

resolution instrument D1A. Furthermore the profile for CeF_3 was calculated at intervals of 0.05° . In this case the isotropic temperature factors of the F atoms were individually refined. The arguments in favour of $P\bar{3}c1$ are the same as with LaF_3 . Final coordinates and temperature factors are given in Table 2 and the profile is shown in Fig. 2.

Table 3. *Interatomic distances for LaF_3 and CeF_3*

	LaF_3	CeF_3
Ln—2 F(2)	2.421 (5)	2.400 (3)
Ln—1 F(3)	2.436 (8)	2.419 (5)
Ln—2 F(1)	2.467 (4)	2.445 (3)
Ln—2 F(1)	2.482 (4)	2.460 (5)
Ln—2 F(1)	2.638 (8)	2.621 (5)
Ln—2 F(1)	2.999 (5)	2.974 (4)
F(1)—1 F(1)	2.575 (6)	2.532 (4)
F(1)—1 F(1)	2.688 (7)	2.677 (4)
F(1)—1 F(2)	2.694 (4)	2.668 (3)
F(1)—2 F(1)	2.746 (6)	2.719 (2)
F(1)—1 F(3)	2.755 (5)	2.728 (3)
F(1)—1 F(2)	2.776 (5)	2.761 (2)
F(1)—1 F(2)	2.868 (4)	2.855 (3)

Discussion

Taken with the indirect evidence our results confirm that the structures of LaF_3 and CeF_3 are correctly described by $P\bar{3}c1$ and the important interatomic distances are given in Table 3. The coordination sphere of La contains nine F atoms at distances between 2.421 and 2.638 Å, with two more distant neighbours at 2.999 Å. The coordination around Ce is the same except that the distances are shorter because of the

smaller ionic radius of Ce^{3+} . Distances for CeF_3 have been calculated with our cell constants, those for LaF_3 with the values of Zalkin & Templeton (1953).

The neutron results of LaF_3 and CeF_3 are strikingly similar (Table 2). Considering the very short counting time, the restricted number of data points and the low resolution in the LaF_3 experiment, the results compare very favourably with those on CeF_3 . It is clear that profile analysis of data collected on the low resolution instrument D2 affords a rapid and reliable method for refining simple crystal structures of this type. The higher resolution and thus the more reliable determination of the background gives however a higher precision for the temperature factor refinement.

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The Crystal and Molecular Structure of N,N' -Ethylenebis(thiosalicylideneiminato)cobalt(II), the Sulphur Analogue of a Molecular Oxygen Carrier, N,N' -Ethylenebis(salicylideneiminato)cobalt (II)

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The structure of N,N' -ethylenebis(thiosalicylideneiminato)cobalt(II) has been determined from 2727 diffractometer data and refined by least-squares methods to $R=0.041$. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a=13.978(6)$, $b=15.173(7)$, $c=7.103(4)$ Å, $\beta=98.14(8)^\circ$, $D_m=1.57$, $D_c=1.59$ g cm $^{-3}$ for $Z=4$. The molecules associate to form centrosymmetric dimers, similar to those in $\text{Co}(\text{salen})$. The coordination about Co is best described as square-pyramidal with the metal atom raised 0.181(1) Å out of the basal plane toward the apical S atom. The Co–S(apical) length is 2.444(1) Å.

Introduction

Synthetic molecular oxygen carriers are the object of much study (Basolo, 1974; Henrici-Olivé & Olivé,

1974). N,N' -Ethylenebis(salicylideneiminato)cobalt(II), $\text{Co}(\text{salen})$, the 'active form' of which absorbs molecular oxygen reversibly in the solid state as well as in solution has undergone extensive investigation (Bayer &

Schretzmann, 1967), several of the inactive (Brückner, Calligaris, Nardin & Randaccio, 1969; de Iasi, Post & Holt, 1971; Calligaris, Minichelli, Nardin & Randaccio, 1970) and active forms (Schaefer & Marsh, 1969; Calligaris *et al.*, 1970) being well characterized by X-ray analysis. The active forms bind dioxygen end-on at the sixth coordination site, the fifth site being occupied by a nitrogen donor.

N,N'-Ethylenebis(thiosalicylideneiminato)cobalt(II), Co(S-salen), is inactive to oxygenation in the solid state and displays several dissimilar properties to the O analogue (van den Bergen, Corrigan, Murray, Slade & West, 1974), the structure of the oxygen complex being dimeric (Brückner *et al.*, 1969; de Iasi, *et al.*, 1971). This paper reports the crystal and molecular structure of Co(S-salen),* which preliminary photography had shown not to be isostructural with Co(salen).

Experimental

Crystal data

C₁₆H₁₄N₂S₂Co, $M = 357.4$, monoclinic, $a = 13.978$ (6), $b = 15.173$ (7), $c = 7.103$ (4) Å, $\beta = 98.14$ (8)°, $U = 1491.0$ Å³. $D_m = 1.57$ (2) g cm⁻³ (by flotation), $Z = 4$, $D_c = 1.59$ g cm⁻³. $F(000) = 732$, $\mu = 14.6$ cm⁻¹ for Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Space group $P2_1/c$ (No. 14) from systematic absences: $h0l$, l odd; $0k0$, k odd. Cell parameters were determined with a Philips PW 1100 X-ray diffractometer computer program (Gatehouse & Mislin, 1974).

Intensity measurements

Intensities were collected from a single crystal, $0.34 \times 0.33 \times 0.15$ mm, with graphite-monochromated Mo $K\alpha$ radiation. A unique data set was collected out to 2θ (Mo $K\alpha$) = 56° by the ω scan technique, with a symmetric scan range of $\pm 0.75^\circ$ in ω (with an allowance for dispersion) from the calculated Bragg angle at a scan rate of 0.05° s⁻¹. Only one reflexion was sufficiently strong to require the insertion of an attenuation filter.

3590 independent reflexions were measured; 2727 obeyed the condition $F_o^2 > 3\sigma(F_o^2)$ and were used in the subsequent calculations. Three standard reflexions, monitored at two-hourly intervals, showed no systematic variations.

The data were processed with a program specifically designed for the diffractometer (Hornstra & Stubbe, 1972). Background-corrected intensities were assigned standard deviations according to

$$\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (\rho I)^2]^{1/2}$$

where CT is the total integrated peak count obtained in scan time t_c ; B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$, and $I = CT - (t_c/t_b)(B_1 + B_2)$. The value of ρ was taken as 0.04 (Corfield, Doedens &

Ibers, 1967). Values of I and $\sigma(I)$ were then corrected for Lorentz and polarization effects but not for extinction or absorption.

Structure determination and refinement

In the least-squares refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is $1/\sigma^2(F_o)$. Scattering factors were those of Cromer & Waber (1965) for Co, S, N, C and Ibers (1962) for H, and the major programs used were *MONLS*, a modified version of the full-matrix least-squares program of Busing, Martin & Levy (1962); *MONDLS*, a block-diagonal least-squares program based on that of Shiono (1968) and the Fourier summation program of White (1965). Diagrams were drawn by *ORTEP* (Johnson, 1965). All major calculations were performed on the Monash University CDC 3200 computer.

Solution of the Patterson map yielded coordinates of the Co and S atoms, and a structure-factor calculation based on these positions gave $R_1 = 0.375$, $R_2 = 0.443$ where

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

and

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

A difference synthesis revealed all remaining non-hydrogen atoms and inclusion of these with all atoms assigned isotropic temperature factors of 3.0 Å² gave $R_1 = 0.278$, $R_2 = 0.284$. After three cycles of full-matrix least-squares refinement the positional and isotropic temperature factors converged to give $R_1 = 0.092$ and $R_2 = 0.116$. Anisotropic thermal parameters were then introduced for all atoms and after several block-diagonal least-squares cycles all parameters converged to give $R_1 = 0.047$, $R_2 = 0.063$.

A difference synthesis revealed the H atoms except those on the C atoms of the ethylenediamine bridge, which were included at idealized positions [Table 1, C-H 0.95 Å, Churchill (1973)], with isotropic thermal parameters of 5.0 Å². Block-diagonal refinement was continued with fixed H parameters and was considered complete when no parameter shift was greater than 0.1σ . The final residuals were for observed reflexions $R_1 = 0.041$, $R_2 = 0.052$; for all reflexions $R_1 = 0.060$,

Table 1. Idealized H atom positions ($\times 10^3$)

	x/a	y/b	z/c
H(C2)*	355	436	304
H(C3)	511	399	470
H(C4)	527	329	768
H(C5)	391	305	913
H(C7)	230	307	926
H(C2')	-187	474	-11
H(C3')	-347	427	-79
H(C4')	-421	352	153
H(C5')	-330	313	438
H(C7')	-195	324	662

* A preliminary report of this work appeared in *J. Inorg. Nucl. Chem. Lett.* (1975).

* H atoms are numbered according to the C atom to which they are attached.

Table 2. Final positional parameters ($\times 10^4$) and anisotropic thermal parameters [$\times 10^3$; $\times 10^4$ for Co, S(1) and S(2)] of the non-hydrogen atoms

Estimated standard deviations are in parentheses. The temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}b^*c^*kl + \dots)]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	462 (1)	4030 (1)	5445 (1)	339 (4)	198 (4)	174 (3)	16 (3)	44 (2)	11 (3)
S(1)	1688 (1)	4201 (1)	3836 (2)	366 (8)	408 (8)	302 (7)	54 (6)	97 (6)	41 (6)
S(2)	-397 (1)	4569 (1)	2876 (2)	358 (7)	229 (6)	178 (6)	3 (5)	27 (5)	0 (5)
N(1)	1225 (4)	3492 (3)	7592 (6)	47 (3)	27 (2)	25 (2)	6 (2)	1 (2)	5 (6)
N(2)	-638 (3)	3565 (3)	6446 (6)	42 (3)	29 (2)	24 (2)	-4 (2)	8 (2)	2 (2)
C(1)	2788 (4)	3928 (4)	5174 (9)	36 (3)	34 (3)	51 (4)	3 (3)	4 (3)	-7 (3)
C(2)	3617 (5)	4088 (5)	4318 (12)	43 (4)	62 (5)	77 (4)	0 (4)	18 (4)	2 (4)
C(3)	4534 (6)	3872 (7)	5248 (15)	38 (4)	90 (7)	108 (7)	-1 (4)	9 (5)	-8 (6)
C(4)	4637 (6)	3471 (7)	7016 (15)	43 (4)	83 (6)	106 (7)	7 (4)	-13 (4)	-15 (6)
C(5)	3838 (6)	3318 (6)	7887 (12)	50 (4)	70 (5)	72 (5)	7 (4)	-18 (4)	-6 (4)
C(6)	2902 (5)	3504 (4)	6997 (9)	40 (3)	36 (3)	50 (4)	4 (3)	-5 (3)	-6 (3)
C(7)	2125 (5)	3349 (4)	8056 (9)	59 (4)	38 (3)	33 (3)	9 (3)	-8 (3)	1 (3)
C(8)	604 (6)	3244 (7)	9046 (10)	60 (5)	129 (8)	38 (4)	22 (5)	17 (3)	45 (5)
C(1')	-1592 (4)	4196 (4)	2561 (8)	38 (3)	24 (3)	30 (3)	-1 (2)	0 (2)	-5 (2)
C(2')	-2153 (5)	4403 (5)	809 (10)	53 (4)	47 (4)	40 (4)	-4 (3)	-7 (3)	3 (3)
C(3')	-3103 (6)	4140 (6)	428 (11)	56 (5)	74 (6)	60 (5)	-12 (4)	-25 (4)	6 (4)
C(4')	-3532 (5)	3682 (6)	1747 (13)	37 (4)	87 (6)	79 (6)	-14 (4)	-6 (4)	2 (5)
C(5')	-3000 (5)	3476 (5)	3479 (11)	39 (4)	64 (5)	62 (5)	-10 (4)	7 (3)	1 (4)
C(6')	-2025 (4)	3733 (4)	3922 (9)	39 (3)	35 (3)	38 (3)	-3 (3)	5 (3)	-7 (3)
C(7')	-1541 (5)	3485 (4)	5769 (8)	47 (4)	37 (3)	36 (3)	-7 (3)	14 (3)	1 (3)
C(8')	-354 (6)	3181 (8)	8379 (10)	63 (5)	177 (11)	35 (4)	-30 (6)	-3 (4)	52 (6)

$R_2=0.057$. * A final difference synthesis had no major characteristics greater than $0.5 \text{ e } \text{\AA}^{-3}$. Final positional

* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. 31141 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Bond lengths (\AA) and selected angles ($^\circ$), with estimated standard deviations in parentheses

Co—S(1)	2.206 (2)	S(1)—Co—S(2)	84.2 (1)
Co—S(2)	2.195 (1)	N(1)—Co—N(2)	86.2 (2)
Co—N(1)	1.915 (4)	S(1)—Co—N(1)	94.4 (2)
Co—N(2)	1.918 (4)	S(2)—Co—N(2)	94.2 (1)
S(1)—C(1)	1.739 (6)	Co—S(1)—C(1)	112.4 (2)
S(2)—C(1')	1.748 (6)	Co—S(2)—C(1')	112.7 (2)
N(1)—C(7)	1.273 (9)	Co—N(1)—C(7)	134.2 (4)
N(2)—C(7')	1.291 (8)	Co—N(1)—C(8)	110.3 (4)
N(1)—C(8)	1.488 (10)	Co—N(2)—C(7')	133.6 (4)
N(2)—C(8')	1.492 (9)	Co—N(2)—C(8')	111.2 (4)
Co—S(2')	2.444 (1)	S(1)—C(1)—C(6)	125.2 (5)
C(1)—C(2)	1.404 (10)	S(2)—C(1')—C(6')	124.9 (4)
C(2)—C(3)	1.395 (11)	C(1')—C(2')—C(3')	120.6 (7)
C(3)—C(4)	1.385 (15)	C(2')—C(3')—C(4')	121.1 (8)
C(4)—C(5)	1.371 (13)	C(3')—C(4')—C(5')	119.4 (8)
C(5)—C(6)	1.411 (10)	C(4')—C(5')—C(6')	121.2 (7)
C(6)—C(1)	1.411 (9)	C(5')—C(6')—C(1')	118.9 (6)
C(6)—C(7)	1.435 (10)	C(6')—C(1')—C(2')	118.7 (6)
C(1')—C(2')	1.409 (9)	C(1')—C(6')—C(7')	124.6 (5)
C(2')—C(3')	1.376 (11)	N(2)—C(8')—C(8)	114.4 (7)
C(3')—C(4')	1.371 (13)	N(1)—C(7)—C(6)	128.5 (6)
C(4')—C(5')	1.380 (11)	N(2)—C(7')—C(6')	128.6 (6)
C(5')—C(6')	1.410 (9)	C(1)—C(2)—C(3)	120.9 (7)
C(6')—C(1')	1.400 (9)	C(2)—C(3)—C(4)	120.2 (9)
C(6')—C(7')	1.438 (8)	C(3)—C(4)—C(5)	119.8 (9)
C(8)—C(8')	1.359 (11)	C(4)—C(5)—C(6)	121.4 (8)
		C(5)—C(6)—C(1)	119.2 (6)
		C(6)—C(1)—C(2)	118.5 (6)
		C(1)—C(6)—C(7)	124.7 (6)
		N(1)—C(8)—C(8')	114.7 (7)

and thermal parameters are in Table 2, with their estimated standard deviations derived from the inverse least-squares matrix. Bond lengths and angles are in Table 3.

Results and discussion

The asymmetric unit contains one Co(S-salen) unit, but the structure can be more accurately described as

Table 4. Equations of least-squares planes and distances of individual atoms (\AA) from the planes

X , Y and Z are coordinates in \AA referred to an orthogonal system of axes having X along a , Y in the ab plane and Z along c^* . Fractional coordinates x, y, z in the system are related to X, Y, Z by the matrix equation

$$\begin{bmatrix} 13.978 & 0 & -1.006 \\ 0 & 15.172 & 0 \\ 0 & 0 & 7.031 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

(I) Plane through S(1), S(2), N(1), N(2)

$$0.0071X - 0.8937Y - 0.4485Z + 7.0003 = 0$$

Co	-0.181 (1)	S(2)	-0.109 (1)
		N(1)	-0.122 (4)
S(1)	0.108 (1)	N(2)	0.123 (4)

(II) Plane through C(1)—C(7), S(1)

$$-0.0240X - 0.9109Y - 0.4120Z + 6.9943 = 0$$

S(1)	0.030 (1)	C(4)	0.027 (11)
C(1)	-0.014 (6)	C(5)	0.015 (9)
C(2)	-0.017 (8)	C(6)	-0.005 (6)
C(3)	-0.017 (11)	C(7)	-0.019 (6)

(III) Plane through C(1')—C(7'), S(2)

$$0.3415X - 0.8605Y - 0.3780Z + 7.0156 = 0$$

S(2)	-0.003 (1)	C(4')	-0.002 (9)
C(1')	0.009 (6)	C(5')	0.001 (7)
C(2')	-0.003 (7)	C(6')	-0.002 (6)
C(3')	0.001 (9)	C(7')	-0.001 (6)

being built of discrete centrosymmetric dimers (Fig. 1), the dimeric structure being essentially the same as in the inactive form of Co(salen) (Brückner *et al.*, 1969; de Iasi *et al.*, 1971). Fig. 1 also indicates the labelling of the atoms. Dimerization occurs through the sharing of one S atom from each S-salen ligand, with two Co atoms, the Co-S apical bond being 2.444 (1) Å. The Co...Co distance in the dimer is 3.24 Å.

Coordination about Co is best described as square pyramidal with the metal atom displaced 0.181 (1) Å

from the plane of the four coordinating atoms towards the apical S atom of the second molecule (Table 4).

In Co(salen) the Co-O lengths differ by 0.07 Å, the lengthening being ascribed to the additional coordination bond in which one of the O atoms is involved, but in the present compound there is no significant difference between the two Co-S bonds, 2.206 (2) and 2.195 (1) Å, but they are longer than that found in the monomeric Co(II) complex, Co (SacSac)₂, 2.16 Å (Beckett & Hoskins, 1967).

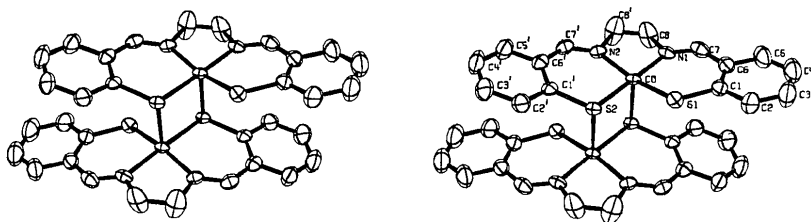


Fig. 1. A stereoscopic view of the molecular dimer. Thermal ellipsoids for all atoms have been drawn at the 50% probability level. H atoms have been omitted for clarity.

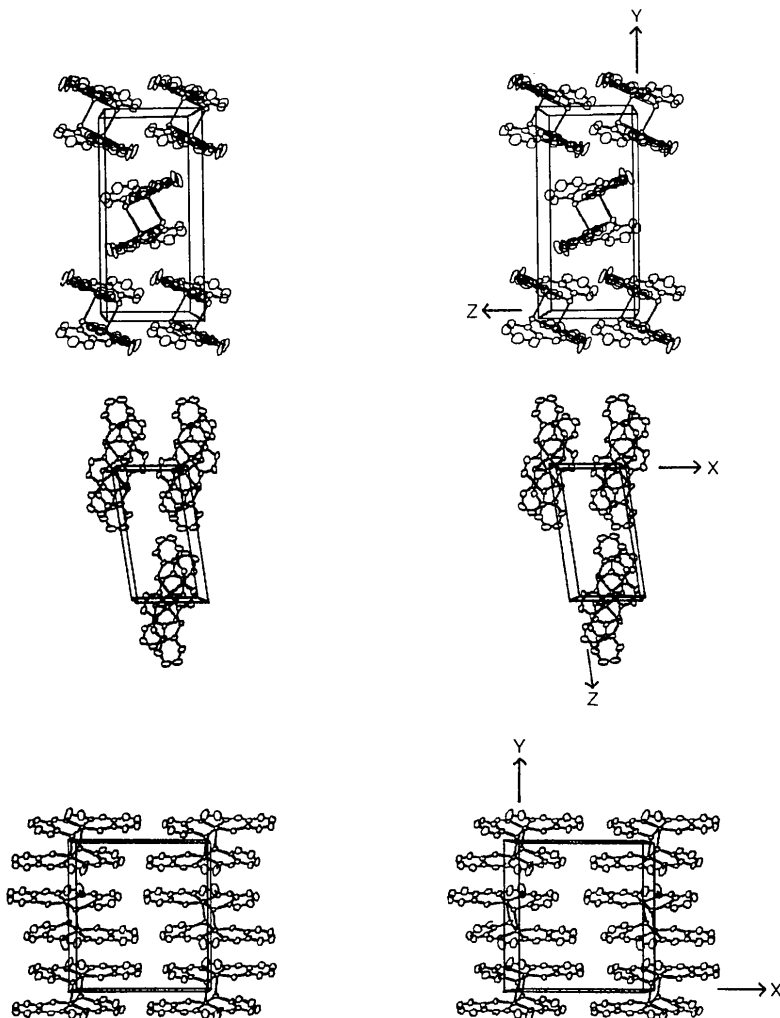


Fig. 2. Molecular packing diagrams, viewed down a, b and c respectively.

The difference in length between the Co-S(2') bridge bond and the Co-S(1) coordination bond is *ca* 0.24 Å, whereas in the O analogue the difference is *ca* 0.35 Å, implying that the S dimer is more strongly bonded. This may explain why Co(S-salen) is not coordinated by pyridine and its low oxygen sensitivity in solution (van den Bergen *et al.*, 1974) compared with Co(salen).

Bond lengths within the ligand, excluding the C-S lengths which are normal (Table 3), are essentially the same as those found in the salen ligand in several related complexes (Calligaris, Nardin & Randaccio, 1972), the major apparent exception being the very short C(8)-C(8') length, 1.359 (11) Å. This shortening is due to considerable librational movement of these two atoms, as can be seen in Fig. 1. Correction of the bond length for this thermal motion (Busing, Martin & Levy, 1964) yields the more reasonable value, 1.498 (8) Å. It is not apparent at this stage if this anomalous behaviour is due entirely to thermal motion or slight disorder of the ethylenic C atoms.

Bond angles around Co are similar to those in Co(salen), S-Co-S being slightly closed in comparison with O-Co-O and the other three coordination angles being slightly more open compared with those in Co(salen). Bond angles within the S-salen ligand are comparable to those in the salen ligand of Co(salen) (Brückner *et al.*, 1969) with three notable differences. The Co-S-C angles (Table 3) have closed by more than 10° compared with the corresponding angles in Co(salen) [128.4 (10) and 123.2 (8)°], and the N-C7(C7')-C6(C6') angles have opened by *ca* 4°. These differences may be ascribed to the dissimilarity in coordination and C-X (X=S or O) lengths in Co(S-salen) and Co(salen), the remainder of the ligand being relatively rigid, due to electron delocalization, and less capable of dissipating bond length change. The other deviation in bond angle is around the ethylenic C(8) and C(8'), these angles having opened up some 8° with respect to the corresponding angles in Co(salen). This change may not be significant because of the large thermal excursions of these atoms.

Table 5. Intermolecular distances (Å) within the dimeric unit

Second atom is related to the first by the symmetry code $-x, 1-y, 1-z$.

Co-S(2)	2.445	S(2)-C(8)	3.584
Co-Co	3.240	S(2)-C(8')	3.717
Co-C(1')	3.333	S(2)-C(7)	3.975
Co-N(2)	3.908	C(1)-C(1')	3.774
S(1)-C(6')	3.517	C(1)-C(6')	3.786
S(1)-C(7')	3.530	C(6)-C(2')	3.705
S(1)-C(1')	3.547	C(6)-C(1')	3.926
S(1)-S(2)	3.659	C(6)-C(3')	3.958
S(1)-N(2)	3.688	C(7)-C(2')	3.504
S(2)-N(1)	3.162	C(7)-C(1')	3.812
S(2)-N(2)	3.185	N(1)-C(1')	3.549
S(2)-S(2)	3.331	N(1)-C(2')	3.571

The closest intermolecular approach between dimers is C(8')-N(2) ($x, \frac{1}{2}-y, \frac{1}{2}+z$) 3.488 Å; the closest Co-S contact between dimers is Co-S(1) ($x, \frac{1}{2}-y, \frac{1}{2}+z$) of 5.62 Å.

The close approach of the two molecules in the dimer necessitates the bending away of the two halves of the S-salen ligand in an umbrella conformation, the angle between the two planes (Table 4) being 21.4°, which is very similar to the 22.2° found in Co(salen). Intermolecular contact distances less than 4.0 Å in the dimer are in Table 5. Fig. 2 gives a view of the packing down each axial direction, indicating that within the crystal, as in Co(salen), no voids are present, thus rendering the complex, in the solid state, less susceptible to oxygen attack.

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