 1-Benzylimidazole and 2,3-dimethyl-2,3-dinitrobutane were purchased from Aldrich Chemical Co. 1-Benzylimidazole was purified by sublimation. Oxygen gas was dried by passage through concentrated H₂SO₄, KOH(s) and 3A Linde Molecular Sieves. Commercially available tetrahydrofuran was distilled from benzophenone ketyl prior to use. Analyses were carried out at the analytical facility in our laboratories.

Preparation of the Schiff Base. 2,3-Diamino-2,3-dimethylbutane was prepared according to published procedures.¹⁵ A 0.58-g amount of this substituted ethylenediamine was added dropwise to a refluxing solution of 1.30 g of salicylaldehyde in 7 ml of ethanol. After 15 min of stirring the solution was allowed to cool. Yellow needles of the Schiff base were collected, washed with ethanol, and dried under vacuum; yield 1.10 g (66%). Anal. Calcd for C₂₀H₂₄N₂O₂: C, 74.04; H, 7.46; N, 8.64. Found: C, 73.96; H, 7.43; N, 8.56.

Preparation of (N,N'-(1,1,2,2-tetramethylethylene)bis(salicylideneiminato))cobalt(II). A 0.70-g sample of the Schiff base was completely dissolved in 10 ml of hot methanol, and 0.54 g of cobalt(II) acetate tetrahydrate in 15 ml of hot methanol was slowly added. After

Table I. Crystal Data for Co(C₂₀H₂₂N₂O₂)(C₁₀H₁₀N₂)(O₂)·C₄H₈O

Fw	643.64	β	93.596 (5)°
Space group	$P2_1/c$, C_2h^5	V	3189 Å ³
Z	4	ρ_{calcd}	1.340 g cm ⁻³
a	11.485 (1) Å	F_{000}	1356 electrons
b	14.566 (1) Å	μ (Mo K α)	6.104 cm ⁻¹
c	19.102 (1) Å		

refluxing for 15 min the solution was slowly cooled to room temperature. The cobalt complex is soluble in methanol and had to be precipitated with approximately 10 ml of water. All operations were carried out under nitrogen. The orange, microcrystalline product was dried for 16 h under vacuum; yield 0.66 g (79%). Anal. Calcd for Co(C₂₀H₂₂N₂O₂): C, 62.99; H, 5.82; N, 7.35. Found: C, 62.48; H, 5.76; N, 7.35.

Preparation of Dioxygen (N,N'-(1,1,2,2-tetramethylethylene)bis(salicylideneiminato))(1-benzylimidazole)cobalt(II) Tetrahydrofuranate, Co(saltmen)(1-BzImid)(O₂)·THF. A 25-mg sample of Co(saltmen) and 10 mg of 1-benzylimidazole were completely dissolved in 2 ml of THF in a 25-ml volumetric flask. This solution was cooled to -18 °C with a stream of oxygen gas flowing over the solution. The color of the solution darkened upon cooling. Crystallization sometimes occurred spontaneously after a few hours, but the best formed crystals were obtained by seeding the solution. The dark red crystals were isolated by quickly filtering the cold solutions. Treating the crystals with polar organic solvents such as acetone or chloroform caused evolution of oxygen gas.

X-Ray Data Collection. Preliminary Weissenberg and precession films indicated the monoclinic space group $P2_1/c$ (No. 14) from the systematic absences of $l = 2n + 1$ for $h0l$ data and $k = 2n + 1$ for $0k0$ data. It was possible to obtain only a rough estimate of the density of the crystals because of the lability of the dioxygen in most solvents. This crude measurement indicated that there was at least one molecule of THF per molecule of monomer. Because the crystals are relatively stable, no special precautions were necessary in handling them, contrary to our experience with similar compounds.

A crystal of approximate dimensions 0.25 × 0.30 × 0.43 mm was placed on a Daxex-automated General Electric quarter-circle diffractometer with the [100] axis nearly coincident with the ϕ axis of the diffractometer. The 2θ values of 12 manually centered reflections were used in a least-squares procedure to obtain the lattice parameters given in Table I. Graphite monochromatized Mo K α radiation (λ 0.71073 Å) was used for data collection.

The θ - 2θ scan method was used with the x-ray beam collimated to 1.0 mm, at a takeoff angle of 3°. Data were collected between 2θ values of 4 and 45° with a scan range which varied linearly from 1.9 to 2.2° at these extremes. A scan speed of 2° min⁻¹ was employed with 15-s stationary-background counts at the beginning and end of the scans. Three reflections were measured every 75 reflections to serve as a check on possible crystal decay or system malfunction. No variations other than those attributable to counting statistics were noted. After Lorentz and polarization corrections were made and the systematically absent reflections were eliminated, a total of 4162 independent reflections were available. The standard deviations in the intensities were estimated from the formula $\sigma^2(I) = S + (B_1 + B_2)T^2 + (pS)^2$ where S , B_1 , and B_2 are respectively the scan counts and the two background counts, T is the conversion factor to correct for the difference between the time spent on the scan and backgrounds, and $(pS)^2$ is the usual correction factor with p taken to be 0.02. Because the transmission coefficients only varied from 0.833 to 0.874, absorption corrections were neglected.

Solution and Refinement of the Structure. Initial coordinates for almost all of the atoms in the structure with the exception of the phenyl carbon atoms in the benzylimidazole ligand and the atoms in the tetrahydrofuran molecule were obtained from an E map produced by the program MULTAN 74.^{16,17} The remaining nonhydrogen atoms were easily found by Fourier difference syntheses, although it was not possible to identify the oxygen atom in the tetrahydrofuran molecule initially. Positions of most of the hydrogen atoms were idealized at a distance of 0.96 Å from their respective carbon atoms. Fourier difference syntheses revealed the positions of hydrogen atoms bonded to the methyl carbon atoms. Eventually, the positional and isotropic thermal parameters of all of the hydrogen atoms except those of the THF molecule were varied.

The only complication in the refinement resulted from high thermal motion of the THF solvent molecule (Figure 2). At first, C(31) was

Table II. Atomic Parameters^a

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	A	B	C
Co	592 (0.4)	1357 (0.4)	1946 (0.3)	41 (0.3)	43 (0.3)	40 (0.3)	3 (0.3)	1 (0.2)	3 (0.3)	0.191	0.206	0.213
O(1)	965 (2)	2254 (2)	1282 (1)	51 (2)	49 (2)	48 (2)	-6 (2)	2 (1)	10 (2)	0.196	0.221	0.248
O(2)	-963 (2)	1544 (2)	1576 (1)	45 (2)	63 (2)	53 (2)	6 (2)	-5 (1)	15 (2)	0.185	0.234	0.271
O(3)	265 (2)	2296 (2)	2586 (1)	65 (2)	52 (2)	64 (2)	0 (2)	12 (2)	-5 (2)	0.222	0.241	0.268
O(4)	1019 (3)	2921 (2)	2735 (2)	97 (3)	64 (2)	84 (2)	-6 (2)	12 (2)	-17 (2)	0.233	0.294	0.322
N(1)	2138 (2)	1189 (2)	2334 (2)	42 (2)	45 (2)	48 (2)	2 (2)	-3 (2)	-2 (2)	0.195	0.210	0.231
N(2)	218 (2)	463 (2)	2615 (1)	38 (2)	45 (2)	42 (2)	0 (2)	2 (2)	3 (2)	0.195	0.200	0.217
N(3)	787 (3)	393 (2)	1208 (2)	50 (2)	46 (2)	41 (2)	0 (2)	0 (2)	-2 (2)	0.199	0.215	0.226
N(4)	648 (3)	-874 (2)	590 (2)	59 (2)	59 (2)	54 (2)	1 (2)	0 (2)	-16 (2)	0.200	0.241	0.273
C(1)	1964 (4)	2661 (3)	1256 (2)	68 (3)	40 (3)	37 (2)	-1 (2)	12 (2)	-7 (2)	0.172	0.210	0.263
C(2)	2072 (4)	3367 (3)	765 (2)	85 (4)	52 (3)	53 (3)	-6 (3)	8 (3)	8 (2)	0.208	0.247	0.293
C(3)	3102 (5)	3798 (3)	690 (2)	115 (4)	63 (4)	78 (4)	-22 (3)	22 (3)	8 (3)	0.218	0.284	0.354
C(4)	4079 (4)	3588 (3)	1101 (3)	82 (4)	70 (4)	94 (4)	-30 (3)	26 (3)	-7 (3)	0.206	0.283	0.347
C(5)	4020 (4)	2909 (3)	1593 (2)	66 (3)	58 (3)	88 (4)	-4 (3)	15 (3)	-5 (3)	0.236	0.249	0.303
C(6)	2975 (3)	2436 (3)	1688 (2)	55 (3)	42 (3)	59 (3)	-9 (2)	10 (2)	-6 (2)	0.193	0.225	0.258
C(7)	2999 (3)	1706 (3)	2184 (2)	43 (3)	54 (3)	66 (3)	-2 (2)	-2 (2)	-7 (2)	0.203	0.230	0.264
C(8)	-1871 (3)	1083 (3)	1760 (2)	35 (2)	64 (3)	50 (3)	9 (2)	0 (2)	-5 (2)	0.181	0.219	0.261
C(9)	-2970 (4)	1311 (3)	1436 (2)	53 (3)	72 (3)	76 (3)	7 (3)	-6 (2)	7 (3)	0.215	0.271	0.287
C(10)	-3946 (4)	857 (4)	1608 (2)	41 (3)	100 (4)	97 (4)	18 (3)	-12 (3)	-8 (3)	0.184	0.301	0.339
C(11)	-3907 (4)	163 (4)	2091 (2)	41 (3)	103 (4)	91 (4)	-12 (3)	12 (3)	-11 (3)	0.194	0.291	0.335
C(12)	-2873 (4)	-72 (3)	2412 (2)	51 (3)	74 (3)	68 (3)	-5 (3)	8 (2)	-2 (3)	0.221	0.260	0.275
C(13)	-1842 (3)	377 (3)	2263 (2)	38 (2)	59 (3)	44 (3)	-1 (2)	7 (2)	0 (2)	0.188	0.214	0.243
C(14)	-805 (3)	129 (3)	2670 (2)	50 (3)	47 (3)	47 (3)	-2 (2)	7 (2)	1 (2)	0.207	0.220	0.231
C(15)	1181 (3)	212 (3)	3153 (2)	48 (3)	63 (3)	41 (3)	7 (2)	-4 (2)	12 (2)	0.178	0.230	0.262
C(16)	2331 (3)	373 (3)	2800 (2)	47 (3)	52 (3)	55 (3)	2 (2)	-12 (2)	14 (2)	0.176	0.228	0.270
C(17)	1048 (4)	-774 (3)	3410 (2)	76 (4)	83 (4)	78 (3)	5 (2)	-11 (3)	40 (3)	0.190	0.284	0.350
C(18)	1059 (4)	897 (4)	3768 (2)	65 (3)	122 (4)	43 (3)	5 (3)	-8 (2)	-3 (3)	0.196	0.265	0.351
C(19)	2628 (4)	-455 (3)	2335 (2)	64 (3)	58 (3)	81 (3)	14 (2)	-8 (3)	3 (3)	0.210	0.266	0.300
C(20)	3345 (4)	507 (3)	3351 (2)	57 (3)	67 (3)	67 (3)	4 (2)	-14 (2)	6 (3)	0.206	0.262	0.287
C(21)	1588 (4)	408 (3)	707 (2)	68 (3)	53 (3)	56 (3)	-4 (2)	17 (2)	2 (2)	0.212	0.235	0.276
C(22)	1504 (4)	-363 (3)	325 (2)	72 (3)	65 (3)	58 (3)	6 (3)	21 (2)	-2 (3)	0.208	0.257	0.288
C(23)	241 (3)	-396 (3)	1120 (2)	47 (3)	59 (3)	48 (3)	1 (2)	6 (2)	-11 (2)	0.197	0.220	0.257
C(24)	304 (4)	-1810 (3)	375 (2)	73 (4)	79 (4)	78 (4)	-4 (3)	0 (3)	-38 (3)	0.200	0.273	0.341
C(25)	1250 (4)	-2475 (3)	520 (2)	71 (3)	45 (3)	48 (3)	-12 (2)	-1 (2)	-1 (2)	0.199	0.221	0.277
C(26)	1682 (4)	-2628 (4)	1201 (2)	90 (4)	97 (4)	59 (3)	-25 (3)	5 (3)	3 (3)	0.242	0.263	0.345
C(27)	2559 (6)	-3228 (4)	1342 (3)	157 (6)	73 (4)	103 (5)	-33 (4)	-40 (4)	37 (4)	0.219	0.290	0.455
C(28)	3002 (6)	-3704 (4)	817 (4)	190 (7)	61 (4)	200 (8)	53 (4)	-109 (6)	-43 (5)	0.205	0.287	0.584
C(29)	2592 (6)	-3569 (4)	147 (3)	227 (8)	140 (6)	123 (6)	104 (6)	-66 (5)	-91 (5)	0.192	0.319	0.601
C(30)	1717 (5)	-2938 (3)	-5 (2)	138 (5)	73 (4)	62 (3)	32 (3)	-19 (3)	-27 (3)	0.200	0.266	0.406
C(31)	3685 (11)	2962 (6)	3872 (5)	342 (6)	111 (7)	197 (11)	-30 (8)	-108 (10)	-28 (7)	0.286	0.403	0.650
C(32)	3280 (6)	3494 (7)	4372 (5)	114 (6)	228 (10)	192 (10)	-31 (7)	45 (6)	12 (8)	0.299	0.451	0.486
C(33)	4174 (9)	3772 (6)	4806 (3)	182 (8)	219 (9)	108 (6)	-45 (8)	1 (6)	-38 (6)	0.303	0.406	0.503
C(34)	5232 (6)	3598 (6)	4451 (6)	81 (5)	209 (9)	332 (14)	-38 (6)	-62 (6)	-9 (9)	0.234	0.468	0.599
O(5)	4742 (8)	2963 (7)	3884 (5)	238 (10)	418 (13)	414 (12)	79 (9)	11 (8)	-96 (10)	0.449	0.582	0.710

Atom	x	y	z	$B, \text{\AA}^2$	Atom	x	y	z	$B, \text{\AA}^2$
H(1)	143 (3)	353 (2)	48 (2)	5.0 (8)	H(21)	325 (3)	105 (2)	357 (2)	4.8 (8)
H(2)	310 (3)	421 (2)	38 (2)	5.7 (9)	H(22)	336 (3)	-1 (2)	368 (2)	5.5 (9)
H(3)	477 (3)	389 (2)	110 (2)	5.9 (9)	H(23)	208 (2)	90 (2)	66 (1)	3.3 (7)
H(4)	468 (3)	270 (1)	190 (2)	5.0 (9)	H(24)	188 (3)	-53 (2)	-3 (2)	4.8 (9)
H(5)	376 (2)	157 (2)	241 (2)	4.2 (8)	H(25)	-41 (2)	-58 (2)	138 (2)	3.9 (8)
H(6)	-299 (2)	186 (2)	112 (1)	3.0 (7)	H(26)	7 (3)	-177 (2)	-10 (2)	4.1 (8)
H(7)	-459 (3)	106 (2)	140 (2)	5.0 (8)	H(27)	-33 (3)	-191 (2)	56 (2)	6.3 (9)
H(8)	-453 (3)	-15 (2)	222 (2)	6.4 (9)	H(28)	132 (3)	-228 (2)	152 (2)	8.5 (10)
H(9)	-280 (3)	-57 (2)	271 (2)	4.4 (8)	H(29)	287 (3)	-328 (2)	177 (2)	8.8 (11)
H(10)	-89 (2)	-38 (2)	298 (2)	3.8 (8)	H(30)	357 (3)	-406 (3)	92 (2)	8.2 (10)
H(11)	55 (3)	-73 (2)	374 (2)	6.2 (10)	H(31)	293 (3)	-376 (2)	-26 (2)	7.5 (10)
H(12)	100 (3)	-118 (2)	299 (2)	9.6 (11)	H(32)	149 (3)	-282 (2)	-47 (2)	7.2 (10)
H(13)	178 (3)	-89 (2)	369 (2)	6.7 (10)	H(33)	339	236	397	12.0
H(14)	157 (3)	76 (2)	411 (2)	5.1 (8)	H(34)	332	318	344	12.0
H(15)	31 (3)	85 (2)	392 (2)	4.9 (8)	H(35)	273	318	465	12.0
H(16)	143 (3)	163 (2)	370 (2)	4.9 (8)	H(36)	292	404	417	12.0
H(17)	289 (3)	-100 (2)	266 (2)	6.9 (10)	H(37)	421	342	52	12.0
H(18)	315 (3)	-29 (2)	205 (2)	6.8 (10)	H(38)	414	441	491	12.0
H(19)	191 (3)	-72 (2)	206 (2)	6.8 (10)	H(39)	582	329	474	12.0
H(20)	399 (3)	52 (2)	312 (2)	6.2 (10)	H(40)	555	414	425	12.0

^a The x, y, z fractional coordinates are multiplied by 10^3 in the case of nonhydrogen parameters and by 10^3 otherwise. The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$. The U_{ij} elements are multiplied by 10^3 . Estimated standard deviations in this and the following tables are given in parentheses. $A, B,$ and C designate the root-mean square amplitudes of vibration (\AA).

designated as the oxygen atom. This led to an excess of electron density of 1.3 e \AA^{-3} at the position of O(5) and a hole of similar size at atom C(31). Reversing the assignments of these two atoms greatly improved the Fourier difference map, although least-squares refinement still failed to produce a reasonable model for the THF molecule. When the rest of the model had converged (parameter shifts less than 1σ),

there were still shifts of about 2σ in some of the thermal parameters of the THF molecule. Various attempts to improve the model gave unsatisfactory results without any significant changes in the structural parameters of the dioxygen adduct.

The final least-squares refinement²⁰ with 4262 data (including negative intensities²¹) gave an R index ($R = \sum |F_o - F_c| / \sum F_o$) of 0.069

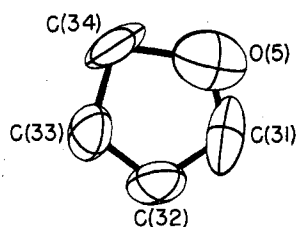


Figure 2. ORTEP drawing of the THF solvate molecule viewed approximately perpendicular to the best molecular plane. Thermal ellipsoids are drawn at the 20% probability level.

Table III. Bond Lengths (Å)

Co-N(1)	1.896 (2)	C(26)-C(27)	1.348 (7)
Co-N(2)	1.894 (2)	C(27)-C(28)	1.346 (8)
Co-O(1)	1.889 (2)	C(28)-C(29)	1.350 (9)
Co-O(2)	1.899 (2)	C(29)-C(30)	1.380 (8)
Co-O(3)	1.889 (2)	C(31)-C(32)	1.34 (1)
Co-N(3)	2.011 (2)	C(31)-O(5)	1.21 (1)
O(3)-O(4)	1.277 (3)	C(32)-C(33)	1.34 (1)
N(1)-C(7)	1.289 (4)	C(33)-C(34)	1.45 (1)
N(2)-C(14)	1.281 (4)	C(34)-O(5)	1.51 (1)
O(1)-C(1)	1.295 (4)	C(2)-H(1)	0.92 (3)
O(2)-C(8)	1.307 (4)	C(3)-H(2)	0.84 (3)
C(1)-C(2)	1.402 (5)	C(4)-H(3)	0.91 (3)
C(1)-C(6)	1.420 (5)	C(5)-H(4)	0.98 (3)
C(2)-C(3)	1.355 (6)	C(7)-H(5)	0.97 (3)
C(3)-C(4)	1.363 (6)	C(9)-H(6)	0.99 (3)
C(4)-C(5)	1.369 (6)	C(10)-H(7)	0.86 (3)
C(5)-C(6)	1.405 (5)	C(11)-H(8)	0.90 (3)
C(6)-C(7)	1.425 (5)	C(12)-H(9)	0.92 (3)
C(8)-C(9)	1.410 (5)	C(14)-H(10)	0.96 (3)
C(8)-C(13)	1.406 (5)	C(17)-H(11)	0.88 (3)
C(9)-C(10)	1.360 (6)	C(17)-H(12)	1.00 (4)
C(10)-C(11)	1.367 (6)	C(17)-H(13)	0.98 (4)
C(11)-C(12)	1.347 (6)	C(18)-H(14)	0.88 (3)
C(12)-C(13)	1.398 (5)	C(18)-H(15)	0.93 (3)
C(13)-C(14)	1.428 (5)	C(18)-H(16)	1.16 (3)
N(1)-C(16)	1.494 (4)	C(19)-H(20)	1.03 (3)
N(2)-C(15)	1.507 (4)	C(19)-H(21)	0.87 (3)
C(15)-C(16)	1.539 (5)	C(19)-H(22)	1.03 (3)
C(15)-C(17)	1.528 (5)	C(20)-H(17)	0.89 (3)
C(15)-C(18)	1.553 (5)	C(20)-H(18)	0.91 (3)
C(16)-C(19)	1.550 (5)	C(20)-H(19)	0.98 (3)
C(16)-C(20)	1.532 (5)	C(21)-H(23)	0.92 (3)
N(3)-C(21)	1.368 (4)	C(22)-H(24)	0.87 (3)
N(3)-C(23)	1.316 (4)	C(23)-H(25)	0.96 (3)
N(4)-C(22)	1.357 (5)	C(24)-H(26)	0.94 (3)
N(4)-C(23)	1.338 (4)	C(24)-H(27)	0.84 (3)
N(4)-C(24)	1.471 (5)	C(26)-H(28)	0.91 (5)
C(21)-C(22)	1.340 (5)	C(27)-H(29)	0.87 (4)
C(24)-C(25)	1.469 (5)	C(28)-H(30)	0.85 (4)
C(25)-C(26)	1.380 (6)	C(29)-H(31)	0.93 (3)
C(25)-C(30)	1.348 (6)	C(30)-H(32)	0.92 (3)

for $F_0 > 0$. The error in an observation of unit weight is 1.51. A final three-dimensional difference synthesis revealed no residual electron density greater than $+0.7 \text{ e } \text{Å}^{-3}$.

Table II gives the final values of the positional and thermal parameters for $\text{Co}(\text{saltmen})(\text{BzIImid})(\text{O}_2) \cdot \text{THF}$. Bond lengths and selected bond angles are given in Tables III and IV. A table of observed and calculated structure factors is available.²²

Results and Discussion

Figure 3 shows the structure of the 1:1 cobalt-dioxygen adduct with the oxygen σ bonded to the metal atom. A stereoscopic view of the arrangement of the well-separated monomers is presented in Figure 4.

The equatorial ligand is nearly planar. Slight deviations from planarity are most aptly described in terms of a stepped-shape conformation for the salicylaldehyde residues with respect to the cobalt coordination plane.²³ Bond lengths and angles within these residues compare well with those in other salen complexes.²⁴ The cobalt atom displays octahedral coordination with all in-plane distances essentially the same,

Table IV. Selected Bond Angles (deg)

N(1)-Co-N(2)	83.9 (1)	C(9)-C(10)-C(11)	122.0 (4)
O(1)-Co-O(2)	84.2 (1)	C(10)-C(11)-C(12)	119.1 (4)
O(1)-Co-N(2)	179.7 (1)	C(11)-C(12)-C(13)	121.4 (4)
O(1)-Co-N(1)	96.1 (1)	C(12)-C(13)-C(14)	117.3 (3)
O(2)-Co-N(2)	95.8 (1)	N(2)-C(14)-C(13)	126.6 (3)
O(2)-Co-N(1)	178.6 (1)	C(7)-N(1)-C(16)	120.6 (3)
O(1)-Co-O(3)	89.8 (1)	N(1)-C(16)-C(15)	106.5 (3)
O(2)-Co-O(3)	85.2 (1)	N(1)-C(16)-C(19)	107.9 (3)
O(3)-Co-N(1)	93.4 (1)	N(1)-C(16)-C(20)	112.8 (3)
O(3)-Co-N(2)	89.8 (1)	C(14)-N(2)-C(15)	119.3 (3)
O(1)-Co-N(3)	88.4 (1)	N(2)-C(15)-C(16)	106.1 (3)
O(2)-Co-N(3)	89.0 (1)	N(2)-C(15)-C(17)	111.3 (3)
N(1)-Co-N(3)	92.4 (1)	N(2)-C(15)-C(18)	105.2 (3)
N(2)-Co-N(3)	91.9 (1)	C(15)-C(16)-C(19)	111.0 (3)
O(3)-Co-N(3)	174.1 (1)	C(15)-C(16)-C(20)	110.8 (3)
Co-O(3)-O(4)	120.0 (2)	C(16)-C(15)-C(17)	112.9 (3)
Co-O(2)-C(8)	125.1 (2)	C(16)-C(15)-C(18)	110.7 (3)
Co-O(1)-C(1)	125.5 (2)	C(17)-C(15)-C(18)	110.2 (3)
Co-N(1)-C(7)	123.4 (3)	C(19)-C(16)-C(20)	107.9 (3)
Co-N(1)-C(16)	115.9 (2)	N(3)-C(21)-C(22)	109.8 (3)
Co-N(2)-C(14)	124.4 (2)	N(3)-C(21)-N(4)	111.4 (3)
Co-N(2)-C(15)	116.0 (2)	C(21)-N(3)-C(23)	105.1 (3)
Co-N(3)-C(21)	126.0 (2)	N(4)-C(22)-C(21)	106.6 (4)
Co-N(3)-C(23)	128.8 (3)	C(22)-N(4)-C(23)	107.0 (3)
O(1)-C(1)-C(2)	118.5 (3)	C(22)-N(4)-C(24)	126.4 (3)
O(1)-C(1)-C(6)	124.5 (3)	C(23)-N(4)-C(24)	126.4 (3)
C(1)-C(2)-C(3)	121.7 (4)	N(4)-C(24)-C(25)	112.0 (3)
C(2)-C(1)-C(6)	117.0 (3)	C(24)-C(25)-C(26)	120.2 (4)
C(1)-C(6)-C(5)	119.1 (4)	C(24)-C(25)-C(30)	120.8 (4)
C(1)-C(6)-C(7)	122.7 (3)	C(25)-C(26)-C(27)	120.9 (5)
C(2)-C(3)-C(4)	121.8 (4)	C(26)-C(25)-C(30)	119.0 (4)
C(3)-C(4)-C(5)	118.9 (4)	C(25)-C(30)-C(29)	119.6 (5)
C(4)-C(5)-C(6)	121.4 (4)	C(26)-C(27)-C(28)	119.8 (5)
C(5)-C(6)-C(7)	118.1 (3)	C(27)-C(28)-C(29)	120.4 (6)
N(1)-C(7)-C(6)	126.9 (3)	C(28)-C(29)-C(30)	120.2 (6)
O(2)-C(8)-C(9)	118.0 (3)	C(31)-C(32)-C(33)	109.3 (8)
O(2)-C(8)-C(13)	125.0 (3)	C(32)-C(31)-O(5)	112.3 (10)
C(8)-C(9)-C(10)	120.6 (4)	C(31)-O(5)-C(34)	110.0 (9)
C(9)-C(8)-C(13)	117.0 (3)	C(32)-C(33)-C(34)	106.9 (7)
C(8)-C(13)-C(12)	119.9 (3)	C(33)-C(34)-O(5)	99.0 (7)
C(8)-C(13)-C(14)	122.7 (3)		

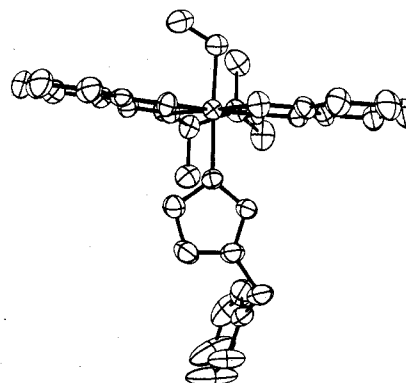


Figure 3. View of the $\text{Co}(\text{saltmen})(\text{BzIImid})(\text{O}_2)$ molecule with thermal ellipsoids drawn at the 40% probability level.

averaging 1.895 (4) Å. The O-Co-N in-plane angles are 95.8 and 96.1°, while the cis O-Co-O and N-Co-N angles are 84.2 and 83.9°, respectively. The axial Co-O bond length of 1.889 (2) Å is indistinguishable from the equatorial metal-ligand distances; the significantly longer Co-N(imidazole) distance of 2.011 (2) Å is most likely the result of steric interaction between the imidazole and the substituted ethylenediamine bridge.

Thermal excursions of almost all of the atoms in the $\text{Co}(\text{saltmen})(\text{BzIImid})(\text{O}_2)$ molecule are reasonable, although slightly short distances observed in the benzyl portion of the imidazole ligand may reflect the high thermal motion of these atoms. Bond lengths within the imidazole base are all normal. The high thermal motion of the THF molecule has been

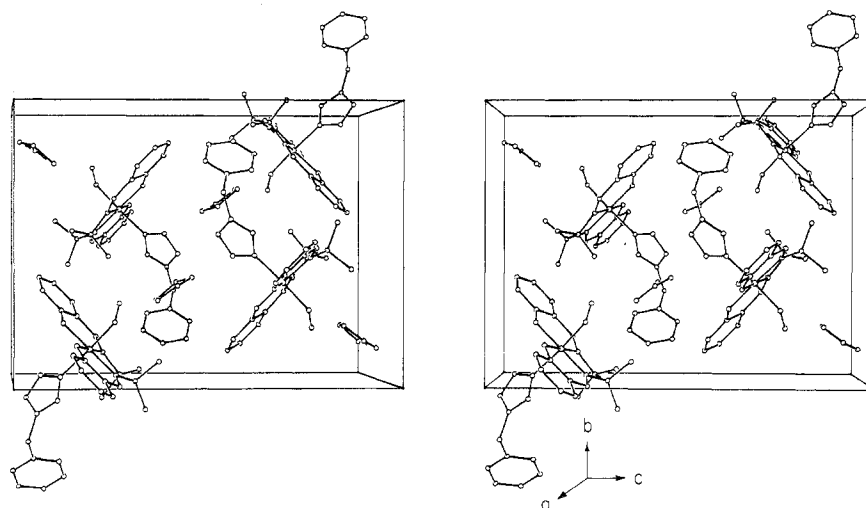


Figure 4. ORTEP stereopair drawing of the crystal packing viewed approximately parallel to a^* . Hydrogen atoms have been omitted for the sake of clarity.

Table V. Comparison of Some Structural Parameters of $\text{Co}(3\text{-Xsaltmen})(1\text{-RImid})(\text{O}_2)$ Complexes

	O—O, Å	M—O—O, deg	M—O ₂ , Å	M—N(Imid), Å	Ref
$\text{Co}(t\text{-Busalten})(\text{BzIImid})(\text{O}_2) \cdot 1.5\text{Me}_2\text{CO}$	1.273 (10)	117.5 (6)	1.873 (7)	1.974 (8)	13
$\text{Co}(3\text{-Fsaltmen})(1\text{-MeImid})(\text{O}_2) \cdot 2\text{Me}_2\text{CO}$	1.302 (3)	117.4 (2)	1.881 (2)	2.004 (3)	14
$\text{Co}(\text{saltmen})(\text{BzIImid})(\text{O}_2) \cdot \text{THF}$	1.277 (3)	120.0 (2)	1.889 (2)	2.011 (2)	This work

alluded to previously (Experimental Section and Figure 2).

The small thermal motion of the dioxygen ligand and its freedom from positional disorder are especially noteworthy. Thus, the O—O distance of 1.277 (3) Å is more precise than that in any other room-temperature structural determination and is as precise as that found in the closely related $\text{Co}(3\text{-Fsaltmen})(1\text{-MeImid})(\text{O}_2)$ molecule at -171°C in which the O—O separation is 1.302 (3) Å. The Co—O—O angle of 120.0 (2) $^\circ$ is exactly that expected for an sp^2 oxygen σ bonded to the cobalt atom. However, significant variations in this angle occur among the structures of σ -bonded dioxygen adducts in which no significant differences in O—O bond lengths exist. Variations can be ascribed to both solid-state packing forces and π bonding from the π^* orbitals of oxygen to filled metal d orbitals (d_{xz} or d_{yz}). It may be that large differences in M—O—O angles are more indicative of slight differences in the electronic nature of coordinated dioxygen than are differences in the O—O distances.²⁵

Table V contains a comparison of some of the structural parameters for the series of closely related monomeric dioxygen adducts which we have studied. The O—O bond lengths²⁶ given are all consistent with the formal representation of a dioxygen adduct of cobalt as a superoxide ion bonded to Co(III) as indicated by both ESR²⁷ and ESCA²⁸ studies. The difference of 0.025 Å between the O—O bond lengths in $\text{Co}(3\text{-Fsaltmen})(1\text{-MeImid})(\text{O}_2)$ and $\text{Co}(\text{saltmen})(\text{BzIImid})(\text{O}_2)$ is marginally significant and indicates a slightly greater electron density in the π^* orbitals of the coordinated dioxygen in the former. This is unexpected, since the electron-withdrawing fluorine substituents should inhibit electron transfer to the π^* orbitals of oxygen. However, qualitative stabilities of these two adducts are consistent with the expected order with $\text{Co}(3\text{-Fsaltmen})(1\text{-MeImid})(\text{O}_2)$ being much less stable. The differences in the Co—O—O angles in Table V are well within the range attributable to the effect of packing forces.

The observation that $\text{Co}(\text{saltmen})(\text{BzIImid})(\text{O}_2)$ is apparently more stable than $\text{Co}(t\text{-Busalten})(\text{BzIImid})(\text{O}_2)$ is also surprising. The *tert*-butyl substituent should enhance the oxygen-carrying ability of the cobalt atom. Although qualitative stabilities based on the time it takes for the crystals to turn the bright red color indicative of oxygen loss are not

exact criteria of stability, the unexpected order is consistent with that found for substituted cobalt chelates of acacen.²⁹

All of the molecules listed in Table V crystallize in the same space group and all cocrystallize with molecules of solvent. In the unit cell of $\text{Co}(t\text{-Busalten})(\text{BzIImid})(\text{O}_2)$ one acetone molecule lies approximately parallel to the axial ligand plane with some of the acetone hydrogen atoms within van der Waals distance of the terminal oxygen atom. A similar packing arrangement occurs for $\text{Co}(3\text{-Fsaltmen})(1\text{-MeImid})(\text{O}_2)$ where two acetone molecules snugly embrace the dioxygen ligand. As shown in Figure 1, the THF molecule in the present structure lies perpendicular to the axial ligand plane. In every case, the terminal oxygen atom is preferentially oriented toward the solvent molecules. Intermolecular solid-state interactions involving these solvent molecules in the three complexes we have studied presumably account for the lack of disorder of the dioxygen ligand, in striking contrast to the disorder observed for almost all of the other σ -bonded M—O₂ complexes.

The mutual orientation of the Co—O—O group and the imidazole plane is the same as that in the other dioxygen adducts listed in Table V; viz., the planes are approximately parallel, in this case with a dihedral angle of 19.2 $^\circ$ between them. In addition to a twist of these two planes about the normal to the cobalt coordination plane, the axially coordinated oxygen and nitrogen atoms are canted away from the normal at angles of 4.6 and 2.6 $^\circ$, respectively. The significance of the mutual orientation of the dioxygen ligand and the axial base has been discussed elsewhere,^{4,8a,13,14} but it is noteworthy that both the parallel and perpendicular orientations occur and both even occur simultaneously in the case of the picket fence porphyrin.

Our original objective in undertaking the study of oxygen-carrying cobalt complexes was to isolate stable 1:1 dioxygen adducts primarily by incorporating steric hindrance into the Co(salen) ligand. Examination of space-filling molecular models indicated that the sterically hindered $\text{Co}(t\text{-Busalten})$ ligand was ideally suited for this purpose. Unexpectedly, diminishing the steric bulk of the substituted salicylaldehyde did not alter the monomeric nature of the isolated products. This is surprising in light of the reported

isolation of only 2:1 adducts of similar cobalt complexes.³⁰ It appears that the conditions under which we prepared these adducts (aprotic, polar solvents at low temperatures in the presence of imidazoles) may account for the difference in results. Physical studies presently in progress may elucidate more fully the thermodynamics and kinetics of the reaction of these ligands with oxygen and the electronic properties of the dioxygen adducts.

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Registry No. Co(saltmen)(BzIImid)(O₂)·THF, 60338-52-5; Co(saltmen), 60306-16-3; 2,3-diamino-2,3-dimethylbutane, 20485-44-3; salicylaldehyde, 90-02-8; H₂saltmen, 60306-02-7.

Supplementary Material Available: A continuation of Table IV, showing H-atom angles, and Table VI, a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Structural Investigation of Two Carbonyl Complexes of Cobalt(I) and Nickel(0) with the Ligand Tris(2-diphenylphosphinoethyl)amine

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The molecular structures of two carbonyl complexes of the ligand tris(2-diphenylphosphinoethyl)amine, np₃, [Co(CO)(np₃)]BPh₄·(CH₃)₂CO and [Ni(CO)(np₃)] have been determined from three-dimensional x-ray data. The cobalt complex crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 12.43 (1), *b* = 20.29 (2), *c* = 23.85 (2) Å, β = 103.0 (1)°, and *Z* = 4. The nickel complex crystallizes in the monoclinic space group *P*2₁ with *a* = 20.44 (1), *b* = 8.87 (1), *c* = 10.34 (1) Å, β = 90.4 (1)°, and *Z* = 2. Counter methods were used and full-matrix least-squares refinements gave final conventional *R* factors of 0.073 and 0.049 for the cobalt and nickel complex, respectively. The cobalt complex has a trigonal bipyramidal geometry whereas the nickel complex has a tetrahedral geometry, the central nitrogen of the ligand being not coordinated. Structural, magnetic, and spectral data of the two complexes are compared with those of the isoelectronic and isostructural metal nitrosyl complexes and discussed on the basis of a qualitative molecular orbital approach.

Introduction

In the course of previous studies performed in this laboratory a variety of 3d metal nitrosyl and carbonyl complexes with the ligand tris(2-diphenylphosphinoethyl)amine, np₃, have been

prepared and characterized.^{1,2} In particular the x-ray structures of the [M(NO)(np₃)]BPh₄ (M = Fe, Co, Ni) complexes have been determined and their spectral and magnetic properties interpreted on the basis of a simplified