

## The Dioxygen Ligand as a Bridging Group. Structure of Potassium Decacyano- $\mu$ -superoxo-dicobaltate(III) Monohydrate

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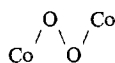
The structure of the superoxo-bridged binuclear anion  $[(\text{CN})_5\text{CoO}_2\text{Co}(\text{CN})_5]^{5-}$  has been determined. A comparison of the bond distances and angles of this ion with those previously obtained for the corresponding peroxocyno complex and the peroxo- and superoxoammine complexes has led to a better understanding of the bonding within the bridging dioxygen group and its bonding to cobalt. Crystals of the compound  $\text{K}_5[\text{Co}_2\text{O}_2(\text{CN})_{10}]\cdot\text{H}_2\text{O}$  were used in a three-dimensional single-crystal X-ray diffraction study. They are triclinic with unit cell parameters  $a = 11.707(9) \text{ \AA}$ ,  $b = 19.423(15) \text{ \AA}$ ,  $c = 7.664(7) \text{ \AA}$ ,  $\alpha = 93.92(7)^\circ$ ,  $\beta = 110.36(8)^\circ$ , and  $\gamma = 94.71(8)^\circ$ ; the space group is  $P\bar{1}$  with the rather uncommon number of three formula units per cell. Least-squares refinement using 3399 intensity data measured by a computer-controlled diffractometer led to an  $R$  index of 0.065. The two independent binuclear anions in this structure, one centrosymmetric and the other noncentrosymmetric, both have the bridging superoxo ligand bonded in the "staggered" arrangement; however, the centrosymmetric Co-O-O-Co group is planar by crystallographic symmetry, while the acentric Co-O-O-Co group shows a torsion angle of  $166^\circ$ . The average O-O distance is  $1.26 \text{ \AA}$ , typical of a superoxide grouping, and the Co-O distances average  $1.94 \text{ \AA}$ . The relative conformations of the pentacyanocobalt groups within the binuclear ions differ, the centric ion having eclipsed cyanide ligands and the acentric ion having staggered cyanide ligands. The equatorial Co-C distances average  $1.88 \text{ \AA}$ , and the axial Co-C distances average  $1.84 \text{ \AA}$ . There is substitutional disorder involving one  $\text{K}^+$  ion and one water molecule.

### Introduction

The 2:1 (two cobalt atoms to one  $\text{O}_2$  group) dioxygen complexes of cobalt have been known since 1852, when Fremy<sup>1</sup> isolated a  $\mu$ -peroxo-dicobalt(III) salt from oxygenated ammoniacal cobalt(II) solutions and correctly formulated it as such. Several investigators, notably Werner<sup>2,3</sup> and his students, contributed to the understanding of these compounds in the late nineteenth and early twentieth centuries, using the singly bridged peroxo complexes as intermediates in the synthesis of a wealth of binuclear cobalt complexes containing up to three bridging ligands of various types. The nature of the dioxygen bridge was not well understood until recent years; however, it was recognized by Werner that the complexes fell into two distinct classes, which he termed the peroxocobalt(III,IV) and the peroxocobalt(III,III) types. The (III,IV) description implied nonequivalent cobalt atoms, and later investigators avoided the problem of assigning formal oxidation states to the individual cobalt atoms by reference to magnetic properties. The (III,III) ions became known as "diamagnetic peroxo," and the (III,IV), as "paramagnetic peroxo."

Characterization of the cobalt-dioxygen bonding mode has been a subject of renewed interest in recent years as a model for dioxygen-binding proteins, especially hemoglobin and myoglobin. An X-ray structure determination of the oxygenated form of myoglobin<sup>4</sup> has failed to elucidate the bonding geometry of the dioxygen, although the environment of the binding site was well determined; nor has electronic spectroscopy been of much value for resolution of this problem, since intense transitions due to the porphyrin system obscure the more interesting bands involving the metal and oxygen atoms. Thus, studies of model compounds continue to be useful.

Recently, the paramagnetic "peroxo" complexes have been characterized by esr<sup>5,6</sup> and X-ray structural<sup>7,8</sup> data as Co(III,III) *superoxo* compounds having equivalent cobalt atoms and with the unpaired electron residing primarily on the  $\text{O}_2$  group. In ammine compounds the superoxo bridge, as well as the peroxo bridge in diamagnetic species, has been shown to be staggered, *i.e.*



In the important cyano compounds, the peroxo ion has been

shown to adopt the same bridging configuration;<sup>9</sup> however, no structural information has yet been available for the superoxo complex.

The title compound was first reported in 1961 by Haim and Wilmarth,<sup>10</sup> who characterized the anion as a binuclear, peroxo-bridged Co(III,IV) species. The preparation was accomplished by a one-electron oxidation, using a variety of oxidants, of the  $[(\text{CN})_5\text{CoO}_2\text{Co}(\text{CN})_5]^{6-}$  ion, which was formed by air oxidation of  $\text{Co}(\text{CN})_5^{3-}$  ion. The potassium salt was thought by them to be the pentahydrate. The compound has recently been prepared in a more easily purified form through replacement of ammonia ligands by cyanide ions in the preformed  $\mu$ -superoxo-decaammine(5+) ion.<sup>6</sup> In that study, the potassium salt was believed to be the monohydrate. ESR results showed the ion to have a  $^{59}\text{Co}$  hyperfine structure and  $g$  value very similar to that of the decaammine, indicating that the cobalt-superoxo bonding is very similar in the two ions, with the unpaired electron perhaps more localized on the bridge in the decacyanide. While the magnetic and spectral evidence suggests that the  $\mu$ -superoxo-decacyanide has the same "staggered" configuration as has been established for the  $\mu$ -superoxo- and  $\mu$ -peroxo-decaammines, one might suspect that the  $\pi$ -bonding nature of the cyanide ligands would make the percyano system more prone to forming a symmetric,  $\pi$ -bonded structure with the dioxygen ligand perpendicular to the Co-Co axis, as was once proposed for the decaammines<sup>11,12</sup> and as has been demonstrated to occur in some 1:1 complexes of dioxygen with Co, Ir, Rh, and Pt.<sup>13</sup> In order to establish the configurations of these cyano complexes, we have carried out crystal structure studies of potassium salts of the paramagnetic species  $[(\text{CN})_5\text{CoO}_2\text{Co}(\text{CN})_5]^{5-}$  and the diamagnetic species  $[(\text{CN})_5\text{CoO}_2\text{Co}(\text{CN})_5]^{6-}$ . In the diamagnetic compound, we found<sup>9</sup> the Co-O-O-Co grouping to have the staggered configuration typical of the other peroxo compounds; we report here the structure of the paramagnetic superoxo compound.

### Experimental Section

The zinc salt of the  $[(\text{CN})_5\text{CoO}_2\text{Co}(\text{CN})_5]^{5-}$  ion was prepared from  $[\text{Co}_2\text{O}_2(\text{NH}_3)_{10}](\text{SO}_4)(\text{HSO}_4)_3$  by the method of Mori, Weil, and Kinnaird.<sup>6</sup> Using this salt as the starting material, attempts were made to crystallize the ion with a variety of cations, including  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $(\text{C}_4\text{H}_9)_4\text{N}^+$ , and  $\text{Co}_2\text{O}_2(\text{NH}_3)_{10}^{5+}$ . All these attempts yielded powders or intractable oils except for  $\text{K}^+$ , which,

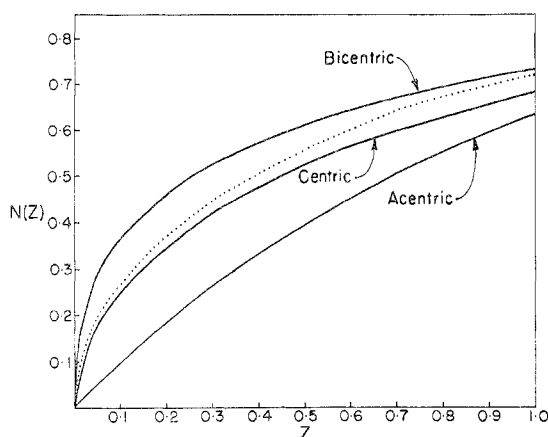


Figure 1. Howells, Phillips, and Rogers<sup>14</sup> zero-moment plots of the experimental data and theoretical curves for the first three hyper-symmetric distributions. The bicentric distribution, as tabulated by Rogers and Wilson,<sup>15</sup> arises from a noncrystallographically centrosymmetric motif in a centric space group.

with difficulty, could be made to form rather poor single crystals magenta in color. The  $K^+$  salt was coerced to crystallize from aqueous solution by addition of a 1:1 mixture of methanol and ethanol at  $0^\circ$  followed by slow cooling to  $-15^\circ$ ; however, the tendency to oil or to form small, scaly, dendritic crystals was pronounced. Large single crystals which sometimes grew could not successfully be retrieved from the mother liquor without disintegration; however, thin bladelike crystals could be removed intact. While the blades were rather small and hideously shaped for the purposes of X-ray diffraction, they yielded clean diffraction patterns, and the structure was determined using them.

Preliminary Weissenberg photography indicated a triclinic crystal system, and a density determination by flotation in a  $CCl_4$ - $CHBr_3$  mixture established the number of formula units in the cell as three. Three is a rather unusual number of formula units, especially for this particular formula. It requires for space group  $P\bar{1}$  that at least one binuclear ion, one  $K^+$  ion, and one water molecule lie on centers of symmetry. Since water molecules are inherently acentric, a completely ordered structure in the centric space group is impossible. Statistical tests on the intensity data (Figure 1), however, suggested the centric space group, and eventual successful refinement confirmed its appropriateness.

A crystal of approximate dimensions  $0.55 \times 0.03 \times 0.09$  mm was placed in a capillary for protection from atmospheric humidity (the compound is somewhat deliquescent) and mounted with its long axis,  $[001]$ , nearly coincident with the  $\phi$  axis of a Datex-automated General Electric quarter-circle diffractometer. Unit cell dimensions were determined from  $2\theta$  values measured for 18 reflections using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda$  0.71069 Å). A Delaunay reduction procedure<sup>16</sup> exposed no higher symmetry. Dimensions of the Delaunay reduced cell and other crystal data are summarized in Table I.

Intensity data were measured by  $\theta$ - $2\theta$  scans using Mo  $K\alpha$  radiation and a proportional counter. The X-ray beam was collimated to 1 mm, and the takeoff angle was  $3^\circ$ . Scans were made at a constant rate of  $1^\circ \text{ min}^{-1}$ , and backgrounds were counted for 30 sec at each extreme of the scan. Scan widths varied linearly with  $2\theta$ , having values of  $1.6^\circ$  at  $2\theta = 6^\circ$  and  $2.0^\circ$  at  $2\theta = 29^\circ$ , centered on the weighted mean of the  $\alpha_1$  and  $\alpha_2$  peaks. Five standard reflections were remeasured every 100 reflections. All reflections in one hemisphere with  $4^\circ \leq 2\theta \leq 43^\circ$  were measured at least once, and many weak reflections were remeasured. Of 3399 independent reflections within the hemisphere, 286 (about 8.4% of the total) had measured intensities less than zero. The intensities of the standard reflections declined by about 3% during the 250 hr of measurement, and the data were rescaled to correct for this decline. Lorentz and polarization effects were corrected. For the purposes of absorption corrections, the crystal, which exhibited no faces, edges, or otherwise regular shape, was approximated by a rectangular prism, and the method of gaussian quadrature<sup>17</sup> was applied. No correction was made for absorption due to the capillary. Maximum and minimum transmission coefficients are about 0.94 and 0.81. Observational variances  $\sigma^2(F_o^2)$  were

Table I. Crystal Data

Formula	$K_2[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$
Formula weight	623.6
Space Group	$P\bar{1}, C_1^1$
Z	3
a	11.707 (9) Å
b	19.423 (15) Å
c	7.664 (7) Å
$\alpha$	$93.92 (7)^\circ$
$\beta$	$110.36 (8)^\circ$
$\gamma$	$94.71 (8)^\circ$
V	$1620 (4) \text{ \AA}^3$
$\rho_o$	$1.91 (1) \text{ g cm}^{-3}$
$\rho_c$	$1.918 (5) \text{ g cm}^{-3}$
$\lambda(\text{Mo } K\alpha)$	0.71069 Å
$\mu(\text{Mo } K\alpha)$	$25.7 \text{ cm}^{-1}$

obtained from counting statistics, including an additional term  $(0.02S)^2$ , where  $S$  is the scan count, to account for nonstatistical errors.

**Structure Solution and Refinement.** Initially, extensive efforts to solve the structure by Patterson methods were unsuccessful, several apparent solutions proving to be incorrect. We then turned to direct methods. The origin was established by assigning signs to three reflections of appropriate parities having high  $E$  values and being involved in large numbers of  $\Sigma_2$  relationships; in addition, five reflections of parity type  $eee$  with  $E > 1.5$  were assigned positive signs by  $\Sigma_1$  relationships. Expansion of this starting set through  $\Sigma_2$  relationships of probability greater than 0.95 yielded but 21 additional signs. Two additional reflections were given symbolic signs, but only 94 new phases were developed in terms of these signs. However, when a third symbol was introduced, a total of 368 symbolic phases were developed in addition to the 29 absolute phases. The eight  $E$  maps corresponding to all combinations of symbolic signs were calculated; none of these  $E$  maps indicated an obvious structure to us, but all eight showed a very pronounced hypersymmetry, with pseudocenters of symmetry at  $(1/3, 1/6, 1/6)$  and  $(2/3, 1/3, 1/3)$ .

While hypersymmetry had previously been suspected (see Figure 1), its nature had not been known. It was now apparent that all of the origin-fixing reflections, one of the symbolic reflections, and in fact most of the reflections with large  $E$  values fall into the subset  $h - k - l = 3n$ , and that an approximate structure can be described in terms of a subcell with a volume one-third that of the true unit cell. A Patterson map calculated for this subcell (that is, based on the reflections with  $h - k - l = 3n$ ) was readily interpreted in terms of the positions of one cobalt atom and two potassium atoms per asymmetric unit, leading to the locations of all six cobalt atoms and twelve of the fifteen potassium atoms in the real unit cell. This structure was consistent with one of the  $E$  maps that we had calculated earlier; from this map we assigned positions to the three remaining potassium ions, assuming one of them to lie on a center of symmetry  $(0, 0, 1/2)$  as required for an ordered structure.

Ideally, this structure would exhibit a higher degree of hypersymmetry than the bicentric distribution, since it consists of the bicentric arrangement with an additional, parallel motif lying on a center of symmetry and possesses a translational regularity not present in the simple bicentric pattern. The actual data lie below the theoretical curve of the bicentric distribution, because the actual deviations from the ideal structure are large. Only 12 of the 15 potassium ions lie on the hypersymmetric array, the two independent binuclear ions are decidedly nonparallel, and the conformations of the ligands in the two are quite different.

An initial structure factor calculation led to an  $R$  index of 0.45 for the 2210 reflections with  $(\sin^2 \theta)/\lambda^2$  less than 0.19. A Fourier synthesis then revealed the positions of all ligand atoms and of one water in a general position. Structure factors based on this model yielded an  $R$  index of 0.32; however, a difference map indicated that the potassium ion placed at  $(0, 0, 1/2)$  is, in fact, disordered about that center, occupying with equal probability two positions separated by 2.7 Å.

Machine calculations were carried out using the CRYM crystallographic computing system on IBM 370/155 and 370/158 computers. Scattering factors for  $K^+$ , O, C, N, and  $Co^0$ , including the anomalous dispersion correction  $\Delta f'$  for Co and  $K^+$ , were taken from ref 18. The quantity minimized in the least-squares calculations was  $\sum w(F_o^2 - F_c^2)^2$ , where the weights are  $w = 1/\sigma^2(F_o^2)$ . Refinement of the structure utilized two matrices, one containing all

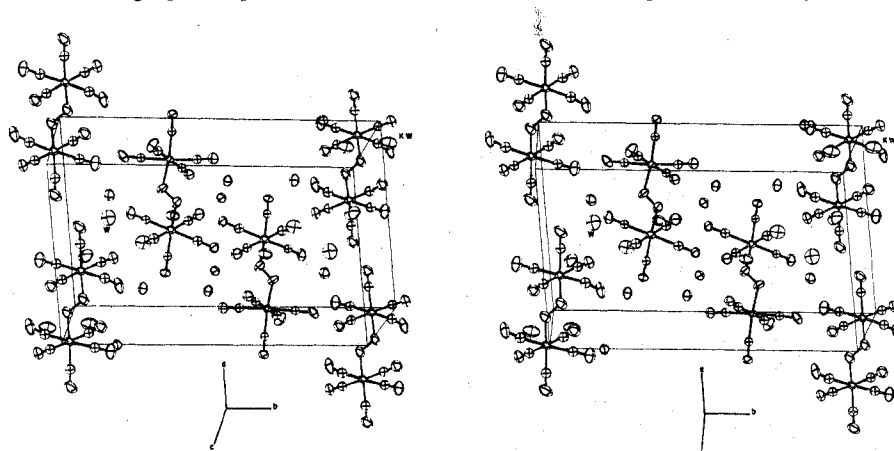


Figure 2. The crystal packing, with the unit cell outlined, viewed parallel to  $c^*$ . The atom labeled W and its symmetry equivalent are ordered water molecules; the atom labeled KW and its symmetry equivalents are disordered water molecule and  $K^+$  "atoms." The stereopair was drawn by ORTEP,<sup>29</sup> representing atoms by 40% probability ellipsoids.

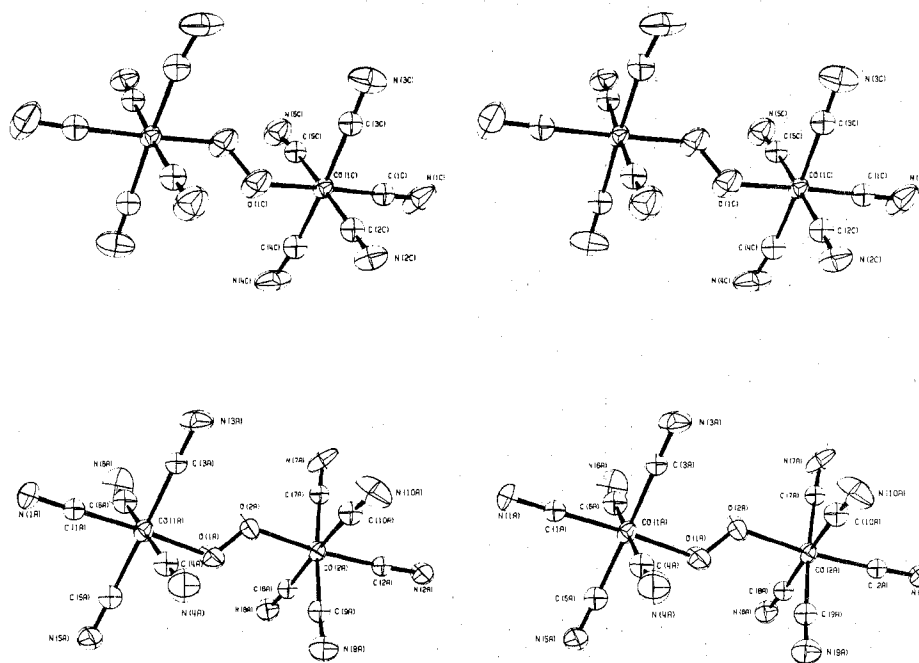


Figure 3. ORTEP<sup>29</sup> stereopairs of the  $[(CN)_5CoO_2Co(CN)_5]^{5-}$  anions C (above) and A. Ellipsoids enclose 40% probability. Both ions are viewed approximately along  $c^*$  with  $a$  horizontal.

positional parameters and the other containing all thermal parameters and the scale factor. All reflections, including those with negative measured values of  $F_o^2$ , were used in the refinement. Convergence was slow. All atoms were given anisotropic thermal parameters, except for the cyanide carbon atoms, which were treated as isotropic. After many cycles of least-squares refinement, convergence was reached at an  $R$  of 0.12 and a "goodness of fit" of 2.28; however, the troublesome disordered potassium ion had unreasonably small thermal parameters. At this point, our model contained two water molecules and three formula units of  $K_5[Co_2O_2(CN)_{10}]$  per cell, while the salt had been previously chemically characterized as the monohydrate.<sup>6</sup> By allowing the population parameter of the disordered potassium ion to refine by least squares, we concluded that the "missing" water molecule actually shares the site occupied by the disordered potassium ion; adding an oxygen atom with half-population at the same position as this potassium ion caused the thermal parameters of the combined potassium and water site (KW) to refine to reasonable values. After a few more cycles of least-squares refinement, convergence was reached with no parameter shifting by more than half its esd. The final values of the  $R$  index ( $R = \sum |F_o - |F_c|| / \sum F_o$ ) are 0.065 for the 1821 reflections with  $F_o > 3\sigma(F_o)$  and 0.106 for the 3113 reflections with  $F_o > 0$ . The goodness of fit,  $[\sum w(F_o^2 - F_c^2)^2 / (m - s)]^{1/2}$ , where  $m = 3399$  measurements and  $s = 331$  parameters, is 1.81. Attempts to locate hydrogen atoms of the ordered water molecule were unsuccessful. A three-dimensional difference synthesis

calculated at the conclusion of the refinement indicated no residual peaks greater than  $0.7 \text{ e } \text{\AA}^{-3}$ . A table of observed and calculated structure factors is available.<sup>19</sup>

## Results and Discussion

**General Description of the Structure.** Our structure solution confirms the formulation of the anion as a binuclear decacyano complex and establishes the configuration of the superoxo bridge as that suggested by epr studies, the skewed configuration known to exist in the  $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$  ion.<sup>7,8</sup> The crystal structure of the salt  $K_5[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$  consists of a nearly parallel arrangement of two crystallographically distinct binuclear anions in a 2:1 ratio, one acentric and the other centric, with  $K^+$  ions and water molecules surrounding the anions. Refined positional and thermal parameters for all atoms are contained in Table II, in which the two distinct anions are designated C (for centrosymmetric) and A (for acentric). Figure 2 illustrates the packing of ions in the structure.

**The  $[(CN)_5CoO_2Co(CN)_5]^{5-}$  Anion.** Conformations and thermal ellipsoids of the two anions are shown in Figure 3, and interatomic distances within these ions are given in Figure 4. The centric anion, which has rigorous  $C_i$  symmetry, deviates

Table II. Positional and Thermal Parameters<sup>a</sup>

Atom	x	y	z	$U_{11}$ or B	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Co(1C)	20,950 (16)	3,252 (9)	10,540 (26)	268 (12)	363 (12)	334 (14)	-24 (9)	42 (10)	-3 (10)
Co(1A)	44,973 (16)	32,752 (9)	18,697 (27)	251 (12)	409 (12)	385 (14)	-15 (9)	45 (10)	-29 (10)
Co(2A)	87,377 (15)	35,264 (9)	37,270 (27)	218 (11)	363 (12)	345 (13)	14 (9)	27 (10)	-16 (10)
K(1)	9,864 (29)	42,114 (16)	6,209 (46)	587 (25)	482 (22)	484 (26)	88 (18)	127 (21)	55 (19)
K(2)	23,489 (32)	25,462 (16)	63,843 (48)	770 (27)	435 (22)	473 (25)	81 (19)	191 (21)	-56 (19)
K(3)	42,232 (42)	8,316 (23)	69,346 (76)	948 (36)	929 (33)	1572 (50)	86 (27)	459 (35)	-563 (33)
K(4)	-1,775 (31)	17,428 (16)	92,343 (51)	530 (23)	437 (22)	695 (29)	41 (18)	110 (21)	68 (20)
K(5)	67,461 (30)	15,529 (17)	35,821 (51)	503 (24)	519 (23)	614 (28)	-34 (18)	-5 (21)	10 (20)
K(6)	33,344 (29)	49,052 (16)	63,346 (51)	461 (22)	423 (21)	721 (29)	-33 (17)	185 (21)	-57 (20)
K(7)	66,852 (31)	37,902 (19)	78,526 (57)	492 (25)	915 (30)	796 (33)	-92 (22)	128 (23)	-48 (25)
KW	-356 (53)	6,328 (34)	43,552 (91)	644 (44)	1462 (62)	803 (52)	-45 (42)	69 (39)	100 (46)
O(1C)	343 (9)	263 (5)	-86 (15)	55 (7)	65 (8)	72 (8)	1 (5)	12 (7)	40 (7)
C(1C)	3,767 (13)	418 (7)	2,075 (20)	3.64 (0.34)					
N(1C)	4,816 (12)	484 (7)	2,724 (22)	46 (10)	91 (11)	139 (15)	-10 (8)	4 (10)	56 (11)
C(2C)	2,095 (12)	838 (7)	-968 (20)	3.40 (0.33)					
N(2C)	2,051 (10)	1,156 (6)	-2,235 (17)	63 (9)	45 (8)	47 (9)	-4 (6)	8 (7)	9 (7)
C(3C)	2,162 (12)	-504 (7)	-269 (20)	3.68 (0.34)					
N(3C)	2,195 (13)	-1,040 (6)	-1,031 (19)	115 (12)	57 (9)	71 (11)	15 (8)	32 (10)	-4 (8)
C(4C)	2,007 (13)	1,130 (7)	2,450 (21)	4.02 (0.35)					
N(4C)	1,804 (14)	1,605 (6)	3,285 (19)	150 (14)	37 (8)	77 (11)	-9 (8)	64 (11)	-8 (8)
C(5C)	2,058 (12)	-179 (7)	3,046 (21)	3.52 (0.33)					
N(5C)	1,989 (11)	-479 (6)	4,290 (20)	63 (9)	74 (10)	83 (12)	2 (7)	17 (9)	30 (9)
O(1A)	6,244 (8)	3,604 (4)	3,010 (13)	41 (6)	45 (6)	59 (7)	9 (5)	-2 (6)	-16 (6)
O(2A)	7,028 (8)	3,197 (5)	3,137 (13)	39 (6)	60 (7)	56 (8)	18 (5)	12 (6)	-11 (6)
C(1A)	2,826 (12)	3,022 (6)	742 (18)	2.77 (0.29)					
N(1A)	1,775 (10)	2,872 (5)	-42 (16)	29 (7)	53 (8)	53 (9)	-3 (6)	6 (7)	4 (7)
C(2A)	10,408 (12)	3,731 (6)	4,315 (18)	2.67 (0.29)					
N(2A)	11,443 (10)	3,833 (5)	4,599 (16)	30 (7)	43 (7)	64 (9)	-7 (6)	8 (7)	-18 (7)
C(3A)	4,771 (11)	2,437 (7)	748 (18)	2.73 (0.30)					
N(3A)	4,933 (10)	1,940 (5)	-18 (17)	63 (9)	38 (8)	57 (9)	-2 (6)	2 (8)	-11 (7)
C(4A)	4,493 (12)	3,688 (7)	-253 (20)	3.27 (0.33)					
N(4A)	4,526 (11)	3,938 (6)	-1,580 (20)	68 (10)	76 (10)	82 (12)	14 (8)	30 (9)	26 (9)
C(5A)	4,112 (12)	4,137 (7)	2,722 (19)	3.51 (0.32)					
N(5A)	3,826 (10)	4,674 (6)	3,061 (18)	47 (8)	42 (8)	79 (10)	0 (6)	12 (8)	-11 (7)
C(6A)	4,528 (13)	2,855 (7)	4,030 (22)	3.99 (0.35)					
N(6A)	4,640 (13)	2,605 (8)	5,429 (20)	86 (11)	127 (12)	55 (11)	11 (9)	13 (9)	15 (10)
C(7A)	9,116 (11)	2,722 (7)	4,921 (19)	2.84 (0.30)					
N(7A)	9,365 (10)	2,213 (6)	5,634 (17)	53 (9)	60 (9)	55 (10)	-25 (7)	-9 (7)	13 (7)
C(8A)	8,836 (11)	4,060 (6)	5,901 (19)	2.89 (0.30)					
N(8A)	8,825 (10)	4,383 (6)	7,243 (16)	49 (8)	51 (8)	47 (9)	-2 (6)	12 (7)	-7 (7)
C(9A)	8,419 (12)	4,312 (7)	2,382 (19)	3.16 (0.31)					
N(9A)	8,222 (10)	4,761 (6)	1,383 (16)	56 (8)	47 (8)	42 (9)	0 (6)	10 (7)	-5 (7)
C(10A)	8,625 (12)	3,041 (7)	1,454 (21)	3.50 (0.33)					
N(10A)	8,531 (12)	2,805 (6)	-39 (20)	89 (11)	75 (10)	68 (11)	32 (8)	16 (9)	-9 (9)
O(4)	6,358 (11)	1,668 (6)	7,090 (17)	124 (11)	108 (10)	85 (10)	10 (9)	35 (9)	-3 (8)

<sup>a</sup> Heavy-atom (Co and K) coordinates have been multiplied by  $10^5$ . Light-atom coordinates have been multiplied by  $10^4$ . Anisotropic temperature factor is of the form  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ . Heavy-atom thermal parameters have been multiplied by  $10^4$ . Light-atom  $U$ 's have been multiplied by  $10^3$ . Estimated standard deviations are given in parentheses.

only slightly from  $C_{2h}$  symmetry, the O-O grouping being nearly eclipsed with respect to the equatorial ligands C(5)-N(5). Neglecting the offset due to the O-O bridge, the equatorial ligands of the two cobalt centers are eclipsed, as is usually found to be the case in 2:1 dioxygen-bridged complexes, and the Co-O-O-Co linkage is, of course, exactly planar. The acentric anion has a quite different conformation, having no crystallographic symmetry nor even any close correspondence to noncrystallographic, idealized symmetry. In this ion, the equatorial ligands about the two cobalt atoms are staggered by about  $35^\circ$ ; in addition, there is a twist about the O-O bond, making the superoxide group Co-O-O-Co nonplanar and the planes of the two sets of equatorial ligands nonparallel. The torsion angle about the O-O bond is  $166^\circ$ ; by comparison, this torsion angle in the  $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$  ion is  $180^\circ$  in the pentanitrate salt<sup>8</sup> and  $175^\circ$  in the sulfate tris(bisulfate).<sup>7</sup>

For a peroxo group, simple MO theory predicts the formation of two lone pairs of electrons on each oxygen atom, such that when it bridges two metal atoms, the most stable configuration is predicted when the lone pairs and thus also the coordinated metal atoms are skewed.<sup>20</sup> For a superoxo group, a similar argument predicts  $\pi$ -bonding character and

a planar configuration for the Co-O-O-Co linkage, with maximum overlap of orbitals with  $\pi$  symmetry. However, the present observation of both a planar and a nonplanar  $\mu$ -superoxo complex in the same crystal structure indicates very strongly that packing forces are the most important factor in determining the O-O torsion angle. Anion A is in an ordered environment and presumably adopts a slightly nonplanar conformation to enable it to fit best among the fixed cations. Anion C, however, has as close neighbors two pairs of disordered potassium ions and water molecules (KW); presumably this slight disorder puts less constraint on the anion, and it can adopt the more favored planar conformation. A planar model resulting from a disordering of two or more significantly nonplanar structures is ruled out by the very reasonable thermal parameters of the ligand atoms. We note a similar effect in the  $\mu$ -peroxo ions  $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$  and  $[(CN)_5CoO_2Co(CN)_5]^{6-}$ , in which the O-O torsion angle is apparently dictated by the presence or absence of hydrogen bonds to the bridging oxygen atoms.<sup>9,21,22</sup>

The fact that two different conformations of the same ion are present in the same structure presents us with an opportunity to explore the effects of conformation upon bond lengths; however, the results reveal no major differences

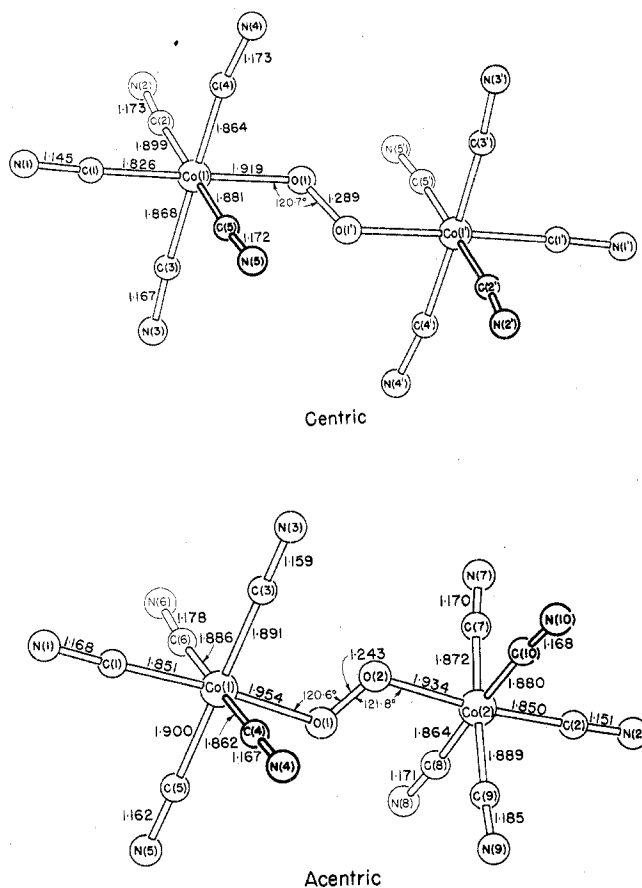


Figure 4. Bond distances and bridging angles for anions C and A. In anion C, esd's are 0.02 Å for O-O and C-N, 0.009 Å for Co-O, and 0.015 Å for Co-C. Values for anion A are similar except for O-O, which has an esd of 0.013 Å.

between the two ions. The Co-Co distances are identical, having values of 4.634 (8) Å for the centric ion and 4.637 (6) Å for the acentric ion. The largest difference between ions A and C is the O-O bond length, the determination of which is a primary interest in this investigation. The centric O-O distance, 1.289 (20) Å, has one of the largest esd's in the structure and differs from that of the acentric ion by 0.046 Å, about twice the esd of the difference. This difference may be real but is of marginal significance. The average O-O distance is 1.262 Å, which agrees well with the value of 1.28 (2) Å seen in potassium superoxide<sup>23</sup> and is probably significantly shorter than the length of 1.31–1.32 Å found in the analogous decaammine complex.<sup>7,8</sup> A similar effect was noted in the  $\mu$ -peroxo system, in which the decacyanide<sup>9</sup> also exhibited a shorter O-O distance (1.447 Å) than the decaammine (1.471 Å).<sup>21,22</sup> The cyano O-O shortening, incidentally, appears to be inconsistent with the findings of Mori, Weil, and Kinnaird<sup>6</sup> that the hyperfine coupling constant  $ACo$  for this ion is smaller than that of the decaammine. The smaller  $ACo$  is interpreted as implying that the spin density (and therefore the electron density) is more localized on the superoxo bridge; this would mean that there is more  $\pi^*$  character to the O-O bond and thus a longer O-O distance. We observe the opposite effect. It seems probable that the inconsistency arises through the assumption that spin density not localized on the cobalt atom must reside on the superoxo bridge. It appears more likely, in view of our results, that the unpaired electron is delocalized into  $\pi$  orbitals of the coordinated cyanide ligands.

Co-O distances range from 1.919 (9) to 1.954 (9) Å and average 1.936 Å. The difference between the largest and smallest of these values is 0.035 Å, which is probably not significant. This average is significantly longer than the

Table III. Bond Angles (deg) in the  $[(CN)_5CoO_2Co(CN)_5]^{5-}$  Ions

The Centric Ion	
O(1C)-Co(1C)-C(1C)	177.3 (6)
C(2C)-Co(1C)-C(5C)	178.7 (6)
C(3C)-Co(1C)-C(4C)	177.4 (7)
O(1C)-Co(1C)-C(2C)	84.6 (5)
C(3C)	92.5 (5)
C(4C)	87.0 (7)
C(5C)	94.2 (5)
C(1C)-Co(1C)-C(2C)	92.8 (6)
C(3C)	88.4 (6)
C(4C)	92.2 (6)
C(5C)	88.4 (7)
C(2C)-Co(1C)-C(3C)	91.6 (7)
C(4C)	90.9 (7)
C(5C)-Co(1C)-C(3C)	88.8 (7)
C(4C)	88.7 (7)
Co(1C)-C(1C)-N(1C)	178.7 (14)
C(2C)-N(2C)	177.6 (12)
C(3C)-N(3C)	176.8 (15)
C(4C)-N(4C)	171.7 (14)
C(5C)-N(5C)	176.8 (14)
Co(1C)-O(1C)-O(1C')	120.7 (10)
The Acentric Ion	
O(1A)-Co(1A)-C(1A)	176.2 (5)
C(3A)-Co(1A)-C(5A)	173.6 (5)
C(4A)-Co(1A)-C(6A)	179.1 (6)
O(1A)-Co(1A)-C(3A)	93.6 (5)
C(4A)	88.0 (5)
C(5A)	89.9 (5)
C(6A)	91.2 (6)
C(1A)-Co(1A)-C(3A)	89.1 (6)
C(4A)	89.4 (6)
C(5A)	87.2 (6)
C(6A)	91.4 (6)
C(3A)-Co(1A)-C(4A)	88.1 (6)
C(6A)	91.5 (6)
C(5A)-Co(1A)-C(4A)	86.6 (7)
C(6A)	93.8 (7)
Co(1A)-C(1A)-N(1A)	177.0 (14)
C(3A)-N(3A)	176.6 (13)
C(4A)-N(4A)	177.7 (14)
C(5A)-N(5A)	173.3 (13)
C(6A)-N(6A)	175.0 (12)
Co(1A)-O(1A)-O(2A)	120.6 (6)
O(2A)-Co(2A)-C(2A)	173.1 (5)
C(7A)-Co(2A)-C(9A)	175.2 (7)
C(8A)-Co(2A)-C(10A)	176.3 (6)
O(2A)-Co(2A)-C(7A)	87.4 (5)
C(8A)	93.0 (5)
C(9A)	94.8 (5)
C(10A)	87.6 (5)
C(2A)-Co(2A)-C(7A)	86.3 (6)
C(8A)	90.2 (6)
C(9A)	91.3 (6)
C(10A)	89.7 (6)
C(7A)-Co(2A)-C(8A)	94.1 (6)
C(10A)	89.6 (6)
C(9A)-Co(2A)-C(8A)	90.1 (6)
C(10A)	86.2 (6)
Co(2A)-C(2A)-N(2A)	176.3 (13)
C(7A)-N(7A)	178.3 (14)
C(8A)-N(8A)	176.0 (12)
C(9A)-N(9A)	173.2 (13)
C(10A)-N(10A)	172.9 (13)
Co(2A)-O(2A)-O(1A)	121.8 (7)
Torsion Angles	
C(2C)-Co(1C)-O(1C)-O(1C')	150.5
C(3A)-Co(1A)-O(1A)-O(2A)	-15.7
C(8A)-Co(2A)-O(2A)-O(1A)	54.6
Co(1A)-O(1A)-O(2A)-Co(2A)	165.9

average value of 1.889 (7) Å found in  $\mu$ -dioxigen-dicobalt complexes with nitrogen-donor ligands.<sup>9</sup> An analogous but larger effect was noted in the reduced form of the ion ( $\mu$ -peroxo), in which the Co-O distance is 1.985 (3) Å. In that structure,  $K_8[Co_2O_2(CN)_{10}](NO_3)_2 \cdot 4H_2O$ , both oxygen atoms of the peroxo bridge act as hydrogen-bond acceptors, which

Table IV. Closest Contacts<sup>a</sup> (Less than 3.3 Å) to the Potassium Ions

K(1)-N(5A)	3.21	K(2)-N(4C)	2.75	K(3)-O(4)	2.83	K(4)-N(4C)	3.21
N(1A)	2.90	N(6A)	3.01	N(2C)	2.93	O(1C)	3.03
N(2A)	3.06	N(2C)	3.01	N(3A)	2.91	N(1A)	2.91
N(8A)	2.98	N(1A)	3.08	N(1C)	2.86	N(10A)	2.79
N(9A)	2.88	N(2A)	3.02			N(7A)	2.85
N(8A')	3.04						
K(5)-N(3A)	3.03	K(6)-N(5A)	2.78	K(7)-N(6A)	3.15	KW-N(4C)	3.11
N(7A)	3.04	N(4A)	2.71	N(8A)	2.87	N(2C)	2.93
N(1C)	2.80	N(2A)	2.80	N(4A)	2.75	N(3C)	3.11
O(2C)	3.24	N(5A)	3.22	N(10A)	3.10	KW'	2.70
O(4)	2.87	N(9A)	3.01	N(9A)	3.08	N(5C)	2.82
N(3C)	2.82	O(1A)	2.88	N(5A)	3.17		
N(5C)	2.92						

<sup>a</sup> Where both C and N atoms of a cyanide ligand are closer than 3.3 Å, only the N atom is listed.

may explain the lengthening of the Co-O distance relative to the present compound; no difference in the Co-O distance was noted between the peroxo and superoxo ions in the decaammine system.

Accompanying the rather long Co-O distance, we also find a shortening of almost 0.04 Å in the trans Co-C distance (average 1.842 (7) Å) relative to the average equatorial distance, 1.880 (4) Å. Again an analogous effect, perhaps slightly smaller, is seen in the reduced decacyano ion,<sup>9</sup> while some of the nitrogen-donor  $\mu$ -dioxygen complexes exhibit the opposite effect, *i.e.*, a slight axial Co-N lengthening. This lengthening is about 0.02 Å in [(NH<sub>3</sub>)<sub>5</sub>CoO<sub>2</sub>Co(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup> and almost 0.05 Å in [(en)<sub>2</sub>(dien)<sub>2</sub>Co<sub>2</sub>O<sub>2</sub>]<sup>4+</sup>,<sup>22,24</sup>

The C-N distances of cyanide ligands range from 1.145 (19) to 1.185 (23) Å and average 1.167 (8) Å. Co-C-N angles deviate from linearity by amounts up to about 8°; such deviations are common in terminal cyanide ions coordinated to transition metals and are probably due to packing effects.

With this knowledge of the geometry of the [(CN)<sub>5</sub>CoO<sub>2</sub>Co(CN)<sub>5</sub>]<sup>5-</sup> ion, we are now in a position to make some generalizations about the structural effects of changing both the ligands and the oxidation state of the dioxygen bridge in the L<sub>5</sub>CoO<sub>2</sub>CoL<sub>5</sub> system, since the structures of the ions [(CN)<sub>5</sub>CoO<sub>2</sub>Co(CN)<sub>5</sub>]<sup>6-</sup>, [(NH<sub>3</sub>)<sub>5</sub>CoO<sub>2</sub>Co(NH<sub>3</sub>)<sub>5</sub>]<sup>5+</sup>, and [(NH<sub>3</sub>)<sub>5</sub>CoO<sub>2</sub>Co(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup> are also known. The peroxides are nonplanar when extensive hydrogen bonding is present and planar otherwise. The superoxides "prefer" the planar configuration but can also tolerate some deviation from planarity if efficient packing necessitates deformation. The amines are characterized by short Co-O bonds, long O-O bonds, and either a lengthening of the axial Co-N bond or no detectable effect upon it. The cyanides are characterized by long Co-O distances, short O-O distances, and a shortening of the axial Co-C length. In these respects, the decacyanide system is the antithesis of the decaammine system.

These observed trends in bond distances in this class of compounds may be interpreted in terms of relative  $\pi$ -accepting character of the ligands involved. While the ammonia molecule coordinates to transition metals wholly by  $\sigma$  donation into d orbitals of the metal, both cyanide and dioxygen possess not only this  $\sigma$ -donation capability but also  $\pi^*$  orbitals capable of accepting electron density from the metal through  $\pi$  overlap with metal d orbitals of proper symmetry. We believe from the results of structural studies of the (NH<sub>3</sub>)<sub>5</sub>CoCN<sup>2+</sup> and (NH<sub>3</sub>)<sub>5</sub>Co(cyano)Co(CN)<sub>5</sub> systems<sup>25-28</sup> that the NH<sub>3</sub> and -CN<sup>-</sup> ligands are approximately equivalent as  $\sigma$  donors, since no structural trans effects were noted in these complexes. Therefore the differences in bond lengths between the  $\mu$ -dioxygen-decaammine and -decacyanide ions must be due to  $\pi$  interactions alone.

A strong Co-O bond and weak Co-N bond (trans lengthening) in the decaammine system is consistent with strong Co-O  $\pi$ -back-donation, since dioxygen is quite clearly a better  $\pi$  acceptor than NH<sub>3</sub>. It should be noted that

metal-to-ligand donation places electron density into  $\pi^*$  orbitals of dioxygen and thus would be expected to weaken and hence lengthen the O-O bond. This is exactly the effect seen in the decaammine ions, which do indeed have long O-O distances. The weak Co-O bond and strong trans Co-C bond of the decacyanide ions also is consistent with this sort of thinking if it is assumed that -CN<sup>-</sup> is a better  $\pi$  acceptor than dioxygen. In competition for  $\pi$  donation from metal d orbitals, cyanide accepts more readily, causing a strengthening of the trans Co-C bond and little strengthening of the Co-O bond, which remains long. This reasoning predicts little more electron density donated into the dioxygen  $\pi^*$  orbitals in the decacyanide complex than in the free superoxide ion, and indeed no lengthening of the O-O bond is noted.

Thus we conclude that cyanide (coordinated through carbon) is a better "electron sink" than dioxygen, in either the peroxo or the superoxo oxidation states. There seems to be little difference between peroxo and superoxo groups in terms of  $\pi$ -bonding capability.

**The Hydrogen Bonding.** Although hydrogen atoms were not located, hydrogen bonds can be postulated from examination of distances between the water molecules and cyanide nitrogen atoms. The ordered water molecule O(4) occupies a position in proximity to (*i.e.*, less than 3.3 Å distant from any atom in) three different binuclear anions, but only one contact can be found indicative of hydrogen bonding; the O(4)-N(6A) distance is 2.86 Å. The disordered water molecule exhibits more possibilities for hydrogen bonding. The "KW" atom, an artifact half-populated with both K<sup>+</sup> and O, is disordered about (0, 0, 1/2) and thus is located between two centric anions related by a unit translation along z. The actual position of the water molecule is poorly known, as its position was constrained to correspond exactly with that of the half-potassium atom, which is probably not realistic. Possible hydrogen-bonding distances are 2.93 Å to N(2C), 3.11 Å to N(3C), 3.11 Å to N(4C), and 2.82 Å to N(5C). The distance of 2.70 Å from KW to its inversion-related equivalent represents in principle another possibility for hydrogen bonding, if in any particular unit cell both positions are simultaneously occupied by water molecules. Each such configuration would, however, require that in another area of the crystal, two K<sup>+</sup> ions also occupy adjacent positions separated by 2.70 Å, which is unreasonably short; therefore, we believe that the statistical centers are due only to the configurations K<sup>+</sup>...H<sub>2</sub>O and H<sub>2</sub>O...K<sup>+</sup> in equal populations.

This structure exhibits a complete lack of hydrogen bonding to the dioxygen ligand, in contrast to the double salt of the  $\mu$ -peroxo ion, K<sub>8</sub>[Co<sub>2</sub>O<sub>2</sub>(CN)<sub>10</sub>](NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O. An attempt was made to crystallize K<sub>5</sub>[Co<sub>2</sub>O<sub>2</sub>(CN)<sub>10</sub>] in the presence of KNO<sub>3</sub> in an effort to effect the sort of stability due to hydrogen bonding observed in the  $\mu$ -peroxo double salt, and small, cherry red crystals were obtained. They are triclinic and appear to contain two formula units of K<sub>6</sub>[Co<sub>2</sub>O<sub>2</sub>(CN)<sub>10</sub>](NO<sub>3</sub>)·H<sub>2</sub>O per cell. These crystals are actually less stable than those of

the simple potassium salt, and no further work was done using them.

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**Registry No.** K<sub>5</sub>[(CN)<sub>5</sub>CoO<sub>2</sub>Co(CN)<sub>5</sub>]-H<sub>2</sub>O, 12145-87-8.

**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 Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40655N.

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## Molecules with an M<sub>4</sub>X<sub>4</sub> Core. IV.<sup>1-3</sup> Crystallographic Detection of a "Step" Configuration for the Cu<sub>4</sub>I<sub>4</sub> Core in Tetrameric Triphenylphosphinecopper(I) Iodide, [PPh<sub>3</sub>CuI]<sub>4</sub>

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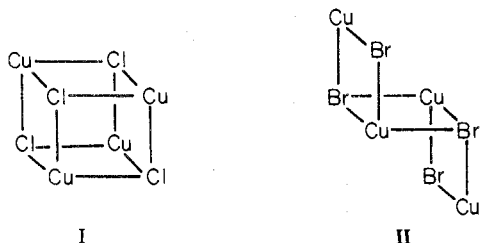
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Tetrameric triphenylphosphinecopper(I) iodide crystallizes in the centrosymmetric monoclinic space group *C*<sub>2</sub>/*c* [*C*<sub>2h</sub><sup>6</sup>; No. 15] with *a* = 25.845 (6) Å, *b* = 16.137 (4) Å, *c* = 18.264 (5) Å, β = 110.75 (2°), *V* = 7123 (3) Å<sup>3</sup>, and *Z* = 4. Single-crystal X-ray diffraction data, complete to 2θ = 35° (Mo Kα radiation), were collected with a Picker FACS-1 automated diffractometer and the structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. The final discrepancy indices are *R*<sub>F</sub> = 6.74% and *R*<sub>wF</sub> = 5.05% for 2255 independent reflections. The molecule has crystallographically dictated *C*<sub>i</sub> (I) symmetry, with the Cu<sub>4</sub>I<sub>4</sub> core defining a "step" structure. Most surprisingly, nonsolvated [Ph<sub>3</sub>PCuI]<sub>4</sub> is both isomorphous and isostructural with the solvated bromo analog, of idealized composition [Ph<sub>3</sub>PCuBr]<sub>4</sub>·2CHCl<sub>3</sub>. Within the [Ph<sub>3</sub>PCuI]<sub>4</sub> molecule, the symmetry-related copper atoms Cu(2) and Cu(2') are in tetrahedral coordination, with Cu(2)-P(2) = 2.242 (4) Å, Cu(2)-I(1) = 2.620 (2) Å, Cu(2)-I(2) = 2.728 (2) Å, and Cu(2)-I(2') = 2.707 (2) Å; the other two symmetry-related copper atoms [Cu(1) and Cu(1')] are in trigonal coordination with Cu(1)-P(1) = 2.228 (5) Å, Cu(1)-I(1) = 2.527 (2) Å, and Cu(1)-I(2) = 2.591 (2) Å. Intramolecular copper...copper distances are (in order) Cu(1)...Cu(2) = Cu(1')...Cu(2') = 2.835 (3) Å, Cu(2)...Cu(2') = 3.404 (4) Å, and Cu(1)...Cu(2') = Cu(1')...Cu(2) = 4.295 (3) Å. Iodine...iodine contacts show considerably less variation, individual values (in order) being I(1)...I(2') = I(1')...I(2) = 4.204 (2) Å, I(2)...I(2') = 4.238 (2) Å, and I(1)...I(2) = I(1')...I(2') = 4.384 (2) Å.

### Introduction

We have shown previously that the Cu<sub>4</sub>Cl<sub>4</sub> core of [PPh<sub>3</sub>CuCl]<sub>4</sub> has the "cubane-like" structure I,<sup>1,5</sup> whereas the Cu<sub>4</sub>Br<sub>4</sub> core of the analogous bromo compound, [PPh<sub>3</sub>CuBr]<sub>4</sub>, has the "step" structure II.<sup>2,5</sup> The overall geometry of Cu<sub>4</sub>X<sub>4</sub>



(X = halogen) cores is not, however, a function only of the identity or size of the halogen atoms; iodo derivatives are known both with a cubane-like core {[AsEt<sub>3</sub>CuI]<sub>4</sub><sup>3,6</sup> and [PEt<sub>3</sub>CuI]<sub>4</sub><sup>3,7</sup>} and with a step structure {(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>Cu<sub>4</sub>I<sub>4</sub>}<sup>8</sup>.

As a continuation of our studies on species with a Cu<sub>4</sub>X<sub>4</sub> core, we decided that a determination of the crystal structure of [PPh<sub>3</sub>CuI]<sub>4</sub> was necessary. Our results, which show the [PPh<sub>3</sub>CuI]<sub>4</sub> molecule to be another member of the growing family of compounds known to have a step structure, are given below.

### Collection of the X-Ray Diffraction Data

A sample of [PPh<sub>3</sub>CuI]<sub>4</sub> was prepared following the procedure of Costa, Reisenhofer, and Stefani.<sup>9</sup> Small diamond-shaped crystals (mp 265–268°) were present in the initial reaction product. Sub-