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# The Crystal and Molecular Structure of μ-Peroxo-bis-[3,3′-diimino-di-n-propylamine-bis-salicylaldehyde cobalt(III)]. $C_6H_5CH_3$*

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The structure of μ-peroxo-bis-[3,3′-diimino-di-n-propylamine-bis-salicylaldehyde cobalt(III)] $C_6H_5CH_3$, $(CoO_2N_3C_{20}H_{23})_2O_2.C_6H_5CH_3$, has been determined by single-crystal X-ray analysis. The red-black salt crystallizes in the monoclinic space group $C2/c$ with unit-cell dimensions $a=10{\cdot}236$ (6), $b=24{\cdot}31$ (2), $c=18{\cdot}02$ (1) Å, and $\beta=104{\cdot}06$ (6)°; $Z=4$. The measured density of 1·37 (3) g.cm$^{-3}$ agrees well with the value of 1·39 (1) g.cm$^{-3}$ calculated for four formula units in the cell. Three-dimensional intensity data were collected on a Datex-automated General Electric diffractometer using Co $K\alpha$ radiation. The structure was determined by Patterson and Fourier methods and refined by Fourier and least-squares techniques to an $R$ index of 0·12 for 1185 reflextions. Oxygen atoms of the salicylaldehyde groups are arranged in *cis* positions in the octahedra around the cobalt atoms while the imine nitrogen atoms are *trans*. The molecule crystallizes around a twofold axis with a skew, nonplanar Co–O–O–Co bridge arrangement. The O–O distance of 1·45 (2) Å and the torsion angle around this bond of 149° indicate that the $O_2$ group is best formulated as a peroxide ($O_2^{2-}$) ion.

A similar molecule can be crystallized from acetonitrile or acetone. Crystals obtained from these solvents are also monoclinic, space group $P2/c$, with approximate cell dimensions $a=10{\cdot}35$ (1), $b=11{\cdot}39$ (1), and $c=17{\cdot}23$ (1) Å; $\beta=101{\cdot}5(1)$°. Partial data from a poorly formed crystal indicate a similar Co–O–O–Co arrangement about a twofold axis.

## Introduction

An interesting chemical reaction, which is of vital importance from a biological viewpoint, is the reversible bonding of an $O_2$ molecule to a metal chelate compound. A few naturally occurring molecules of this sort are known, but these are so large that it is difficult to determine the detailed geometry of the oxygen–metal bond. In recent years some simpler compounds which exhibit this important oxygen-carrying property have been synthesized (Vogt, Faigenbaum & Wiberley, 1963). Because the synthetic oxygen-carrying molecules are relatively small, it should be possible to obtain valuable information concerning the detailed geometry of the oxygen–metal bond from them.

Pfeiffer, Breith, Lubbe & Tsumaki (1933) prepared the first compound of this type, bis-salicylaldehyde-ethylenediimine cobalt(II). This compound and the related diimino-di-n-propylamine-salicylaldehyde cobalt(II) were studied extensively by Calvin, Bailes & Wilmarth (1946) and by Bailes & Calvin (1947). The ethylene-diimine complex reversibly absorbs oxygen in a 2:1 metal-to-$O_2$ ratio, whereas the diimino-di-n-propylamine complex absorbs oxygen in a 1:1 ratio. However, our present structural result shows that the diimino-di-n-propylamine complex can also react with oxygen in a 2:1 ratio.

We have grown crystals of the diimino-di-n-propylamine salicylaldehyde cobalt compound from toluene, acetone, and acetonitrile and report here the structure of the one of these which formed the best crystals. All our products appear to be inactive forms of the compound, as they fail to change color when heated, a characteristic of the reversible oxygen carriers. From this observation we expect them to contain cobalt(III) atoms and oxygen in the form of peroxide ion (Vogt *et al.*, 1963; Schaefer, 1968).

It is interesting to note that, whereas Calvin reported that oxygen pressures of several hundred pounds per square inch were needed to form the oxygen adduct of this compound, we were able to produce an irreversibly oxidized form of the compound in toluene solution with very little oxygen present or in acetonitrile or acetone solutions in contact with the air.

## Experimental

A sample of 3,3′-diimino-di-n-propylamine-bis-salicylaldehyde cobalt(II) was prepared by reacting cobaltous acetate with the Schiff base using essentially the method described by Bailes & Calvin (1947). The material precipitated from the alcohol solution and was washed with water in a nitrogen atmosphere. A hot, saturated solution of the compound in toluene was placed in a

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Dewar flask and allowed to cool overnight within the nitrogen atmosphere*. A black precipitate was observed the following day, so the solution was filtered and the filtering apparatus was allowed to stand overnight to dry the crystals. The filter paper was removed and the precipitate was found to be a powder. On the reverse side of the filter paper, however, small crystals had formed as the solvent evaporated after filtration. Most of the crystals, which appeared single to the eye, gave very confused diffraction patterns indicating twinning or other disorder. Repeated preparations, varying cooling and/or evaporation rates, and other techniques failed to produce better material. The crystals produced on the bottom of the filter paper, although not of high quality, were the best we could obtain and were therefore used for our structure determination†.

Weissenberg photographs revealed systematic absences of *hkl* with $h+k$ odd and of *h0l* with *l* odd, indicating space groups *Cc* or *C*2/*c*; a satisfactory structure was found in the latter. Cell dimensions were determined by a least-squares fit to values of $2\theta$ measured on the diffractometer for 28 reflections. Density was measured by flotation in an aqueous solution of potassium iodide. Crystal data are given in Table 1.

Table 1. *Crystal data*

| | |
|---|---|
| Space group *C*2/*c* | Formula: $Co_2O_6N_6C_{47}H_{54}$ |
| $a=10{\cdot}236\pm0{\cdot}007$ Å | Molecular weight = 916·86 g.mole$^{-1}$ |
| $b=24{\cdot}21\pm0{\cdot}02$ | $Z=4$ |
| $c=18{\cdot}02\pm0{\cdot}01$ | $F_{000}=1902{\cdot}48$ electrons |
| $\beta=104{\cdot}06\pm0{\cdot}06°$ | Molecular symmetry: 2 |
| $D_m=1{\cdot}37\pm0{\cdot}03$ g.cm$^{-3}$ | Co $K\alpha_1=1{\cdot}78892$ Å |
| $D_x=1{\cdot}393\pm0{\cdot}001$ g.cm$^{-3}$ | Co $K\alpha_2=1{\cdot}79278$ Å |

An approximately rectangular crystal measuring about $0{\cdot}05\times0{\cdot}07\times0{\cdot}09$ mm was chosen for collection of three-dimensional intensity data. Each intensity was measured at least twice on a General Electric diffractometer, using a $\theta$–$2\theta$ scan technique with a scan rate of 0·5° per minute or, for some low-angle data, 1° per minute. Backgrounds were collected for fifty seconds on either side of the scan range, which was set at 4° at $2\theta=10°$ and increased linearly to 5° at $2\theta=130°$. The high mosaic character of the crystal required this large scan range so as to include all of the rather broad peaks.

The higher-angle data which we collected were very weak and had large standard deviations; for this reason all *F*'s which had values less than twice their standard deviations were assigned zero intensity and zero weight. In addition, the (315) reflection for which the two intensity measurements differed widely was assigned zero weight.

A total of 1756 reflections were measured, of which 1185 with $I\geq2\sigma(I)$ were used in the final refinement. The intensities were corrected for background and for Lorentz and polarization effects to obtain a set of $F^2$ values and their standard deviations, obtained from the equation

$$\sigma(F^2)=\{1/\mathrm{Lp}[S+\tfrac{1}{2}(B_1+B_2)\,(t/50)^2+(0{\cdot}02S)^2]\}^{\frac{1}{2}},$$

where *S* is the number of counts measured, Lp is the Lorentz and polarization correction, *B* is the number of counts recorded for the background measurement and *t* is the scan time in seconds. The term 0·02*S* is an empirical constant, included to account for errors other than those due to counting statistics (Busing & Levy, 1957).

The calculated value of $\mu R_{\max}$ for this small crystal was 0·13 ($\mu=21{\cdot}2$ cm$^{-1}$); for this reason we neglected any correction for absorption.

### Determination and refinement of the structure

All calculations were carried out on an IBM 360/75 computer using the *CRYM* X-ray crystallographic system. Form factors for Co, N, C, and O were taken from *International Tables for X-ray Crystallography* (1962); those for hydrogen were taken from Stewart, Davidson & Simpson (1965). The quantity minimized

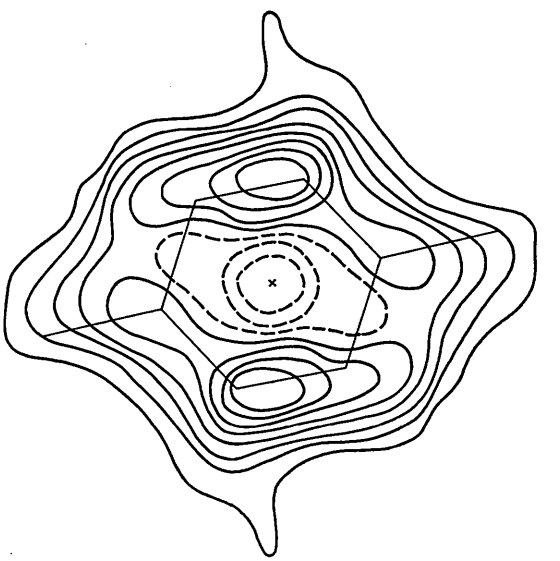

Fig. 1. Difference map in the plane of the toluene molecule. Contours are at intervals of 0·2 e.Å$^3$ beginning at 0·2 e.Å$^3$. Dashed contours represent decreasing electron density.

* The toluene contained dissolved oxygen, as the only precaution taken to remove it was to boil the toluene.

† A different material is produced upon crystallization in air from acetonitrile or acetone. Pictures of poor crystals indicate the monoclinic space group *P*2/*c* with unit-cell dimensions $a=10{\cdot}35$ (1), $b=11{\cdot}39$ (1), $c=17{\cdot}23$ (1) Å, and $\beta=101{\cdot}5$ (1)°. Intensity data from Co $K\alpha$ radiation were collected to 60° in $2\theta$, using a crystal obtained from acetonitrile. Patterson and Fourier techniques gave approximate coordinates for the cobalt atom and the atoms of the surrounding octahedron. Because of the poor quality of the data, we could not continue with the structure analysis; yet it is interesting to note that the partial structure is almost identical with the one described here. Unit-cell dimensions are similar except for a halving of the *b* axis, the cobalt atoms are positioned in the same way relative to a twofold axis, and an $O_2$ group appears to bridge the two cobalt atoms. The Co–Co distance is about 4·6 Å.

by the least-squares method was $\Sigma w(F_o^2-F_c^2)^2$ where $w=1/\sigma^2(F_o^2)$.

The effects of anomalous dispersion of the cobalt atom due to the use of cobalt radiation were accounted for by adding $\Delta f'=-2{\cdot}19$ electrons to the scattering curve of cobalt (Cromer, 1965). The effects of $\Delta f''=0{\cdot}74$ electrons were neglected for this centric structure.

A three-dimensional Patterson synthesis was calculated using only data collected for values of $2\theta$ less than 60°. A prominent feature of this map was a peak, about 4·6 Å from the origin, on the section $v=0$. It was interpreted as an intramolecular Co–Co vector, indicating a twofold axis parallel to **b** and, hence, space group $C2/c$. A subsequent three-dimensional electron-density map, phased by the cobalt atoms, indicated the positions of the six ligand atoms surrounding the cobalt atom. At this point the $R$ index ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$) was 0·52. The data set was expanded to include all reflections with $2\theta<90°$, and additional atoms were added gradually during several cycles of least-squares and Fourier refinement; when all the C, N, and O atoms of the complex had been located, the $R$ index was 0·35. Several cycles of full-matrix least-squares refinement, including the positional and isotropic temperature parameters of the 27 atoms that had been located, led to an $R$ index of 0·22.

Calculations gave a difference map whose most prominent feature suggests the presence of a toluene molecule of crystallization, oriented perpendicular to a twofold axis, and therefore, disordered (Fig. 1). These atoms were added but their parameters were not refined; two more cycles of least-squares refinement of other atom parameters reduced the $R$ index to 0·16. Next, the hydrogen atoms in the structure were added, placed at computed positions 1·0 Å from the carbon and nitrogen atoms; their positional and thermal parameters were never refined.

The remaining data, having $2\theta$ values between 90 and 110°, were added to the refinement, and the cobalt atom and the six ligand atoms were allowed to vibrate

Table 2. *Final parameters of the atoms*

Values in parentheses are estimated standard deviations. All positional and anisotropic thermal parameters have been multiplied by $10^4$. The anisotropic temperature factors are of the form $\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$. The column headed 'Pop.' indicates the fractional occupancy of the atomic site, if other than 1·0.

| | $x$ | $y$ | $z$ | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 3421 (3) | 3913 (1) | 6331 (2) | 83 (4) | 17 (1) | 44 (1) | −3 (4) | 28 (4) | −3 (2) |
| O(1) | 5030 (10) | 3728 (4) | 7101 (5) | 104 (16) | 26 (3) | 32 (5) | −9 (12) | 29 (18) | −3 (6) |
| O(2) | 4383 (11) | 3632 (5) | 5639 (6) | 109 (18) | 30 (4) | 47 (6) | −16 (13) | 59 (17) | −16 (7) |
| O(3) | 1920 (11) | 4148 (5) | 5545 (7) | 136 (19) | 20 (3) | 52 (6) | 12 (12) | −4 (18) | −21 (7) |
| N(1) | 4099 (15) | 4657 (6) | 6227 (7) | 169 (26) | 27 (5) | 27 (7) | 7 (18) | 37 (22) | 11 (9) |
| N(2) | 2672 (13) | 3187 (6) | 6301 (9) | 61 (21) | 28 (4) | 41 (8) | −11 (15) | 11 (21) | −15 (10) |
| N(3) | 2574 (14) | 4089 (5) | 7185 (8) | 137 (23) | 12 (4) | 61 (8) | 11 (14) | 90 (22) | −12 (8) |

| | $x$ | $y$ | $z$ | $B$(Å)$^2$ |
|---|---|---|---|---|
| C(1) | 5156 (22) | 4759 (8) | 5995 (11) | 6·2 (6) |
| C(2) | 5973 (20) | 4357 (9) | 5798 (10) | 6·4 (5) |
| C(3) | 5635 (20) | 3808 (9) | 5642 (10) | 5·5 (5) |
| C(4) | 6513 (23) | 3450 (9) | 5391 (11) | 8·0 (6) |
| C(5) | 7831 (24) | 3642 (11) | 5381 (12) | 9·5 (6) |
| C(6) | 8058 (21) | 4158 (10) | 5522 (12) | 7·9 (6) |
| C(7) | 7318 (23) | 4552 (9) | 5725 (11) | 9·0 (6) |
| C(8) | 1893 (20) | 2985 (7) | 5712 (12) | 5·4 (5) |
| C(9) | 1337 (18) | 3251 (9) | 4985 (12) | 5·2 (5) |
| C(10) | 1353 (19) | 3827 (9) | 4972 (12) | 6·1 (5) |
| C(11) | 672 (19) | 4087 (8) | 4259 (12) | 6·3 (5) |
| C(12) | 41 (21) | 3758 (10) | 3638 (13) | 7·3 (6) |
| C(13) | 64 (21) | 3183 (10) | 3703 (13) | 8·3 (6) |
| C(14) | 639 (22) | 2939 (9) | 4359 (13) | 7·4 (6) |
| C(15) | 3237 (20) | 5133 (8) | 6348 (12) | 7·0 (5) |
| C(16) | 2832 (19) | 5108 (8) | 7087 (11) | 6·6 (5) |
| C(17) | 1929 (19) | 4638 (9) | 7139 (10) | 6·2 (5) |
| C(18) | 2989 (19) | 2871 (8) | 7025 (12) | 6·3 (5) |
| C(19) | 2235 (20) | 3117 (9) | 7563 (11) | 7·5 (6) |
| C(20) | 1630 (18) | 3680 (8) | 7320 (10) | 5·6 (5) |
| HN(3) | 3377 | 4089 | 7631 | 7 |
| HC(1) | 5407 | 5145 | 5953 | 7 |
| HC(4) | 6220 | 3055 | 5255 | 7 |
| HC(5) | 8494 | 3379 | 5241 | 7 |
| HC(6) | 8977 | 4274 | 5481 | 7 |
| HC(7) | 7643 | 4936 | 5809 | 7 |
| HC(8) | 1647 | 2594 | 5766 | 7 |
| HC(11) | 667 | 4493 | 4209 | 7 |

| | $x$ | $y$ | $z$ | $B$(Å)$^2$ | Pop. |
|---|---|---|---|---|---|
| HC(12) | −424 | 3928 | 3132 | 7 | |
| HC(13) | −433 | 2966 | 3259 | 7 | |
| HC(14) | 634 | 2526 | 4390 | 7 | |
| HC(15) | 2441 | 5146 | 5923 | 7 | |
| HC(15) | 3790 | 5474 | 6371 | 7 | |
| HC(16) | 2308 | 5444 | 7123 | 7 | |
| HC(16) | 3625 | 5075 | 7509 | 7 | |
| HC(17) | 1135 | 4639 | 6701 | 7 | |
| HC(17) | 1610 | 4690 | 7628 | 7 | |
| HC(18) | 2751 | 2479 | 6937 | 7 | |
| HC(18) | 3980 | 2906 | 7267 | 7 | |
| HC(19) | 1477 | 2855 | 7578 | 7 | |
| HC(19) | 2849 | 3142 | 8075 | 7 | |
| HC(20) | 927 | 3638 | 6825 | 7 | |
| HC(20) | 1205 | 3818 | 7719 | 7 | |
| | Toluene molecule | | | | |
| C(21) | 5725 | 3400 | 3188 | 15 | |
| C(22) | 6301 | 3400 | 2613 | 15 | |
| C(23) | 5547 | 3400 | 1920 | 15 | |
| C(24) | 6139 | 3400 | 1296 | 15 | ½ |
| HC(21) | 6300 | 3400 | 3723 | 15 | |
| HC(22) | 7305 | 3400 | 2706 | 15 | |
| HC(23) | 4033 | 3400 | 3526 | 15 | ½ |
| HC(24) | 5404 | 3395 | 748 | 15 | ¼ |
| HC(24) | 5876 | 3740 | 889 | 15 | ¼ |
| HC(24) | 6820 | 3740 | 1169 | 15 | ¼ |
| HC(24) | 7292 | 3395 | 1310 | 15 | ¼ |
| HC(24) | 6820 | 3050 | 1169 | 15 | ¼ |
| HC(24) | 5876 | 3050 | 889 | 15 | ¼ |

## Table 3. *Observed and calculated structure factors* ($\times 10$)

An asterisk indicates the reflexion was not used in the refinement.

anisotropically. During the final cycles of least-squares refinement, a total of 144 parameters were adjusted. In the final cycle the maximum shift was 0·7 e.s.d.

The final $R$ index is 0·12, and the weighted $R$ index $\{R_w=[\Sigma w(F_0^2-F_c^2)^2/\Sigma w(F_o)^4]^{\frac{1}{2}}\}$ is 0·16. The goodness of fit $[\Sigma w(F_o^2-F_c^2)^2/(m-s)]^{\frac{1}{2}}$ is 1·95, where $m$ is the number of data used (1185) and $s$ is the number of parameters refined. Final coordinates and temperature coefficients are given in Table 2 and the final observed and calculated structure factors are given in Table 3.

At a number of stages during the refinement, attempts were made to adjust the coordinates of the atoms of the toluene molecule, but they failed: least-squares adjustment led to unrealistic geometry and temperature factors, and difference maps had features (ranging up to $\pm 1{\cdot}0$ e.Å$^{-3}$) that we could not interpret in a reasonable manner. We ultimately returned to our original interpretation (Fig. 1), in which the crystallographic twofold axis passes through the center of the benzene ring and the methyl group is distributed, with equal probability, among two sites on ring carbon atoms *para* to one another. The C(ring)–C(ring) distances were set equal to 1·30 Å and the C(ring)–C(methyl) distance to 1·40 Å; both values are about 0·1 Å less than the standard distance, reflecting the large temperature factors ($B\simeq 15$ Å$^2$) necessary to approximate the diffuse electron density. The hydrogen atoms were similarly placed in assumed positions, those of the methyl group being represented by six half-weight sites evenly distributed on a circle.

Formal standard deviations in bond lengths range from 0·01 to 0·03 Å and in the bond angles from 0·5 to 1·5°. In general the smaller values of the uncertainties are associated with bonds near the center of a molecule. We emphasize here that as a result of the small size and high mosaicity of the crystals, the accuracy of the intensity measurements is relatively low and the apparent thermal motions of the atoms are high. The result was a structure determination of considerably lower precision than usual. Indeed, our values for the C–C distance in the benzene rings $A$ and $F$ differ from expectation values by amounts suggesting that the e.s.d.'s in this part of the molecule should be about 0·05 Å instead of 0·03 Å. In the central, more rigid portion of the molecule, agreement with expected values is more satisfactory.

## Description and discussion of structure

The molecule crystallizes as a dimer around a twofold rotation axis (Fig. 2). The cobalt atoms are bridged by an O–O group having an O–O distance of 1·45 (2) Å; the torsion angle Co–O–O–Co around this bond is 149°. These values are typical of a peroxo group (Abrahams, Collins & Lipscomb, 1951) and compare well with the values of 1·47 (1) Å and 146° found in decaammine-$\mu$-peroxo-dicobalt disulfate tetrahydrate (Schaefer, 1968). Bond angles involving nonhydrogen atoms are given in Table 4.

The octahedron surrounding the cobalt atom comprises three oxygen atoms and three nitrogen atoms. The two oxygen atoms contributed by the salicylaldehyde groups are *cis* while the imine nitrogen atoms are *trans* (see Fig. 2). This arrangement places the three coordinated oxygen atoms in a plane nearly perpendicular to the plane of the three coordinated nitrogen atoms and forces the planes of the two salicylaldehyde groups to be almost perpendicular to one another.

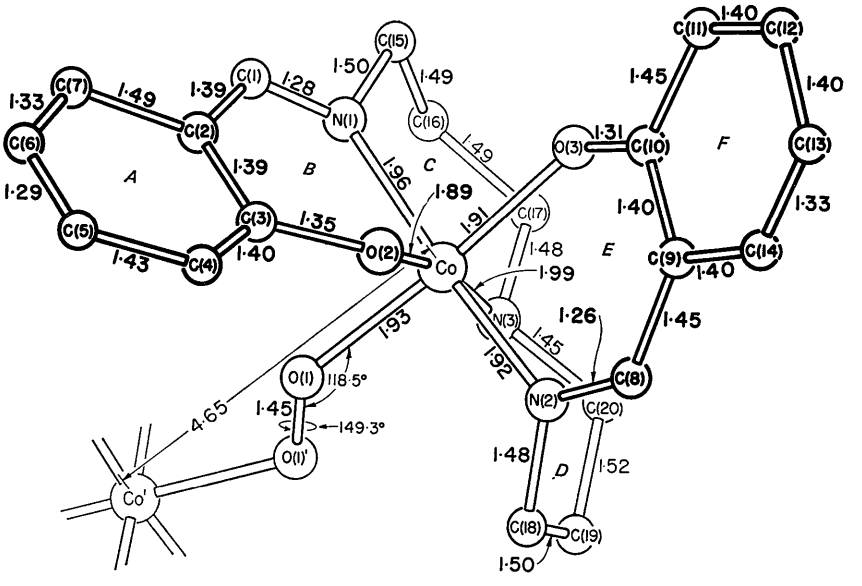


Fig. 2. Bond distances. Letters identify the various rings (see text). The e.s.d's of the bond distances shown are about as follows: Co–Co, 0·005; Co–N or –O, 0·013; O–O, 0·013; C–N or C–O, 0·025; C–C, 0·033 Å.

The two salicylaldehyde groups are related to their adjoining propylamine groups differently, the Co–N(3) bond being nearly parallel to rings *A* and *B* (see Fig. 2) but perpendicular to *E* and *F*. Thus, rings *A*, *B*, and *C* are roughly coplanar while rings *E* and *F* are roughly perpendicular to *D*. Note that ring *C* has a different conformation than *D*. A view down the Co–N(3) bond (Fig. 2) shows the reason. With ring *C* in the more stable chair conformation, the torsion angle N(1)–Co–N(3)–C(17) must be about ±60°. Since N(3) is 4-coordinate and hence bonds tetrahedrally, the torsion angle N(1)–Co–N(3)–C(20) must be about 180°, forcing bonds Co–N(2) and N(3)–C(20) to be coplanar. This, in turn, forces ring *D* to assume the less stable boat conformation (Fig. 2). The conformation could be reversed (*C* a boat and *D* a chair) only if atoms C(17) and C(20) were rotated 60° about the Co–N(3) bond. This rotation, however, would cause the halves of the dimer to come closer together and therefore result in an enlargement of the torsion angle around the O–O bond.

Although the O–O distance of 1·45 Å compares reasonably well with the value 1·47 Å found in $H_2O_2$, the torsion angle of 149° differs significantly from the 90° angle found in that molecule, probably for steric reasons. The closest intramolecular distance across the twofold axis (excluding the bonded oxygen atoms) brings atoms N(3) and C(2′) to within 3·6 Å.

The molecular packing is shown in Fig. 3. The closest intermolecular distance brings atoms C(8) and C(14′) [related to C(14) by a center of symmetry] to within 3·4 Å.

Temperature factors for the carbon atoms were re-

Table 4. *Bond angles involving nonhydrogen atoms*

| | | | |
|---|---|---|---|
| O(1)—Co—O(2) | 84·3 (5)° | N(1)—C(1)—C(2) | 124·0 (19)° |
| O(1)—Co—N(1) | 91·3 (5) | C(1)—C(2)—C(3) | 126·4 (20) |
| O(1)—Co—N(2) | 94·1 (5) | C(1)—C(2)—C(7) | 115·1 (19) |
| O(2)—Co—N(2) | 85·3 (6) | C(3)—C(2)—C(7) | 118·5 (19) |
| O(3)—Co—O(1) | 174·9 (5) | C(2)—C(3)—O(2) | 119·6 (18) |
| O(3)—Co—O(2) | 94·2 (6) | C(4)—C(3)—O(2) | 119·0 (19) |
| O(3)—Co—N(1) | 83·8 (6) | C(4)—C(3)—C(2) | 120·9 (20) |
| O(3)—Co—N(2) | 90·6 (6) | C(5)—C(4)—C(3) | 118·7 (20) |
| N(1)—Co—O(2) | 91·0 (6) | C(6)—C(5)—C(4) | 116·1 (23) |
| N(1)—Co—N(2) | 173·0 (5) | C(7)—C(6)—C(5) | 132·0 (23) |
| N(3)—Co—O(1) | 87·1 (6) | C(2)—C(7)—C(6) | 113·3 (20) |
| N(3)—Co—O(2) | 169·0 (5) | N(2)—C(6)—C(9) | 128·1 (17) |
| N(3)—Co—O(3) | 94·9 (6) | C(8)—C(9)—C(10) | 117·2 (18) |
| N(3)—Co—N(1) | 96·1 (6) | C(8)—C(9)—C(14) | 119·9 (19) |
| N(3)—Co—N(2) | 88·4 (6) | C(14)–C(9)—C(10) | 122·2 (20) |
| Co—O(1)–O(1′) | 118·5 (7) | O(3)—C(10)–C(11) | 117·6 (18) |
| Co—O(2)–C(3) | 121·9 (11) | C(9)—C(10)–O(3) | 126·0 (19) |
| C(10)–O(3)–Co | 121·9 (12) | C(9)—C(10)–C(11) | 116·4 (19) |
| Co—N(1)–C(1) | 123·9 (13) | C(10)–C(11)–C(12) | 119·2 (19) |
| Co—N(1)–C(15) | 117·6 (12) | C(11)–C(12)–C(13) | 120·6 (20) |
| C(1)—N(1)–C(15) | 118·2 (16) | C(12)–C(13)–C(14) | 121·0 (22) |
| C(8)—N(2)–Co | 123·2 (13) | C(13)–C(14)–C(9) | 120·3 (21) |
| C(18)–N(2)–Co | 116·9 (12) | N(1)—C(15)–C(16) | 113·5 (16) |
| C(18)–N(2)–C(8) | 119·9 (16) | C(15)–C(16)–C(17) | 113·6 (16) |
| Co—N(3)–C(20) | 114·7 (10) | C(16)–C(17)–N(3) | 114·9 (16) |
| C(17)–N(3)–Co | 115·0 (10) | C(19)–C(18)–N(2) | 109·0 (16) |
| C(17)–N(3)–C(20) | 108·7 (14) | C(20)–C(19)–C(18) | 114·2 (16) |
| | | N(3)—C(20)–C(19) | 115·1 (16) |

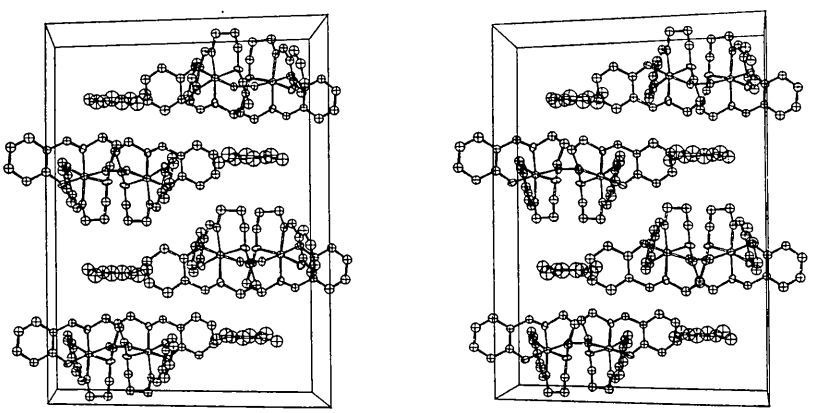

Fig. 3. Stereo diagram of contents of a unit cell (outlined), viewed down the *a* axis with *b* vertical.

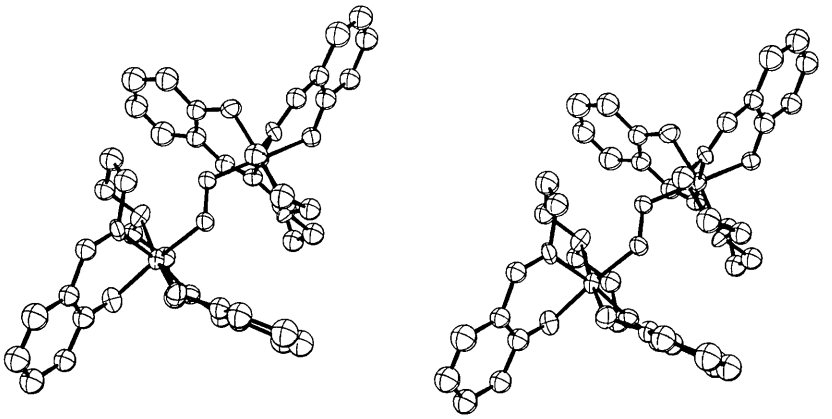

Fig. 4. Stereoscopic view of the molecule.

fined isotropically; the final values reflect the high thermal motion in this crystal. The temperature factors of the nitrogen, oxygen, and cobalt atoms were refined anisotropically. The largest mean-square displacement along a principal axis is 0·11 Å$^2$ for atom O(3); the most elliptical atom is N(3), its longest and shortest axes being 0·10 and 0·03 Å$^2$ respectively. These ellipsoids are represented graphically in Fig. 4.

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