Inorganic Chemistry, Vol. 14, No. 11, 1975 **2595**

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A σ-Bonded Dioxygen Adduct of the Pentacyanocobaltate(II) Anion. Crystal Structure of $[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$

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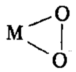
Received March 25, 1975

AIC50223S

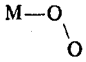
The crystal structure of $[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$ reveals a pseudooctahedral $[Co(CN)_5(O_2)]^{3-}$ complex that is best described as a σ-bonded cobalt(III) superoxide. Comparison with other σ-bonded dioxygen complexes shows that this is the probable mode of bonding of dioxygen in biological oxygen transport molecules. The O_2 ligand has been refined as a noncrystallographic twofold disorder of two bent Co–O_2 groups. The Co–O_1–O_2 angle is 153.4 (21)° with a Co–O_1 distance of 1.906 (14) Å and an O_1–O_2 distance of 1.240 (17) Å. The five Co–C bond lengths average 1.92 (1) Å with average C–N bond lengths of 1.10 (2) Å. The five water molecules form a hydrogen-bonding network around the complex. The red-brown crystals of $[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$ conform to space group $P2_1$ with a = 10.444 (4) Å, b = 14.105 (8) Å, c = 14.392 (6) Å, β = 108.63 (2)°, Z = 2, ρ_{obsd} = 1.15 g/cm³, and ρ_{calcd} = 1.16 g/cm³. Intensity data were collected by automated diffraction methods using θ–2θ scans and stationary backgrounds. For the 2315 reflections with $F^2 > 3\sigma(F^2)$, the structure has refined to R_1 = 7.1% and R_2 = 7.6%. The synthesis and characterization of the salts $[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot DMF$, $[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot 3H_2O$, $[N(C_2H_5)_3(CH_2C_6H_5)]_3[Co(CN)_5(O_2)]\cdot {}^1/_2DMF$, and $[N(CH_2C_6H_5)_2(CH_3)_2]_3[Co(CN)_5(O_2)]$ are also reported. The full structure analysis of $[N(CH_2C_6H_5)_2(CH_3)_2]_3[Co(CN)_5(O_2)]$ shows a random positional disorder between CN and O_2 groups. This appears to occur in many of the other salts but does not occur in the structure reported here for $[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$. This order, which is apparently due to hydrogen bonding of the cyanide groups, has been tested using several models in least-squares refinements.

Introduction

The bonding mode of dioxygen in transition metal complexes has been debated and studied for many years. This interest has centered primarily on biological oxygen transport molecules such as hemoglobin. X-Ray studies on oxymyoglobin and oxyhemoglobin have been made, but the resolution is insufficient to reveal the mode of bonding of dioxygen to the iron atom.[2] A variety of monomeric oxygen adduct complexes have been made over the years. X-Ray structures have been determined for a number of these compounds. They fall into two general types, the π-bonded



and the σ-bonded



structures. Both of these bonding modes have been proposed for oxyhemoglobin, with Pauling[3] favoring the σ-bonded structure and Griffith[4] the π-bonded. Recent X-ray structure reports of $[Co(bzacen)(py)(O_2)]$,[5,6] $[Co(salenC_2H_4py)(O_2)]$,[7] and especially Collman's "picket fence" iron porphyrin complex[8] give strong support to the nonlinear σ-bonded structure. The cobalt complexes are appropriate models for the heme proteins since the properties of oxycobalt myoglobin and oxycobalt hemoglobin indicate that dioxygen binds to cobalt in the same way that it binds to iron in the native proteins.[9,10] The $[Co(CN)_5(O_2)]^{3-}$ ion is the simplest such example of a simple cobalt–oxygen adduct complex.

The $[Co(CN)_5(O_2)]^{3-}$ anion was first proposed as a possible intermediate in the formation of the $[(CN)_5Co–O_2–Co(CN)_5]^{6-}$ anion based on ESR studies.[11] The structure of this peroxo-bridge dimer has been reported recently.[12] The $[Co(CN)_5(O_2)]^{3-}$ ion was characterized in more detail by White and coworkers.[13] In contrast to aqueous solutions, the reaction of $[Co(CN)_5]^{3-}$ with O_2 in DMF is faster than the reaction with $[Co(CN)_5(O_2)]^{3-}$. This is apparently due to the close approach of two trinegative anions in the latter reaction. The result is that $[Co(CN)_5(O_2)]^{3-}$ is a product instead of an intermediate. Because of the continuing interest in this complex, especially in relation to oxygen transport systems, the X-ray crystal structure of $[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$ was undertaken. A preliminary communication of this structure has been published in which the complex was reported as an essentially linear Co–O_2 group.[14] A model is proposed in this paper which reformulates the structure as a disordered bent Co–O_2 complex.

Table I. Summary of Crystal Data

Molecular formula	$[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$
Mol wt	701.86
Space group	$P2_1$
Cell constants[a]	
a	10.444 (4) Å
b	14.105 (8) Å
c	14.392 (6) Å
β	108.63 (2)°
V	2008.9 Å³
Formula units/cell	2
Calcd density	1.16 g/cm³
Obsd density	1.15 g/cm³
Crystal dimensions	0.02 × 0.02 × 0.03 cm
Linear absorption coeff, μ	4.3 cm⁻¹

[a] Ambient temperature of 23°. Mo Kα_1 radiation, λ 0.70926 Å.

Experimental Section

Preparation of $[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$. A dimethylformamide (DMF) solution of $[N(Et)_4]_3[Co(CN)_5]$ was prepared under an anhydrous nitrogen atmosphere as previously described.[13] The solution was exposed to air of moderate humidity at room temperature for a few hours without stirring or agitation. Red-brown crystals of $[NEt_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$ slowly deposited. The crystals are stable in air with no loss in solvent of crystallization. Anal. Calcd for $[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$ (formula weight 701.86): C, 49.6; H, 10.0; N, 16.0. Found: C, 50.0; H, 10.0; N, 16.3.

Unit Cell and Diffraction Data. A series of precession photographs showed that the crystal was monoclinic and exhibited the absences $0k0$, $k \neq 2n$. These absences are consistent with space groups $P2_1$ (C_2^2, No. 4) and $P2_1/m$ (C_{2h}^2, No. 11).[15] As shown by the subsequent solution of the structure, $P2_1$ is the correct space group. The density of several crystals was determined by the flotation method in toluene–1,1-dichloroethane solutions. The measured density was 1.15 g/cm³; the calculated density is 1.16 g/cm³ for two formula units per cell. Crystal data are summarized in Table I. Intensity data were collected on an automated Picker FACS-1 four-circle diffractometer.[16-19] The data were processed as described previously with a parameter p, introduced to prevent overweighting strong reflections, chosen as 0.04. Equivalent reflections were averaged. The R factor for averaging is 5.5%.

Solution and Refinement of the Structure. The structure was solved by the application of heavy-atom techniques.[16] Full-matrix least-squares refinements were carried out for the 2315 reflections with $F^2 > 3\sigma(F^2)$.[20-23] The positions of the cobalt and eight light atoms were found from the three-dimensional Patterson map. Subsequent difference Fourier and least-squares calculations located the remainder of the nonhydrogen atoms.

All of the nonhydrogen atoms were refined anisotropically. It was found that the atoms for the dioxygen ligand displayed extremely high anisotropic thermal motion. A "twofold" disorder model was devised in which two independently varied isotropic oxygen atoms generated two symmetry-related atoms. The details of the model are discussed later. All of the nonhydrogen atoms refined to R_1 = 7.5%[24] in space group $P2_1$. When the enantiomorphous structure was refined (tested by reversing the sign of the k index), the R factor went to R_1 = 8.1% indicating that the configuration originally chosen was correct. A contribution from the hydrogen atoms was made after all of the nonhydrogen atoms had refined. The methylene and methyl hydrogen positions for the three tetraethylammonium cations were calculated based on idealized tetrahedral geometry and a C–H bond length of 0.95 Å.[25] The numbering scheme for the atoms in Table II and the following tables and figures is as follows: O_1 and O_2 are the atoms of the O_2 ligand (with $O_{1'}$ and $O_{2'}$ the twofold disorder related atoms), C_1 through C_5 and N_1 through N_5 are cyanide atoms, N_6 through N_8 are NEt_4^+ atoms. The NEt_4^+ carbon atoms are designated by alkylammonium group number and then sequenced within the group. Thus C_{31} is the methylene carbon atom of the first ethyl group for the third alkylammonium ion while C_{32} is the corresponding methyl group atom. The methylene hydrogen atoms were calculated as fixed groups. Those for which the thermal parameter refined to be 25 or less are listed sequentially as H_1 through H_8. The one hydrogen located in a water molecule (O_5) is H_9. The remaining hydrogen atoms were refined as fixed methyl rigid groups in which only the rotation angle around the local trigonal axis was refined. The structure refined to R_1 = 7.1% and R_2 = 7.6%. The final error in an observation of unit weight is 2.19.[24] The largest contribution to this value was found in the low-angle reflection data resulting from an imperfect description of the disorder model in the structure. The final difference Fourier showed no peak greater than 0.48 e/Å^3 (approximately 10% of a carbon atom). Table II gives the positional and thermal parameters for the nonhydrogen atoms. Positional parameters and isotropic thermal parameters for the individual hydrogen atoms are listed in Table III. Table IV lists the root-mean-square (rms) amplitudes of vibration of the nonhydrogen atoms derived from the anisotropic thermal motion.[26]

X-Ray Studies of Other Salts of the $[Co(CN)_5(O_2)]^{3-}$ Anion. After the initial preparation of the pentahydrate, four other salts of the oxygen adduct were prepared and initial X-ray studies undertaken: **(1)** $[NEt_4]_3[Co(CN)_5(O_2)]\cdot DMF$, **(2)** $[NEt_4]_3[Co(CN)_5(O_2)]\cdot 3H_2O$, **(3)** $[NEt_3Bz]_3[Co(CN)_5(O_2)]\cdot {}^1/_2DMF$, **(4)** $[NBz_2Me_2]_3[Co(CN)_5(O_2)]$ (Bz = benzyl, Et = ethyl, Me = methyl). For compounds **1**–**3** only precession photographs were made from which cell constants and a preliminary space group were determined. For compound **4**, the $[NBz_2Me_2]^+$ salt, a complete X-ray structure determination was made.

$[NEt_4]_3[Co(CN)_5(O_2)]\cdot DMF$ was prepared by bubbling anhydrous O_2 gas through an ca. 0.2 M solution of $[NEt_4]_3[Co(CN)_5]$ in DMF. Crystals of this salt slowly deposited after a few hours at room temperature. The red-brown, platelike crystals lose solvent of crystallization very rapidly when removed from the original solution. Crystals were immediately sealed in thin-walled glass capillaries for X-ray precession photographs. The space group is $P2_1/c$; a = 10.44 Å, b = 34.80 Å, c = 21.93 Å, and β = 93.9°.[27] For eight formula units per cell, ρ_{calcd} = 1.14 g/cm^3 and ρ_{obsd} = 1.15 g/cm^3. Because of the large number of nonhydrogen atoms in two formula units the size of the computational problem would have been prohibitively large.

$[NEt_4]_3[Co(CN)_5(O_2)]\cdot 3H_2O$ was prepared by bubbling O_2 gas through a DMF solution of ca. 0.2 M $[NEt_4]_3[Co(CN)_5]$ and afterward adding water to the solution to make an approximately 10% H_2O–90% DMF solution. This deep red-brown solution was then immediately cooled at −20°; red-brown cube-shaped crystals slowly deposited over a period of several hours. The crystals are stable when exposed to atmosphere. Anal. Calcd for $[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot 3H_2O$ (formula weight 665.83): C, 52.31; H, 9.99; N, 16.83. Found: C, 51.58; H, 9.84; N, 16.72.

Precession photographs showed absences $h + k + l \neq 2n$ and $h0l$, $h \neq 2n$, that were consistent with monoclinic space group $I2/a$ or Ia (alternate setting of $C2/c$ or Cc).[15] The cell constants measured from the films are a = 13.51 Å, b = 14.54 Å, c = 19.92 Å, and β = 96.00°; Z = 4; ρ_{calcd} = 1.14 g/cm^3 and ρ_{obsd} = 1.14 g/cm^3.

$[NEt_3Bz]_3[Co(CN)_5(O_2)]\cdot {}^1/_2DMF$. A solution of $[NEt_3Bz]_3[Co(CN)_5]$ was prepared by treating $[NEt_3Bz]CN$[28] with $CoCl_2$ in stoichiometric amounts in DMF. A color change from yellow to red-brown occurred when O_2 was bubbled through the solution. Diethyl ether was slowly added to the $[Co(CN)_5(O_2)]^{3-}$ solution by a vapor diffusion method described previously,[29] and red-brown crystals formed. Since the crystals slowly lose solvent of crystallization upon long exposure to the atmosphere, they were sealed in capillaries for X-ray studies by the precession method. The space group is also $I2/a$ or Ia with cell constants a = 16.66 Å, b = 21.09 Å, c = 13.95 Å, and β = 102.92°. For Z = 4, ρ_{calcd} = 1.16 g/cm^3 and ρ_{obsd} = 1.16 g/cm^3.

$[NBz_2Me_2]_3[Co(CN)_5(O_2)]$. The deep yellow solution of $[NBz_2Me_2]_3[Co(CN)_5]$ was made by allowing stoichiometric amounts of $[NBz_2Me_2]CN$[28] to react with $CoCl_2$ in DMF. The red-brown color characteristic of the $[Co(CN)_5(O_2)]^{3-}$ anion was formed by bubbling O_2 through the solution. For an ca. 0.1 M solution, crystals slowly formed over a few hours at room temperature. The dark red-brown crystals are indefinitely stable in air. Anal. Calcd for $[N(C_7H_7)_2(CH_3)_2]_3[Co(CN)_5(O_2)]$ (formula weight 900.05): C, 70.73; H, 6.72; N, 12.45. Found: C, 70.64; H, 6.35; N, 12.60.

Precession photographs showed that the space group is also $I2/a$ or Ia, and preliminary cell constants were calculated. Intensity data were collected by automatic diffractometer methods as described earlier.[19] The space group is $I2/a$ as determined by the subsequent solution of the structure. The least-squares refined cell constants are a = 15.523 (3) Å, b = 15.190 (3) Å, c = 21.713 (5) Å, and β = 91.756 (7)°; Z = 4; ρ_{calcd} = 1.168 g/cm^3 and ρ_{obsd} = 1.166 g/cm^3. The structure was solved by direct methods of phasing using the program MULTAN.[16] The Co atom is on a crystallographic inversion center at $^1/_4$, $^1/_4$, $^1/_4$. The three independent ligands are linear and indistinguishable from a cyanide group. Thus, the dioxygen ligand is statistically disordered about all six positions of the octahedral complex with each ligand approximating five-sixths of a cyanide and one-sixth of a dioxygen. One of the two crystallographically independent $[NBz_2Me_2]^+$ cations is situated on a twofold axis while the second cation is located on a general position. For 1240 independent reflections with $F^2 > 3\sigma(F^2)$ and all atoms with isotropic thermal parameters, the structure refined to R_1 = 8.7%. No further refinement was carried out since the $[Co(CN)_5(O_2)]^{3-}$ complex was randomly disordered.

The results of the $[NBz_2Me_2]_3[Co(CN)_5(O_2)]$ structure can be used in evaluating the probable structures of $[NEt_4]_3[Co(CN)_5(O_2)]\cdot 3H_2O$ and $[NEt_3Bz]_3[Co(CN)_5]\cdot {}^1/_2DMF$ which also crystallize in space group $I2/a$ (or Ia). The similar patterns of intensities found in the precession photographs of the three crystals make it highly probable that they are analogous in structure, with a disordered $[Co(CN)_5(O_2)]^{3-}$ anion on an inversion center.

The Dioxygen Disorder Model

As shown by the structural results of the $[NBz_2Me_2]_3[Co(CN)_5(O_2)]$ salt, the $[Co(CN)_5(O_2)]^{3-}$ anion tends to disorder randomly among its six diatomic ligands. That this positional disorder does not occur in $[NEt_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$ is attributed to the noncentric crystal symmetry and especially the hydrogen-bonding network in which the anion is surrounded by five waters of crystallization (Table VI). Nevertheless, a close examination is warranted, especially since the dioxygen ligand appeared almost linear in early refinements and was reported as such in a preliminary report of the structure.[14] The occupancy parameter for the atoms in the least-squares calculations[16] was varied for the 12 atoms to verify that the ligand called dioxygen is unique compared to the other five ligands. Two different refinements were carried out in this test. In the first, all of the ligands were refined with carbon and nitrogen atomic scattering factors and the occupancy, positional, and anisotropic thermal parameters were varied.[29] In the second refinement, all of the ligands were called dioxygens with the same variables as before. The results of both occupancy refinements are given in Table V. The consistent results show that O_x is unique when compared to C_1 through C_5. For the first refinement the average occupancy

Table II. Positional and Thermal Parameters ($\times 10^4$) for the Atoms in $[NEt_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$

	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	-.14183(12)[b]	0[c]	.19343(9)	100.5(14)	41.3(7)	40.6(7)	.7(15)	22.6(7)	-.7(10)
O_1	-.1513(30)	.1311(11)	.2224(25)	8.2(4)[d]					
O_2	-.2105(17)	.2029(10)	.2373(16)	7.6(4)[d]					
O_1'[e]	-.1802	.1240	.2285	8.2[d]					
O_2'[e]	-.1506	.2080	.2506	7.6[d]					
C_1	.6976(10)	.0036(14)	.0855(8)	110(12)	67(6)	48(6)	5(16)	16(8)	13(11)
C_2	.0203(11)	-.0083(13)	.3024(8)	106(12)	53(8)	47(6)	-7(12)	10(7)	-1(9)
C_3	.8859(10)	.8716(9)	.1640(8)	120(14)	42(8)	42(6)	17(8)	29(7)	-3(6)
C_4	-.0402(11)	.0399(8)	.1132(8)	106(13)	68(8)	37(6)	-4(7)	31(8)	12(5)
C_5	.2446(11)	.4599(8)	-.2790(9)	103(14)	58(7)	55(7)	-9(7)	34(9)	-2(6)
N_1	.6069(10)	.0122(15)	.0188(8)	146(12)	127(11)	70(7)	54(14)	0(8)	-2(11)
N_2	.1108(11)	-.0108(12)	.3672(8)	165(14)	86(9)	73(7)	-1(12)	32(9)	0(10)
N_3	.9053(10)	.7982(9)	.1452(8)	159(15)	57(7)	75(7)	12(8)	38(9)	-13(6)
N_4	.0179(11)	.0549(10)	.0641(9)	163(14)	91(8)	74(8)	-4(9)	40(9)	11(6)
N_5	.3023(12)	.4383(9)	-.3271(10)	160(16)	88(8)	108(9)	4(9)	80(10)	-10(7)
N_6	.3280(9)	.2283(8)	.2519(7)	117(12)	64(7)	49(6)	5(8)	20(7)	-12(6)
N_7	.0229(8)	.1661(7)	-.4196(6)	95(10)	60(6)	39(5)	-3(6)	5(6)	-12(5)
N_8	-.6899(9)	-.2241(8)	.1105(8)	112(11)	72(7)	79(8)	1(7)	44(8)	-20(6)
O_3	.3545(8)	.0133(10)	-.1343(6)	170(10)	111(8)	81(5)	-20(10)	24(6)	-20(8)
O_4	.1553(10)	.1068(7)	-.0749(7)	215(14)	79(7)	87(7)	17(8)	68(8)	10(6)
O_5	-.2985(10)	.3773(7)	.2882(7)	220(15)	94(7)	74(6)	-0(8)	49(8)	-2(6)
O_6	-.3435(9)	.4180(9)	.4706(7)	164(12)	146(10)	91(7)	-2(9)	24(8)	-27(7)
O_7	.3758(15)	.4128(16)	-.5045(12)	301(23)	264(22)	173(14)	-60(18)	75(15)	-124(16)
C_{11}	.4191(20)	.2343(22)	.3526(14)	239(27)	248(31)	97(13)	0(24)	63(17)	-13(17)
C_{12}	.4101(19)	.1349(18)	.4120(14)	257(28)	181(22)	117(13)	-17(20)	63(16)	71(15)
C_{13}	.360(4)	.1528(28)	.1998(17)	784(97)	350(47)	106(17)	422(61)	132(36)	27(23)
C_{14}	.4605(22)	.1236(24)	.1778(19)	255(32)	244(31)	175(23)	125(28)	84(24)	-12(23)
C_{15}	.1762(16)	.2250(14)	.2433(14)	190(23)	124(14)	133(14)	-21(14)	73(15)	-14(13)
C_{16}	.1296(18)	.3123(22)	.2846(14)	224(27)	229(26)	115(16)	8(22)	43(17)	-55(17)
C_{17}	.3585(18)	.3187(21)	.2087(20)	153(22)	168(22)	174(23)	-25(18)	21(19)	30(18)
C_{18}	.2529(22)	.3295(18)	.1005(16)	285(34)	166(22)	111(15)	65(22)	38(20)	64(16)
C_{21}	.0151(15)	.2742(11)	-.4124(9)	244(23)	76(10)	50(8)	-38(12)	38(11)	2(7)
C_{22}	.0338(19)	.3252(12)	-.4991(14)	260(29)	74(12)	90(13)	-20(14)	11(16)	4(10)
C_{23}	-.0849(15)	.1258(12)	.4912(9)	201(21)	81(11)	54(8)	4(12)	1(11)	-21(8)
C_{24}	-.2320(12)	.1531(14)	.4851(14)	100(15)	128(15)	152(15)	-2(12)	25(12)	-27(12)
C_{25}	.1541(13)	.1326(13)	-.4297(11)	156(18)	113(13)	105(11)	20(13)	59(12)	-20(11)
C_{26}	.2789(15)	.1680(17)	-.3495(15)	124(20)	167(19)	142(17)	-24(16)	-6(15)	-28(16)
C_{27}	.0009(13)	.1299(10)	-.3257(9)	191(19)	74(9)	72(9)	-36(11)	34(10)	-13(8)
C_{28}	-.0036(18)	.0245(11)	-.3152(12)	332(29)	70(14)	88(10)	-41(14)	15(14)	1(9)
C_{31}	-.358(3)	.1745(20)	-.1681(21)	557(77)	116(20)	173(26)	-61(30)	200(41)	-43(19)
C_{32}	-.2448(24)	.1199(16)	-.1813(19)	415(43)	109(14)	199(24)	78(20)	169(29)	-20(16)
C_{33}	-.2523(22)	.3359(19)	-.1760(19)	292(33)	157(20)	186(23)	-20(20)	155(25)	43(18)
C_{34}	-.3353(20)	.3459(20)	-.2868(15)	253(31)	213(24)	94(15)	-1(22)	-37(17)	86(17)
C_{35}	-.2021(23)	.2611(17)	-.0112(17)	310(35)	134(19)	152(19)	45(23)	65(23)	47(18)
C_{36}	-.1535(26)	.3480(17)	.0466(16)	419(46)	108(17)	103(15)	-69(22)	-8(20)	-34(13)
C_{37}	-.4375(16)	.3237(15)	-.1012(17)	150(21)	133(15)	184(20)	44(14)	87(18)	33(15)
C_{38}	-.5040(19)	.2761(15)	-.0396(19)	235(24)	137(17)	274(28)	41(18)	218(24)	48(17)

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[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)]$.

[b] Standard deviations of the least significant figures are given here and elsewhere in parentheses.

[c] The y parameter of the Co atom is fixed at 0 to define the origin.

[d] Isotropic thermal parameter, Å^2 (x 1).

[e] Positional and thermal parameters determined by the "two-fold" disorder model.

of C_1 through C_5 is 0.97 (5) while O_x refines to 1.44 (6). In the second refinement, C_1 through C_5 averages 0.61 (4) while O_x refines to an occupancy of 1.03 (5). The result for the second atom of the ligands is not as striking as that for the atom adjacent to the cobalt. This is not unexpected since N and O are more likely alike in their scattering properties than C and O. Also, the "twofold" disorder in the oxygen ligand is much more pronounced in the second oxygen and contributes to the diffuseness of the electron density. Taken as a whole, however, these refinements clearly indicate that the dioxygen and cyanide ligands are not disordered with one another.

The twofold disorder model that is used to describe the orientation of the dioxygen ligand in the $[Co(CN)_5(O_2)]^{3-}$ anion can be compared to the model used by Ibers and coworkers.[30,31]

The highly anisotropic thermal motion of the apparently linear dioxygen ligand[14] suggests the possibility of a twofold disorder of two O_2 groups about the linear $Co–O_x–O_y$ axis (where O_x and O_y are the anisotropic "atoms" refined previously). The X-ray diffraction data alone cannot unam-

Table III. Positional and Thermal Parameters of Hydrogen Atoms

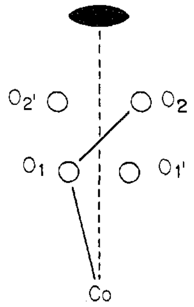
Atom	x	y	z	B, Å
H_1	0.392	0.288	0.383	20
H_2	0.508	0.246	0.351	25
H_3	0.293	0.158	0.134	21
H_4	−0.075	0.058	0.494	19
H_5	−0.084	0.155	−0.323	6
H_6	0.071	0.155	−0.271	8
H_7	0.165	0.812	0.170	16
H_8	0.238	0.900	0.146	25
H_9	−0.328	0.424	0.237	11
H_{10}[a]	0.233	0.395	0.086	23[b]
H_{11}	0.287	0.303	0.052	23
H_{12}	0.168	0.298	0.095	23
H_{13}	−0.048	0.329	−0.557	15
H_{14}	0.060	0.390	−0.482	15
H_{15}	0.100	0.292	−0.516	15
H_{16}	−0.246	0.172	0.547	19
H_{17}	−0.302	0.202	0.438	19
H_{18}	−0.242	0.101	0.465	19
H_{19}	0.265	0.164	−0.288	23
H_{20}	0.364	0.132	−0.342	23
H_{21}	0.291	0.230	−0.366	23
H_{22}	0.075	0.017	−0.267	18
H_{23}	−0.078	−0.007	−0.297	18
H_{24}	−0.006	−0.005	−0.376	18

[a] The parameters of this and following hydrogens were determined by group refinement of methyl hydrogens. [b] This value and following ones are group thermal parameters.

biguously distinguish between the model previously reported[14] and that given here. Although the increase in R_2 (7.3 to 7.6%) is somewhat larger than statistically predicted from the decrease in the number of variables, we prefer the disorder model reported here for the following reasons. (1) It explains the anomalously high thermal motion of the oxygen atoms. (2) The derived standard deviations of the oxygen atoms are much smaller in the disordered model (even though no constraints are applied to the positional parameters for an individual O_2 group). (3) The resultant Co–O–O bond lengths and angle are more consistent with chemical experience and expectation.

The standard deviations for the derived parameters do, of course, *assume the correctness of the model described.*

The twofold axis was defined by a vector from the Co position to the position of O_y. The positional and isotropic thermal parameters x, y, z, and B were refined for atoms O_1 and O_2. A least-squares constraint was imposed[32] to generate the twofold-related positions of $O_{1'}$ and $O_{2'}$ with the same thermal motion as O_1 and O_2, respectively:



In the final least-squares refinement, the parameters of O_1 and O_2 did not shift more than 50% of their calculated standard deviations. The calculated distance between O_1 and $O_{1'}$ is 0.35 Å, and that for O_2 and $O_{2'}$ is 0.59 Å. The computational details of the disorder model are presented in ref 28.

Description of the Structure

The stereoscopic crystal packing diagram in Figure 1 shows the structure to consist of discrete $[Co(CN)_5(O_2)]^{3-}$ anions, $[NEt_4]^+$ cations, and water molecules of crystallization. This figure and the thermal parameters in Table IV show the large apparent thermal motion of the Et_4N^+ cations.[33] This is a common phenomenon for tetraalkylammonium salts as no attempt was made to resolve this disorder–thermal portion of the structure since it has little or no effect on the structure of the $[Co(CN)_5(O_2)]^{3-}$ anion. The $[Co(CN)_5(O_2)]^{3-}$ anion, shown in Figure 2, has an octahedral geometry with a nonlinear σ-bonded dioxygen ligand. The dioxygen exhibits a

Table IV. Root-Mean-Square Amplitudes of Vibration along Principal Axes (Å × 10^3)

Atom[a]	Axis 1	Axis 2	Axis 3	Atom	Axis 1	Axis 2	Axis 3
Co	192.7(19)	204.4(19)	223.4(16)	C_{14}	256(23)	407(27)	547(34)
C_1	197(22)	241(13)	272(20)	C_{15}	283(18)	334(22)	378(21)
C_2	201(17)	229(19)	252(15)	C_{16}	296(24)	334(20)	505(29)
C_3	172(18)	208(16)	257(15)	C_{17}	269(20)	373(27)	464(29)
C_4	157(18)	231(14)	271(15)	C_{18}	247(25)	387(21)	461(29)
C_5	202(18)	229(15)	251(14)	C_{21}	210(18)	255(18)	370(17)
N_1	213(18)	285(16)	394(19)	C_{22}	267(21)	281(22)	396(19)
N_2	263(12)	289(12)	294(16)	C_{23}	197(20)	290(18)	353(18)
N_3	210(17)	276(14)	291(13)	C_{24}	223(17)	332(20)	414(21)
N_4	248(14)	284(13)	311(13)	C_{25}	233(18)	312(18)	360(20)
N_5	219(16)	299(14)	338(14)	C_{26}	227(22)	387(22)	433(26)
N_6	199(15)	238(13)	272(14)	C_{27}	230(17)	272(16)	335(16)
N_7	171(14)	232(12)	260(12)	C_{28}	249(24)	284(17)	442(18)
N_8	204(14)	248(13)	306(13)	C_{31}	294(27)	343(29)	552(39)
O_3	252(12)	308(8)	349(14)	C_{32}	223(24)	414(25)	495(27)
O_4	257(10)	274(12)	341(12)	C_{33}	237(22)	409(24)	465(28)
O_5	256(11)	308(12)	330(11)	C_{34}	186(26)	394(24)	530(29)
O_6	268(12)	303(11)	398(14)	C_{35}	300(24)	394(21)	435(32)
O_7	288(16)	386(15)	589(24)	C_{36}	230(26)	367(25)	513(27)
C_{11}	288(18)	345(21)	501(32)	C_{37}	232(20)	347(22)	439(24)
C_{12}	241(23)	357(20)	480(27)	C_{38}	176(23)	350(23)	543(26)
C_{13}	218(32)	324(27)	824(49)				

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[a] The isotropic oxygen atoms are not included.

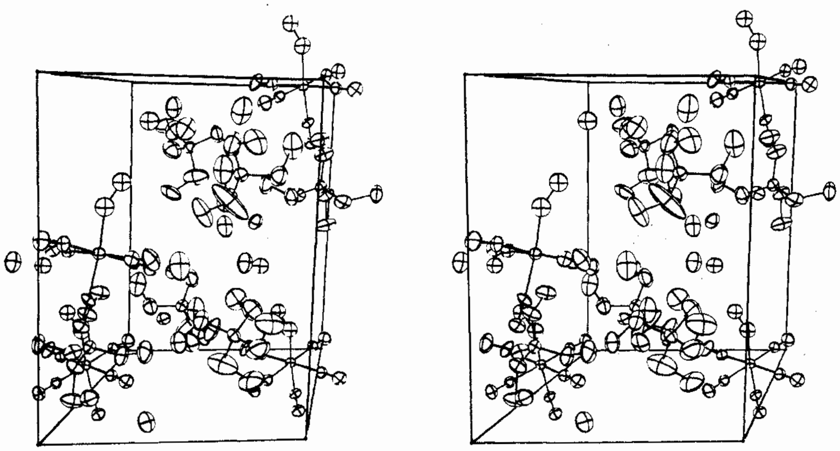

Figure 1. Stereoscopic view of the packing and unit cell contents of $[NEt_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$. The vertical axis is *b*, and the horizontal axis is *a*. The origin is the left rear lower corner of the cell. The shapes of the atoms represent 30% probability contours of the thermal motion.

Table V. Occupancy Refinements for the Ligand Atoms of the $[Co(CN)_5(O_2)]^{3-}$ Complex

	Refinement 1[a]		Refinement 2[b]	
Ligand	Atom 1[c]	Atom 2	Atom 1	Atom 2
C_1N_1	1.08 (5)	1.01 (4)	0.69 (3)	0.84 (4)
C_2N_2	0.98 (5)	0.92 (4)	0.60 (3)	0.80 (4)
C_3N_3	0.82 (5)	1.04 (4)	0.50 (3)	0.90 (4)
C_4N_4	0.99 (5)	1.06 (4)	0.64 (3)	0.89 (4)
C_5N_5	0.97 (5)	1.14 (5)	0.61 (4)	0.98 (4)
Av CN	0.97 (5)	1.03 (4)	0.61 (4)	0.88 (4)
O_xO_y	1.44 (6)	0.87 (5)	1.03 (5)	0.71 (5)

[a] All ligands refined as C–N. [b] All ligands refined as O–O.
[c] Atom 1 is the atom adjacent to the Co; atom 2 is the atom from the Co.

Table VI. Bond Distances in $[NEt_4][Co(CN)_5(O_2)]\cdot 5H_2O$

Atoms	Distance, Å	Atoms	Distance, Å
Co–O_1	1.904 (14)	N_6–C_{11}	1.46 (2)
Co–C_1	1.888 (11)	N_6–C_{13}	1.40 (3)
Co–C_2	1.909 (12)	N_6–C_{15}	1.55 (2)
Co–C_3	1.903 (12)	N_6–C_{17}	1.50 (3)
Co–C_4	1.887 (11)	C_{11}–C_{12}	1.66 (3)
Co–C_5	1.957 (12)	C_{13}–C_{14}	1.26 (3)
		C_{15}–C_{16}	1.51 (3)
O_1–O_2	1.240 (17)	C_{17}–C_{18}	1.60 (3)
C_1–N_1	1.119 (12)		
C_2–N_2	1.096 (12)	N_7–C_{21}	1.53 (2)
C_3–N_3	1.105 (13)	N_7–C_{23}	1.52 (2)
C_4–N_4	1.089 (12)	N_7–C_{25}	1.50 (2)
C_5–N_5	1.096 (13)	N_7–C_{27}	1.53 (2)
		C_{21}–C_{22}	1.51 (2)
O_3–N_1	2.844 (13)	C_{23}–C_{24}	1.56 (2)
O_3–O_4	2.817 (13)	C_{25}–C_{26}	1.52 (2)
O_3–O_5	2.846 (14)	C_{27}–C_{28}	1.50 (2)
O_4–N_3	2.881 (16)		
O_4–N_4	2.904 (15)	N_8–C_{31}	1.65 (3)
O_5–O_6	2.869 (13)	N_8–C_{33}	1.53 (2)
O_5–O_2	2.805 (17)	N_8–C_{35}	1.53 (3)
O_5–O_2'	2.977 (17)	N_8–C_{37}	1.54 (2)
O_6–N_2	2.956 (16)	C_{31}–C_{32}	1.48 (3)
O_6–O_7	3.066 (17)	C_{33}–C_{34}	1.56 (3)
O_7–N_5	2.914 (19)	C_{35}–C_{36}	1.48 (3)
		C_{37}–C_{38}	1.45 (3)

twofold disorder about an axis perpendicular to the plane of the four equatorial cyanides. The Co–O_1 and O_1–O_2 distances are 1.906 (14) and 1.240 (17) Å, respectively. The Co–C and C–N distances average 1.92 (1) and 1.10 (2) Å, respectively. These bond distances and others are listed in Table VI. The Co–O_1–O_2 angle is 153.4 (21)°. The Co–C–N angles are all virtually linear. Table VII summarizes the bond angles in the structure.

The five water molecules of crystallization are within hydrogen-bonding distance of O_2, of the five cyanide nitrogen atoms, and of each other forming an interconnected network about the $[Co(CN)_5(O_2)]^{3-}$ anion (see Figure 1). The water oxygen O_3 is linked to O_4 and O_5; O_5 is linked to O_6, and O_6 to O_7. Except for O_7 which is hydrogen bonded to N_5 and O_6, all of the water molecules are linked to either two other waters and a cyanide or two cyanides and one other water (these distances are summarized in Table VI).

The three tetraethylammonium cations are all ordered with the expected tetrahedral geometry about each of the nitrogen atoms. None are in the vicinity of the water molecules. The cations of N_6 (cation 1) and N_8 (cation 3) exhibit much higher thermal motion in the carbon atoms than did those for N_7

Table VII. Bond Angles in $[NEt_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$

Atoms	Angle, deg	Atoms	Angle, deg
C_1-Co-C_2	178.1 (9)	N_6-C_{11}-C_{12}	109.6 (19)
C_1-Co-C_3	90.1 (7)	N_6-C_{13}-C_{14}	138 (4)
C_1-Co-C_4	90.8 (4)	N_6-C_{15}-C_{16}	113.2 (15)
C_1-Co-C_5	90.2 (5)	N_6-C_{17}-C_{18}	108.2 (16)
C_1-Co-O_1	93.4 (11)		
C_2-Co-C_3	88.1 (6)	C_{21}-N_7-C_{23}	112.8 (10)
C_2-Co-C_4	89.8 (4)	C_{21}-N_7-C_{25}	113.0 (10)
C_2-Co-C_5	89.2 (5)	C_{21}-N_7-C_{27}	104.2 (9)
C_2-Co-O_1	88.5 (11)	C_{23}-N_7-C_{25}	104.7 (10)
C_3-Co-C_4	89.6 (5)	C_{23}-N_7-C_{27}	109.9 (9)
C_3-Co-C_5	91.1 (5)	C_{25}-N_7-C_{27}	112.4 (10)
C_3-Co-O_1	174.1 (9)	N_7-C_{21}-C_{22}	113.3 (11)
C_4-Co-C_5	178.8 (5)	N_7-C_{23}-C_{24}	114.0 (11)
C_4-Co-O_1	85.6 (9)	N_7-C_{25}-C_{26}	114.3 (12)
C_5-Co-O_1	93.7 (10)	N_7-C_{27}-C_{28}	116.1 (12)
Co-O_1-O_2	153.4 (21)	C_{31}-N_8-C_{33}	106.8 (15)
Co-C_1-N_1	174.1 (17)	C_{31}-N_8-C_{35}	111.6 (16)
Co-C_2-N_2	177.0 (13)	C_{31}-N_8-C_{37}	106.9 (15)
Co-C_3-N_3	177.3 (11)	C_{33}-N_8-C_{35}	109.5 (14)
Co-C_4-N_4	173.7 (11)	C_{33}-N_8-C_{37}	109.5 (13)
Co-C_5-N_5	179.4 (11)	C_{35}-N_8-C_{37}	112.3 (13)
		N_8-C_{31}-C_{32}	112.8 (21)
C_{11}-N_6-C_{13}	112.6 (16)	N_8-C_{33}-C_{34}	118.8 (18)
C_{11}-N_6-C_{15}	114.0 (11)	N_8-C_{35}-C_{36}	115.6 (17)
C_{11}-N_6-C_{17}	101.8 (15)	N_8-C_{37}-C_{38}	116.5 (15)
C_{13}-N_6-C_{15}	110.2 (22)		
C_{13}-N_6-C_{17}	107.9 (20)		
C_{15}-N_6-C_{17}	109.9 (13)		

Table VIII. Summary of Structural Results for Complexes with a σ-Bonded Dioxygen Ligand

Compd	M–O,[a] Å	O–O, Å	M–O–O, deg	Ref
$[Co(bzacen)(py)(O_2)]$	1.86	1.26 (4)	126 (2)	5
$[Co(salenC_2H_4py)()_2)]$		1.1	136	*b*
$[Co(acacen)(py)(O_2)]$	1.95 (5)		*c*	37
$[Co(t\text{-}Bsalten)(bzImid)(O_2)]$	1.882 (6)	1.257 (10)	118.5 (5)	36
$[Co(CN)_5(O_2)]^{3-}$	1.906 (14)	1.240 (17)	153 (2)	This study
$[Fe(O_2)(N\text{-}Meimid)\text{-}$	1.75 (2)	1.23 (8)[d]	135 (4)[d]	8
$(\alpha,\alpha,\alpha,\alpha\text{-}TpivPP)]$		1.26 (8)	137 (4)	

[a] M is the metal atom. [b] As cited in ref 8. [c] Reported only to have a "bent" Co–O_2 group. [d] There are two crystallographically independent disordered O_2 molecules in this structure.

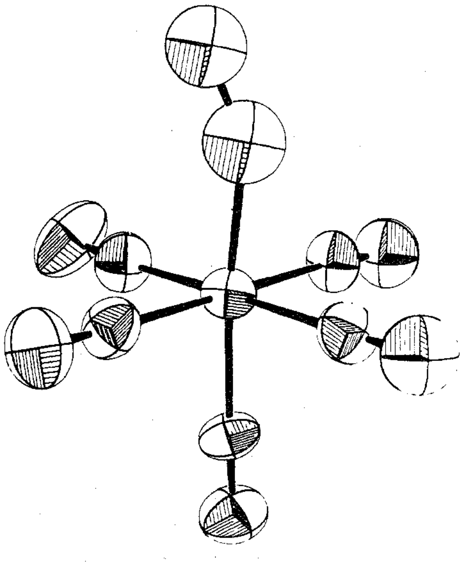

Figure 2. Perspective view of the dioxygen adduct complex, $[Co(CN)_5(O_2)]^{3-}$. For clarity, only one of the twofold disordered dioxygen ligands is shown (the uppermost vertical ligand). The atoms are drawn at the 50% probability contour.

(cation 2). This observation is also evident in the agreement within cation 2 with the expected N–C and C–C bond lengths of 1.48 and 1.54 Å, respectively.[34] The various bond angles for the atoms in the cations are listed in Table VII.

Discussion

All of the Co–O_2 adducts reported to date have been of limited precision due to either poor crystal quality or unresolved disorder problems.[35] However, the present structural results clearly confirm the bent σ-bonded nature of the Co–O_2 adduct and also establish the detailed bond lengths and angles. The σ-bonded nature of the Co–O_2 adducts was originally proposed by Hoffman et al. from ESR studies.[38] The ESR spectra of $[Co(acacen)(py)(O_2)]$[38] and $[Co(CN)_5(O_2)]^{3-}$ [11,13,39] have all been interpreted as cobalt(III) complexes of the superoxide anion. This is also supported by ESCA studies of $[Co(bzacen)(py)(O_2)]$ which concluded that the cobalt was in the +3 oxidation state.[40]

Reports that the O_2 of oxygen adducts of cobalt(II) complexes contain π-bonded oxygen[41] or neutral O_2 in the $^1\Delta$ ground state[42] can be rejected as due to problems in data interpretation and synthetic experimental errors, respectively.[43] The available structural information summarized in Table VIII clearly supports the formulation of the cobalt compounds as superoxide complexes of cobalt(III). The ideal superoxide bond length of 1.28 Å[44] is substantially that found in the most accurate structures, since corrections for thermal motion will increase slightly each of the reported O–O distances. The greater Co–O–O angle found in the $[Co(CN)_5(O_2)]^{3-}$ anion as compared with the neutral Schiff base adducts can be ascribed to a weak Co–O–O angle bending force constant in these compounds and the interaction of the negative charge of the terminal oxygen atom with the four adjacent cyanide anions in the $[Co(CN)_5(O_2)]^{3-}$ complex. In contrast, the terminal oxygens in the neutral Schiff base adducts have adjacent ligand atoms which are either neutral or slightly positively charged.

In conclusion, from the structural results of the $[Co(CN)_5(O_2)]^{3-}$ anion and the other compounds in Table VIII, it can be inferred that dioxygen binds to all such Fe(II) and Co(II) complexes, including the related biological oxygen transport and storage compounds, through only one oxygen atom.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation through Grants GP-29764, GP-36977A, and GP-10510.

Registry No. $[N(C_2H_5)_4]_3[Co(CN)_5(O_2)]\cdot 5H_2O$, 56247-13-3; $[NEt_4]_3[Co(CN)_5(O_2)]\cdot DMF$, 56247-14-4; $[NEt_4]_3[Co(CN)_5(O_2)]\cdot 3H_2O$, 56247-15-5; $[NEt_3Bz]_3[Co(CN)_5(O_2)]\cdot {}^1/_2DMF$, 56247-17-7; $[NBz_2Me_2]_3[Co(CN)_5(O_2)]$, 56247-18-8.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50223S-11-75.

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(6) Abbreviations for compounds in this paper: Co(bzacen), *N,N'*-ethylenebis(benzoylacetone iminato)cobalt(II); py, pyridine; Co(salenC₂H₄py), α,α'-[2-(2'-pyridyl)ethyl]ethylenebis(salicylideniminato)cobalt(II); Fe(α,α,α,α-TpivPP), *meso*-tetrakis(α,α,α,α-*o*-pivalamidophenyl)porphinatoiron(II); Co(salen), *N,N'*-ethylenebis(salicylideniminato)cobalt(II); Co(t-Bsalten), *N,N'*-(1,1,2,2-tetramethyl)ethylenebis(3-*tert*-butylsalicylideniminato)cobalt(II); Co(acacen), *N',N'*-ethylenebis(acetylacetone iminato)cobalt(II); *N*-MeImid, *N*-methylimidazole; bzImid, 1-benzylimidazole.

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a function and error program by Busing and Levy; Johnson's ORTEP, a thermal ellipsoid plot program; FAME, a structure factor normalization program by Dewar; MULTAN, a direct-methods program by Main, Woolfson, and Germain.

(17) The data crystal was a red-brown regular parallelepiped with dimensions 0.02 × 0.02 × 0.03 cm. The crystal was mounted in a thin-walled glass capillary with the b axis nearly parallel to the ϕ axis of the diffractometer. The unit cell constants and crystal orientation were determined by a least-squares refinement using the setting angles for nine carefully centered reflections. The crystal gave ω scan widths at half-height of 0.10° for several low-angle reflections. The data were collected in the θ–2θ scan mode with a scan rate of 2°/min from 0.70° below the $K\alpha_1$ peak to 0.70° above the $K\alpha_1$ peak. Stationary-crystal, stationary-counter background counts of 4 sec each were taken at the start and end of each scan. Intensity data for the unique form $\pm h,+k,+l$ were collected to a 2θ angle of 52°, above which there were no significant intensity data. A symmetry-equivalent form $\pm h,k,-l$ was collected to 40°. The mirror-related form, $\pm h,-k,l$ was also collected out to $2\theta = 45°$. During the data collection the intensities of the 201, 060, and $01\bar{6}$ reflections were measured as standards after every 60 reflections. The standards showed a variation of about 10% throughout the experiment. The F^2 values from the intensity data were corrected for this fluctuation in the standards as described in ref 18. Copper foil attenuators were automatically inserted if the counting rate approached 10^4 counts/sec. The takeoff angle for X-ray tube was 2° and the Bragg 2θ angle for the graphite monochromator was 12.16°. The detector was located 32 cm from the source and had a 7 × 7 mm receiving aperture. The pulse height analyzer was set to a 95% window centered on the Mo $K\alpha$ peak.

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(20) In all refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting factor, w, is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for the nonhydrogen atoms were taken from the tabulations of Cromer and Mann.[21] Hydrogen scattering factor values were those calculated by Stewart, Davidson, and Simpson.[22] Corrections for anomalous dispersion effects for Co were made using the $\Delta f'$ and $\Delta f''$ values of Cromer.[23]

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Reaction of Diethylamine with Mercaptide-Bridged Binuclear Cobalt(III) and Iron(III) Thioxanthate Complexes. Crystal Structure of $Co_2(SC_2H_5)_2(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_3$[1]

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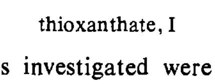
Received March 10, 1975

AIC50178O

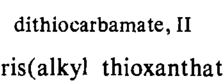
The ethyl mercaptide bridged dimers $Co_2(SC_2H_5)_2(S_2CSC_2H_5)_n[S_2CN(C_2H_5)_2]_{4-n}$, $n = 1$–3, and the mononuclear complex $Co(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_2$ have been synthesized by allowing diethylamine to react with $[Co(SC_2H_5)(S_2CSC_2H_5)_2]_2$. Proton NMR, electronic, and infrared spectral data are reported for these compounds, and an interesting proton NMR solvent effect is examined. The chromatographic procedure for product separations also yielded $Co[S_2CN(C_2H_5)_2]_3$ and other unstable materials. The same reaction performed with $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ led only to the formation of $Fe[S_2CN(C_2H_5)_2]_3$ in tetrahydrofuran and $FeCl[S_2CN(C_2H_5)_2]_2$ in chloroform. The molecular structure of the complex $Co_2(SC_2H_5)_2(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_3$, determined in a single crystal X-ray diffraction study, contains the mercaptide-bridged binuclear $Co_2(SC_2H_5)_2$ core. Its geometry closely resembles that reported earlier for $[Co(SC_2H_5)(S_2CSC_2H_5)_2]_2$. The nonbonded Co···Co distance is 3.350 (4) Å, and the average Co–S bond lengths are 2.251 (3) Å to the bridging ethyl mercaptide ligands, 2.268 (3) Å to the equatorial 1,1-dithiolate sulfur atoms in the plane of the Co_2S_2 rhombus, and 2.290 (3) Å to the out-of-plane, axial sulfur atoms. The thioxanthate ligand is equally disordered among the four terminal 1,1-dithiolate coordination sites. The molecule crystallizes in the triclinic space group $P\bar{1}$ with lattice constants $a = 8.150$ (7) Å, $b = 10.352$ (7) Å, $c = 13.613$ (11) Å, $\alpha = 68.60$ (2)°, $\beta = 79.11$ (2)°, and $\gamma = 109.90$ (3)°, with $Z = 1$. Full-matrix refinement converged at $R_1 = 0.050$.

Introduction

Previous reports from this laboratory[2-6] have described the synthesis and characterization of iron(III) and cobalt(III) complexes of the thioxanthate ligand, I. Among the compounds investigated were the tris(alkyl thioxanthates) of cobalt(III). These complexes undergo carbon disulfide elimination reactions[4] to form the mercaptide-bridged dimers $[Co(SR)(S_2CSR)_2]_2$, eq 1. In the iron(III) system, only



thioxanthate, I



dithiocarbamate, II

$$2Co(S_2CSR)_3 \rightarrow [Co(SR)(S_2CSR)_2]_2 + 2CS_2 \qquad (1)$$

mononuclear tris(*tert*-butyl thioxanthato)iron(III) was isolated, the other alkyl thioxanthates forming $[Fe(SR)(S_2CSR)_2]_2$ under the conditions of the reaction.[2,3,7] The physical properties of these complexes have been extensively investigated and the crystal structures of $(t\text{-}C_4H_9SCS_2)_3Fe$,[5] $(C_2H_5SCS_2)_3Co$,[6] $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$,[3] and