phénomène a aussi été observé par Yawney *et al.* (1973) dans le propionate de cuivre solvaté par la *p*-toluidine.

Si nous excluons de la comparaison des distances celles des carbones du bout de la chaîne carbonée des ions propionates, le Tableau 4 montre que les propionates de cuivre solvatés par la pyridine et les picolines ont des points communs: l'entourage du cuivre est constitué de quatre atomes d'oxygène distants en moyenne de 1,970 Å, d'un atome d'azote situé à 2,161 Å et de l'autre atome de cuivre du dimère, qui est placé à 2,642 Å. On constate aussi que la distance Cu···Cu varie dans le même sens que la distance Cu···N à l'intérieur d'un même composé. A travers ces solvates, les caractéristiques moyennes de l'ion propionate sont: C(1)–O = 1,249, C(1)–C(2) = 1,536 et C(2)–C(3) = 1,505 Å [en excluant les valeurs faussées par une agitation thermique importante de l'atome C(3)], O–C(1)–O = 125,6, O–C(1)–C(2) = 117 et C(1)–C(2)–C(3) = 112,8°.

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Structural Chemistry of the $\{CoNO\}^8$ Group. III.* The Structure of *N,N'*-Ethylenebis(salicylideneiminato)nitrosylcobalt(II), Co(NO)(salen)†

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The crystal and molecular structure of Co(NO)(salen), $C_{16}H_{14}N_3O_3Co$, has been determined by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/c$ with eight molecules in a cell of dimensions $a = 14{\cdot}417$ (7), $b = 11{\cdot}982$ (7), $c = 17{\cdot}481$ (9) Å, and $\beta = 100{\cdot}39$ (4)°. Least-squares refinement of the structure based on the 4479 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ gave a conventional R factor of 0·048. The two crystallographically independent molecules have nearly identical five-coordinate tetragonal-pyramidal coordination about the Co atoms with the nitrosyl occupying the apical position in a bent geometry [Co–N–O = 127·0 (4)°]. In contrast, the salen ligands of the two independent molecules have significantly different conformations which are attributed to crystal packing.

Introduction

The preparation of *N,N'*-ethylenebis(salicyclideneiminato)cobalt(II), Co(salen), was described by Tsumaki (1938). This complex, as well as many other Schiff-base complexes of cobalt, has since been extensively studied, largely because of the ability of many of these to reversibly bind dioxygen. Structural, spectroscopic and thermodynamic studies have shown that the stabilities of dioxygen adducts of Schiff-base complexes of cobalt(II) are very dependent upon the nature of the Schiff base and upon crystal-packing effects (Avdeef & Schaefer, 1976, and references therein).

A quite different behavior is found for reactions of nitric oxide (NO) with Schiff-base complexes of transition metals. A study of several Co(salen) com-

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* Part II: Johnson, Enemark, Feltham & Swedo (1976).

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plexes which have various phenyl ring substituents showed that all react irreversibly with nitric oxide to form diamagnetic 1:1 adducts such as Co(NO)(salen) (Earnshaw, Hewlett & Larkworthy, 1965). On the other hand, the stability and magnetic properties of NO adducts of analogous iron complexes of salen ligands are very dependent upon the substituents on the phenyl rings of the salen ligand (Earnshaw, King & Larkworthy, 1968). As part of a continuing interest in metal nitrosyl complexes we have undertaken structural investigations of some *M*(NO)(salen) complexes. Herein, we describe the structure of Co(NO)(salen).

Experimental

A sample of Co(NO)(salen) prepared by the method of Earnshaw, Hewlett & Larkworthy (1965) and recrystallized from DMF/MeOH was kindly furnished by Dr O. Ileperuma. Preliminary precession photographs (Mo *Kα*) on a multi-faceted crystal of approximate dimensions 0·5 × 0·5 × 0·5 mm indicated that the crystals are monoclinic. The systematic absences of $h0l$ when $l = 2n + 1$, and $0k0$ when $k = 2n + 1$ are unique for the space group $P2_1/c$ (No. 14). The unit-cell parameters (at 23 ±2°C) are a = 14·417 (7), b = 11·982 (7), c = 17·481 (9) Å, and β = 100·39 (4)°. These parameters were determined from a least-squares refinement of the setting angles of twenty automatically centered reflections from diverse regions of reciprocal space having $2\theta \simeq 35°$ (Mo $K\bar{\alpha}$, λ = 0·71069 Å). The observed density of 1·59 g cm^{-3}, determined by flotation in carbon tetrachloride/*n*-heptane, agrees with the calculated density of 1·59 g cm^{-3} for eight formula units of Co(NO)(salen) per unit cell. Thus, there are two formula units per asymmetric unit.

The crystal used for the preliminary precession photographs was also utilized for data collection, and 5900 unique data were collected on a Picker FACS-I four-circle diffractometer using an incident-beam monochromator equipped with a graphite crystal to obtain Mo *Kα* radiation. The take-off angle was 2·0° and the reflections were collected using the θ–2θ scan technique. The scan range was 1·4° plus the dispersion correction for the splitting of the Mo *Kα* lines. The scan rate was 2·0° min^{-1}, and stationary-crystal, stationary-counter background counts of 10 s were taken at both ends of the scan. The scintillation counter was 34 cm from the crystal with an aperture of 4 × 4 mm. The pulse-height analyzer was set to admit ~90% of the Mo *Kα* peak. Metal foil attenuators having attenuator factors of ~1·7 were inserted into the diffracted beam whenever the counting rate exceeded ~7000 counts s^{-1}. Throughout data collection three standard reflections from diverse regions of reciprocal space were monitored every 100 reflections. None of the standard reflections showed any systematic changes during the time required to collect the data.

The data were reduced to F_o^2 and $\sigma(F_o^2)$ by procedures similar to those previously described (Enemark, Hunt, Reed, Steuck & Walthers, 1970). The intensities were calculated by $I = C - (t_s/t_b)(\mathrm{BH} + \mathrm{BL})$,

Table 1. *Final atomic parameters for molecule* I

x, y, and z are in fractional monoclinic coordinates. The standard deviation of the least significant digit is given in parentheses.

	x	y	z
Co	1·04042 (4)	0·35050 (4)	1·03480 (3)
O(1)	1·09343 (27)	0·40798 (26)	1·13260 (22)
O(2)	1·1507 (3)	0·40252 (25)	1·00351 (24)
O(3)	1·0394 (4)	0·1332 (3)	1·02495 (29)
N(1)	0·9210 (4)	0·33212 (28)	1·06081 (29)
N(2)	0·9773 (4)	0·3336 (3)	0·9316 (3)
N(3)	1·0774 (3)	0·2064 (3)	1·04753 (29)
C(1)	1·0520 (4)	0·4221 (3)	1·1911 (4)
C(2)	1·1043 (5)	0·4701 (4)	1·2616 (3)
C(3)	1·0658 (6)	0·4875 (5)	1·3249 (4)
C(4)	0·9721 (5)	0·4581 (4)	1·3268 (4)
C(5)	0·9197 (6)	0·4150 (4)	1·2593 (4)
C(6)	0·9559 (5)	0·3965 (4)	1·1936 (4)
C(7)	0·8955 (5)	0·3538 (4)	1·1246 (4)
C(8)	0·8508 (4)	0·2841 (4)	0·9967 (4)
C(9)	0·8719 (4)	0·3319 (4)	0·9244 (4)
C(10)	1·0133 (6)	0·3255 (4)	0·8738 (4)
C(11)	1·1148 (6)	0·3389 (3)	0·8699 (4)
C(12)	1·1471 (8)	0·3178 (4)	0·8028 (6)
C(13)	1·2376 (6)	0·3359 (4)	0·7973 (6)
C(14)	1·2995 (8)	0·3791 (5)	0·8630 (6)
C(15)	1·2698 (7)	0·4026 (4)	0·9300 (5)
C(16)	1·1760 (6)	0·3813 (3)	0·9386 (4)

Table 2. *Final atomic parameters for molecule* II

x, y, and z are in fractional monoclinic coordinates. The standard deviation of the least significant digit is given in parentheses.

	x	y	z
Co′	0·58245 (4)	0·04665 (3)	0·91981 (3)
O(1)′	0·54315 (24)	0·17467 (19)	0·96564 (18)
O(2)′	0·48001 (19)	0·07887 (17)	0·84078 (16)
O(3)′	0·75107 (27)	0·0681 (3)	0·8797 (3)
N(1)′	0·65205 (25)	−0·00929 (24)	1·01398 (20)
N(2)′	0·60022 (25)	−0·09590 (22)	0·88101 (22)
N(3)′	0·6802 (3)	0·11111 (29)	0·8852 (3)
C(1)′	0·5773 (3)	0·2175 (3)	1·03457 (26)
C(2)′	0·5456 (4)	0·3207 (3)	1·0540 (3)
C(3)′	0·5769 (5)	0·3683 (4)	1·1260 (4)
C(4)′	0·6446 (5)	0·3116 (4)	1·1806 (3)
C(5)′	0·6735 (4)	0·2109 (4)	1·16458 (27)
C(6)′	0·6446 (3)	0·1578 (3)	1·09069 (26)
C(7)′	0·6728 (3)	0·0466 (3)	1·07836 (25)
C(8)′	0·6729 (4)	−0·1281 (3)	1·0131 (3)
C(9)′	0·6752 (4)	−0·1622 (3)	0·9304 (3)
C(10)′	0·5606 (3)	−0·13869 (26)	0·81469 (28)
C(11)′	0·48865 (28)	−0·08081 (26)	0·76029 (26)
C(12)′	0·4533 (3)	−0·13880 (29)	0·68912 (29)
C(13)′	0·3784 (3)	−0·0926 (4)	0·63890 (28)
C(14)′	0·3381 (3)	0·0040 (3)	0·65678 (27)
C(15)′	0·37153 (29)	0·06112 (27)	0·72548 (26)
C(16)′	0·45003 (28)	0·01975 (26)	0·77743 (23)

where C is the total count, t_s and t_b are the scan time and the total background time, and BH and BL are the two background counts. After the backgrounds had been subtracted from the intensities, standard deviations were assigned by the formula $\sigma(I) = [C + (t_s/t_b)^2(\mathrm{BH} + \mathrm{BL}) + (pI)^2]^{1/2}$, where p, the factor to prevent overweighting strong reflections, was set equal to 0·04. The Lorentz and polarization corrections and the attenuator factors were then applied to I and $\sigma(I)$. The polarization correction was $p = (\cos^2 2\theta_m + \cos^2 2\theta)/(1 + \cos^2 2\theta_m)$, where θ_m is the Bragg angle of the monochromator crystal and θ is the Bragg angle of the reflection being observed. Since the linear absorption coefficient for the compound for Mo $K\alpha$ radiation is only 7·7 cm^{-1} and the crystal was of equant habit, no absorption correction was applied.

Table 3. *Fixed atom positions for the hydrogen atoms*

x, y, and z are in fractional monoclinic coordinates.

	x	y	z
H(2)	1·1686	0·4901	1·2630
H(3)	1·1032	0·5208	1·3692
H(4)	0·9458	0·4669	1·3729
H(5)	0·8552	0·3980	1·2585
H(7)	0·8304	0·3412	1·1288
H(8*A*)	0·7875	0·2976	1·0033
H(8*B*)	0·8508	0·2048	0·9969
H(9*A*)	0·8442	0·4033	0·9136
H(9*B*)	0·8416	0·2921	0·8798
H(10)	0·9726	0·3088	0·8262
H(12)	1·1051	0·2882	0·7592
H(13)	1·2590	0·3199	0·7502
H(14)	1·3644	0·3924	0·8584
H(15)	1·3127	0·4328	0·9721
H(2)′	0·5003	0·3597	1·0175
H(3)′	0·5539	0·4391	1·1378
H(4)′	0·6695	0·3454	1·2292
H(5)′	0·7158	0·1722	1·2038
H(7)′	0·7110	0·0101	1·1213
H(8*A*)′	0·6287	−0·1716	1·0352
H(8*B*)′	0·7293	−0·1472	1·0478
H(9*A*)′	0·6682	−0·2403	0·9220
H(9*B*)′	0·7358	−0·1517	0·9167
H(10)′	0·5790	−0·2114	0·8015
H(12)′	0·4803	−0·2074	0·6772
H(13)′	0·3548	−0·1287	0·5909
H(14)′	0·2855	0·0334	0·6218
H(15)′	0·3416	0·1278	0·7373

The structure was solved by direct methods using the *MULTAN* package and the 400 reflections with the highest values of $|E|$. An E map based upon these reflections revealed both Co, four O, and four N atoms. A series of structure factor calculations, least-squares refinements, and electron-density difference maps revealed the other 36 non-hydrogen atoms.

Refinement of the complete structure was based on F_o with the function $\Sigma\, w(|F_o| - |F_c|)^2$ being minimized; the weights were taken as $w = 4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors for the non-hydrogen atoms were taken from Cromer & Mann (1968). The effects of anomalous scattering for the Co atoms were included in the calculated structure factors; the values of $\Delta f'$ and $\Delta f''$ calculated by Cromer & Liberman (1970) were used. All refinements were carried out using the 4479 data with $F_o^2 > 3\sigma(F_o^2)$. Two cycles of full-matrix isotropic least-squares refinement resulted in $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}095$ and $R_2 = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2]^{1/2} = 0{\cdot}124$. Owing to limitations of core memory it was not possible to do full-matrix anisotropic refinement on all non-hydrogen atoms; therefore, in subsequent cycles the two independent molecules were refined as separate blocks. Initially only the scale factor was common to both blocks. Three cycles of anisotropic refinement on each block gave $R_1 = 0{\cdot}062$ and $R_2 = 0{\cdot}081$. The 28 H atoms were included in idealized positions (C—H distance 0·95 Å)

Table 4. *Selected interatomic distances* (Å) *and angles* (°) *in molecule* I

Co—O(1)	1·873 (3)	O(2)—C(16)	1·278 (12)	C(16)—C(15)	1·411 (17)	C(4)—C(5)	1·381 (7)
Co—O(2)	1·879 (6)	N(1)—C(7)	1·263 (11)	C(1)—C(6)	1·426 (12)	C(13)—C(12)	1·343 (18)
Co—N(1)	1·871 (7)	N(2)—C(10)	1·220 (11)	C(16)—C(11)	1·447 (6)	C(5)—C(6)	1·362 (14)
Co—N(2)	1·879 (4)	N(1)—C(8)	1·483 (4)	C(2)—C(3)	1·342 (13)	C(12)—C(11)	1·362 (17)
Co—N(3)	1·809 (4)	N(2)—C(9)	1·502 (9)	C(15)—C(14)	1·347 (19)	C(6)—C(7)	1·447 (6)
N(3)—O(3)	1·071 (4)	C(8)—C(9)	1·470 (11)	C(3)—C(4)	1·402 (13)	C(11)—C(10)	1·487 (14)
O(1)—C(1)	1·286 (9)	C(1)—C(2)	1·443 (6)	C(14)—C(13)	1·418 (9)		

Co—N(3)—O(3)	128·0 (3)	O(1)—C(1)—C(2)	119·0 (6)	C(13)—C(12)—C(11)	121·3 (7)
O(1)—Co—O(2)	85·21 (18)	O(2)—C(16)—C(15)	119·4 (5)	C(5)—C(6)—C(1)	120·8 (5)
O(1)—Co—N(1)	93·63 (21)	O(1)—C(1)—C(6)	126·1 (5)	C(12)—C(11)—C(16)	121·9 (10)
O(1)—Co—N(2)	164·33 (15)	O(2)—C(16)—C(11)	125·3 (9)	C(5)—C(6)—C(7)	119·7 (9)
O(2)—Co—N(2)	92·59 (24)	C(6)—C(1)—C(2)	114·9 (8)	C(12)—C(11)—C(10)	120·8 (6)
O(2)—Co—N(1)	166·86 (15)	C(11)—C(16)—C(15)	115·3 (10)	C(1)—C(6)—C(7)	119·5 (8)
N(1)—Co—N(2)	85·00 (23)	C(1)—C(2)—C(3)	122·4 (8)	C(16)—C(11)—C(10)	117·2 (9)
Co—O(1)—C(1)	127·1 (4)	C(16)—C(15)—C(14)	121·1 (7)	C(6)—C(7)—N(1)	125·6 (8)
Co—O(2)—C(16)	125·7 (4)	C(2)—C(3)—C(4)	121·6 (5)	C(11)—C(10)—N(2)	126·8 (5)
Co—N(1)—C(7)	128·1 (4)	C(15)—C(14)—C(13)	121·9 (13)	C(7)—N(1)—C(8)	118·7 (7)
Co—N(2)—C(10)	126·8 (6)	C(3)—C(4)—C(5)	117·0 (9)	C(10)—N(2)—C(9)	120·3 (5)
Co—N(1)—C(8)	113·2 (5)	C(14)—C(13)—C(12)	118·6 (13)	N(1)—C(8)—C(9)	106·3 (5)
Co—N(2)—C(9)	113·0 (5)	C(4)—C(5)—C(6)	123·2 (9)	N(2)—C(9)—C(8)	107·2 (3)

Table 5. *Selected interatomic distances* (Å) *and angles* (°) *in molecule* II

Co′–O(1)′	1·865 (3)	O(2)′–C(16)′	1·320 (4)	C(16)′–C(15)′	1·407 (4)	C(4)′–C(5)′	1·323 (7)
Co′–O(2)′	1·8715 (19)	N(1)′–C(7)′	1·297 (5)	C(1)′–C(6)′	1·439 (5)	C(13)′–C(12)′	1·379 (5)
Co′–N(1)′	1·8893 (26)	N(2)′–C(10)′	1·302 (5)	C(16)′–C(11)′	1·383 (5)	C(5)′–C(6)′	1·433 (6)
Co′–N(2)′	1·872 (3)	N(1)′–C(8)′	1·455 (5)	C(2)′–C(3)′	1·381 (6)	C(12)′–C(11)′	1·436 (5)
Co′–N(3)′	1·805 (6)	N(2)′–C(9)′	1·485 (4)	C(15)′–C(14)′	1·391 (5)	C(6)′–C(7)′	1·421 (6)
N(3)′–O(3)′	1·163 (7)	C(8)′–C(9)′	1·509 (10)	C(3)′–C(4)′	1·410 (7)	C(11)′–C(10)′	1·451 (4)
O(1)′–C(1)′	1·321 (4)	C(1)′–C(2)′	1·381 (6)	C(14)′–C(13)′	1·356 (6)		

Co′–N(3)′–O(3)′	126·0 (3)	O(1)′–C(1)′–C(2)′	119·1 (3)	C(13)′–C(12)′–C(11)′	118·2 (4)
O(1)′–Co′–O(2)′	83·51 (10)	O(2)′–C(16)′–C(15)′	117·1 (4)	C(5)′–C(6)′–C(1)′	116·4 (4)
O(1)′–Co′–N(1)′	94·14 (14)	O(1)′–C(1)′–C(6)′	121·5 (4)	C(12)′–C(11)′–C(16)′	121·04 (26)
O(1)′–Co′–N(2)′	167·89 (19)	O(2)′–C(16)′–C(11)′	124·45 (25)	C(5)′–C(6)′–C(7)′	120·5 (3)
O(2)′–Co′–N(2)′	93·56 (10)	C(6)′–C(1)′–C(2)′	119·3 (3)	C(12)′–C(11)′–C(10)′	115·9 (3)
O(2)′–Co′–N(1)′	160·16 (17)	C(11)′–C(16)′–C(15)′	118·40 (29)	C(1)′–C(6)′–C(7)′	122·7 (3)
N(1)′–Co′–N(2)′	84·61 (13)	C(1)′–C(2)′–C(3)′	121·7 (4)	C(16)′–C(11)′–C(10)′	122·9 (3)
Co′–O(1)′–C(1)′	128·29 (24)	C(16)′–C(15)′–C(14)′	119·8 (4)	C(6)′–C(7)′–N(1)′	126·00 (29)
Co′–O(2)′–C(16)′	127·15 (23)	C(2)′–C(3)′–C(4)′	119·3 (5)	C(11)′–C(10)′–N(2)′	122·9 (3)
Co′–N(1)′–C(7)′	125·16 (27)	C(15)′–C(14)′–C(13)′	121·51 (29)	C(7)′–N(1)′–C(8)′	119·9 (3)
Co′–N(2)–C(10)′	127·96 (21)	C(3)′–C(4)′–C(5)′	120·2 (4)	C(10)′–N(2)′–C(9)′	117·6 (3)
Co′–N(1)′–C(8)′	114·59 (23)	C(14)′–C(13)′–C(12)′	121·0 (3)	N(1)′–C(8)′–C(9)′	108·4 (3)
Co′–N(2)′–C(9)′	114·19 (24)	C(4)′–C(5)′–C(6)′	122·9 (4)	N(2)′–C(9)′–C(8)′	105·8 (5)

(Churchill, 1973), and given isotropic temperature factors of 6 Å^2, for the ethylene H atoms, or 5 Å^2, for all other H atoms. The H atom scattering factors were obtained from the calculation of Stewart, Davidson & Simpson (1965). Three more cycles of refinement on each block including the H atoms as fixed contributions gave $R_1 = 0{\cdot}053$ and $R_2 = 0{\cdot}066$; however, the temperature factor of C(13) became non-positive definite. An inspection of F_o's and F_c's indicated that secondary extinction (Stout & Jensen, 1968) was a problem in the crystal. At this point the temperature factor of C(13) was reset to its isotropic value, and both Co atoms, the scale factor, and the secondary-extinction coefficient were incuded in both blocks of the refinement. Two cycles of least-squares refinement on each block converged with $R_1 = 0{\cdot}048$ and $R_2 = 0{\cdot}058$.

The final value for the secondary-extinction coefficient (c) was $1{\cdot}00\,(4) \times 10^{-6}$ (mm^{-1} e^{-2}). This parameter enters the equation for the calculated structure factor in the form (Zachariasen, 1968) $F_c = zF_o$, where $z = \{c\beta C + [1 + (c\beta C)^2]^{1/2}\}^{1/2}$, $\beta = 2(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)$, and $\Sigma\, w(|F_o| - |F_c|/z)^2$ is minimized. With secondary extinction included all the temperature factors remained positive definite.

During the final cycle of least-squares refinement, all of the parameter shifts were less than $0{\cdot}8\sigma$ except for

Table 6. *Root-mean-square amplitudes of vibration* (*in* Å)

	Minimum	Intermediate	Maximum		Minimum	Intermediate	Maximum
Co	0·1678 (7)	0·2055 (10)	0·2332 (11)	Co′	0·1736 (6)	0·1832 (15)	0·1904 (9)
O(1)	0·165 (15)	0·208 (4)	0·280 (4)	O(1)′	0·1904 (28)	0·207 (3)	0·294 (9)
O(2)	0·180 (9)	0·227 (7)	0·274 (4)	O(2)′	0·162 (5)	0·1869 (26)	0·242 (8)
O(3)	0·240 (4)	0·315 (4)	0·472 (13)	O(3)′	0·132 (27)	0·302 (5)	0·312 (4)
N(1)	0·172 (6)	0·226 (8)	0·260 (8)	N(1)′	0·177 (7)	0·201 (8)	0·225 (4)
N(2)	0·166 (19)	0·209 (4)	0·230 (7)	N(2)′	0·175 (4)	0·205 (3)	0·230 (11)
N(3)	0·220 (4)	0·236 (4)	0·335 (12)	N(3)′	0·188 (9)	0·228 (4)	0·288 (11)
C(1)	0·185 (18)	0·206 (4)	0·234 (12)	C(1)′	0·158 (22)	0·197 (4)	0·244 (4)
C(2)	0·211 (5)	0·228 (23)	0·280 (6)	C(2)′	0·204 (8)	0·214 (16)	0·269 (4)
C(3)	0·211 (19)	0·257 (10)	0·308 (8)	C(3)′	0·180 (12)	0·242 (15)	0·325 (5)
C(4)	0·11 (6)	0·282 (6)	0·291 (5)	C(4)′	0·189 (5)	0·221 (18)	0·384 (8)
C(5)	0·244 (6)	0·256 (24)	0·266 (5)	C(5)′	0·182 (12)	0·205 (8)	0·298 (5)
C(6)	0·204 (4)	0·232 (5)	0·258 (24)	C(6)′	0·155 (20)	0·195 (4)	0·263 (5)
C(7)	0·141 (23)	0·233 (4)	0·259 (7)	C(7)′	0·164 (15)	0·195 (4)	0·263 (6)
C(8)	0·177 (5)	0·288 (13)	0·335 (7)	C(8)′	0·181 (4)	0·223 (19)	0·270 (4)
C(9)	0·172 (4)	0·248 (12)	0·316 (9)	C(9)′	0·172 (5)	0·245 (4)	0·306 (14)
C(10)	0·203 (5)	0·222 (5)	0·258 (29)	C(10)′	0·173 (8)	0·182 (12)	0·237 (4)
C(11)	0·183 (14)	0·191 (28)	0·252 (5)	C(11)′	0·174 (4)	0·191 (12)	0·218 (5)
C(12)	0·216 (7)	0·26 (4)	0·292 (5)	C(12)′	0·172 (9)	0·204 (13)	0·255 (4)
C(13)	0·09 (8)	0·257 (10)	0·369 (6)	C(13)′	0·173 (4)	0·224 (14)	0·293 (6)
C(14)	0·226 (9)	0·256 (19)	0·371 (13)	C(14)′	0·186 (4)	0·232 (12)	0·243 (8)
C(15)	0·211 (26)	0·232 (10)	0·288 (7)	C(15)′	0·187 (6)	0·200 (4)	0·219 (11)
C(16)	0·201 (5)	0·229 (10)	0·235 (16)	C(16)′	0·150 (14)	0·194 (4)	0·212 (7)

β_{13} of C(13) which shifted by 1·2σ. The largest peak in the final difference electron density map was 0·34 e Å^{-3}. The standard deviation of an observation of unit weight, defined by $[\Sigma w(|F_o| - |F_c|)^2/(n-m)]^{1/2}$, was 2·11. Here n is the number of observations (4479) and m is the number of variables (416); the ratio $n:m$ was 10·8:1. An analysis of the weighting scheme showed that $w(\Delta F)^2$ was not dependent upon $|F_o|$ or $\sin\theta/\lambda$. Careful examination of the difference electron density maps in the nitrosyl regions did not reveal any disorder. A structure factor calculation on all 5900 reflections gave $R_1 = 0{\cdot}064$ and $R_2 = 0{\cdot}060$.*

The final positional parameters are given in Tables 1 and 2, and the positions of the fixed H atoms are given in Table 3. Selected interatomic distances and angles are given in Tables 4 and 5. The r.m.s. amplitudes of vibration along the principal axes are given in Table 6.

The major programs used for the solution and refinement of this structure were local modifications of the *MULTAN* direct-methods program (Germain, Main & Woolfson, 1971), Ibers's *NUCLS* least-squares program, itself a modification of *ORFLS* (Busing, Martin & Levy, 1962), and Zalkin's *FORDAP* Fourier summation program. Molecular diagrams were drawn with the program *ORTEP* (Johnson, 1965). All major calculations were performed on the University of Arizona CDC 6400 computer.

Description

The crystal structure consists of discrete molecules of Co(NO)(salen). Perspective views of the two molecules with the numbering schemes are given in Fig. 1. Both independent molecules have five-coordinate tetragonal-pyramidal coordination about the Co atoms with the nitrosyl group in the axial position. The nearest contacts to the vacant sixth coordination site are H atoms at 3·43 and 3·44 Å for molecule I and molecule II respectively. The inner coordination sphere and average bond lengths are illustrated in Fig. 2. The individual determinations for the two molecules do not vary significantly from the mean values.

From Fig. 2 it can easily be seen that the $\{CoNO\}^8$ triatomic group† is strongly bent, as observed in the other structurally characterized tetragonal-pyramidal $\{M\text{NO}\}^8$ complexes (Enemark & Feltham, 1974). The $\{CoNO\}^8$ groups in the two independent molecules are ordered and in both cases the O atoms are bent over the ethylene region of the appropriate salen ligand. The average nitrosyl bond length is 1·155 (11) Å (corrected for thermal motion assuming a riding model), and the average Co–N–O angle is 127·0 (4)°. The individual values do not differ significantly from the averages. The Co–NO distances in (I) and (II) of 1·809 (4) and 1·805 (6) Å, respectively, are similar to those observed for other complexes with strongly bent $\{CoNO\}^8$ groups (Enemark & Feltham, 1974).

The distances from the Co atoms to the salen N atoms range from 1·871 (7) to 1·889 (2) Å and those from the Co atoms to the salen O atoms range from 1·865 (3) to 1·879 (6) Å. The Co atoms lie 0·25 Å above the plane through the coordinating N and O atoms of the salen ligand. These distances are consistent with the observed values summarized for Co salen complexes by Calligaris, Nardin & Randaccio (1972).

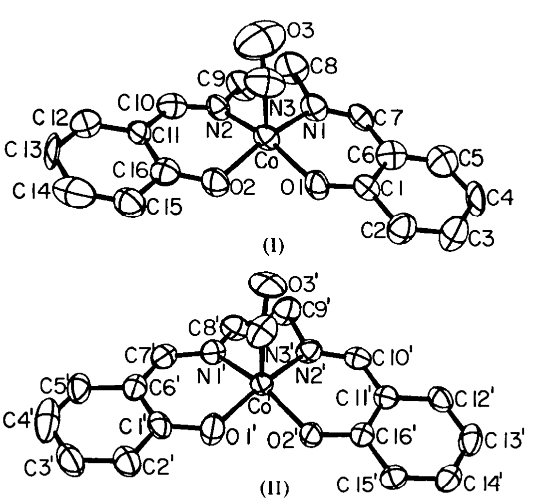

Fig. 1. Perspective views and numbering schemes for (I) and (II). H atoms have been omitted for clarity. The thermal ellipsoids are 50% probability envelopes.

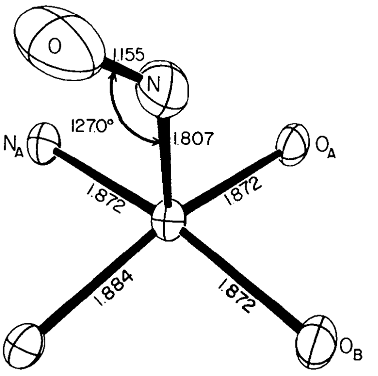

Fig. 2. Perspective view of the inner coordination sphere. The thermal ellipsoids are 20% probability envelopes.

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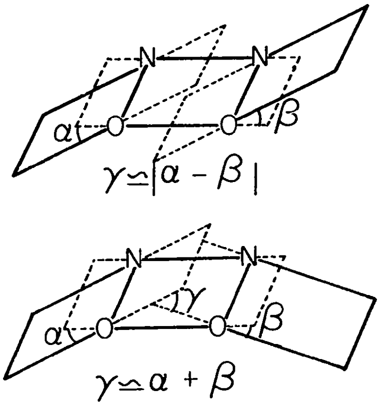
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32955 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† The superscript 8 in $\{CoNO\}^8$ refers to the total number of electrons that are primarily associated with metal d and π^*(NO) orbitals.

The angles about each Co atom are quite normal for salen complexes. The four chelating N—Co—O angles range from 92·6 to 94·1°; the two N—Co—N angles are 85·0 and 84·6°; the two O—Co—O angles are 85·2 and 83·5°. The observed distances and angles within the salen ligands are similar to those in other metal salen complexes which have been structurally characterized.

The two independent molecules differ in the conformations of the salen ligand. The geometry of the salen ligand in these complexes can be conveniently discussed in terms of three planes (Calligaris, Nardin & Randaccio, 1972). A useful reference plane is *C*, the best plane through the four atoms of the salen ligand that are coordinated to the metal atom. Plane *A* consists of the N, O and C atoms of the salicylideneiminato moiety adjacent to the ethylenic C atom that is on the same side of the molecule as the nitrosyl group (above plane *C*). Plane *B* contains the atoms of the salicylideneiminato moiety that is adjacent to the ethylenic C atom that is below plane *C*. The angles between planes *A*, *B* and *C* define three geometries: (1) stepped (top); (2) planar ($\alpha = \beta = \gamma = 0°$); (3) umbrella (bottom).



Line drawings of the two molecules viewed parallel to the best weighted least-squares plane through the coordinating atoms of each salen ligand are given in Fig. 3. The equations for the relevant planes are given in Table 7. Molecule I is essentially of the symmetrically stepped conformation with plane *A* bent down 9·65° with respect to plane *C*, and plane *B* bent up 9·92° with respect to plane *C*. Molecule II is between a planar and an asymmetric umbrella conformation. The angle of 2·74° which plane *B*′ makes with plane *C*′ is due largely to the C and N atoms which are below the coordination plane (see Fig. 3). The phenylene C atoms of plane *B*′ are all coplanar with the coordination plane. The 5·62° angle between planes *A*′ and *C*′ has a substantial contribution from the torsional angle of its phenylene ring, as is evident from Fig. 3. The interplanar angles for (I) and (II) and other related five-coordinate Schiff-base complexes are given in Table 8.

It might be expected that in a symmetrically stepped

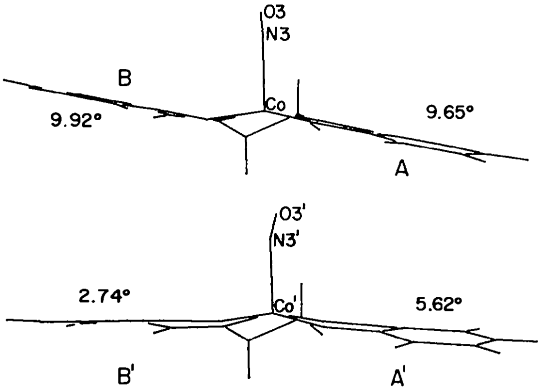


Fig. 3. Line drawings of (I) and (II) viewed parallel to the salen coordination planes.

Table 7. *Equations of least-squares planes and distances* (Å) *of the individual atoms from the planes*

The equations are referred to the crystal axes and *X*, *Y*, and *Z* are fractional monoclinic coordinates.

Plane *A*: O(1), N(1), C(1), C(2), C(3), C(4), C(5), C(6), C(7)

$2\cdot9917X - 11\cdot089Y + 4\cdot7916Z - 4\cdot1643 = 0$

O(1)	0·010 (3)	C(2)	−0·028 (5)	C(5)	0·020 (5)
N(1)	−0·009 (3)	C(3)	−0·033 (6)	C(6)	0·018 (4)
C(1)	0·009 (4)	C(4)	0·022 (5)	C(7)	−0·020 (4)

Plane *B*: O(2), N(2), C(10), C(11), C(12), C(13), C(14), C(15), C(16)

$2\cdot4546X - 11\cdot239Y + 4\cdot6538Z - 2\cdot9494 = 0$

O(2)	0·011 (3)	C(11)	0·016 (4)	C(14)	−0·014 (6)
N(2)	0·026 (3)	C(12)	0·021 (5)	C(15)	−0·039 (5)
C(10)	−0·064 (4)	C(13)	0·013 (5)	C(16)	0·010 (4)

Plane *C*: O(1), O(2), N(1), N(2)

$3\cdot9451X - 11\cdot356Y + 1\cdot9503Z - 1\cdot9075 = 0$

O(1)	−0·018 (3)	N(1)	0·023 (4)
O(2)	0·018 (3)	N(2)	−0·023 (4)

Plane *A*′: O(1)′, N(1)′, C(1)′, C(2)′, C(3)′, C(4)′, C(5)′, C(6)′, C(7)′

$12\cdot104X + 4\cdot8888Y - 8\cdot8152Z + 1\cdot0900 = 0$

O(1)′	0·006 (4)	C(2)′	−0·030 (7)	C(5)′	0·007 (6)
N(1)′	−0·002 (4)	C(3)′	−0·053 (8)	C(6)′	0·048 (6)
C(1)′	0·021 (6)	C(4)′	0·008 (7)	C(7)′	−0·044 (5)

Plane *B*: O(2)′, N(2)′, C(10)′, C(11)′, C(12)′, C(13)′, C(14)′, C(15)′, C(16)′

$10\cdot909X + 5\cdot6229Y - 10\cdot214Z + 2\cdot9407 = 0$

O(2)′	0·033 (3)	C(11)′	0·051 (6)	C(14)′	−0·057 (6)
N(2)′	−0·049 (5)	C(12)′	0·067 (6)	C(15)′	−0·072 (5)
C(10)′	−0·045 (6)	C(13)′	0·022 (6)	C(16)′	0·020 (5)

Plane *C*′: O(1)′, O(2)′, N(1)′. N(2)′

$11\cdot719X + 5\cdot2904Y - 9\cdot0942Z + 1\cdot5614 = 0$

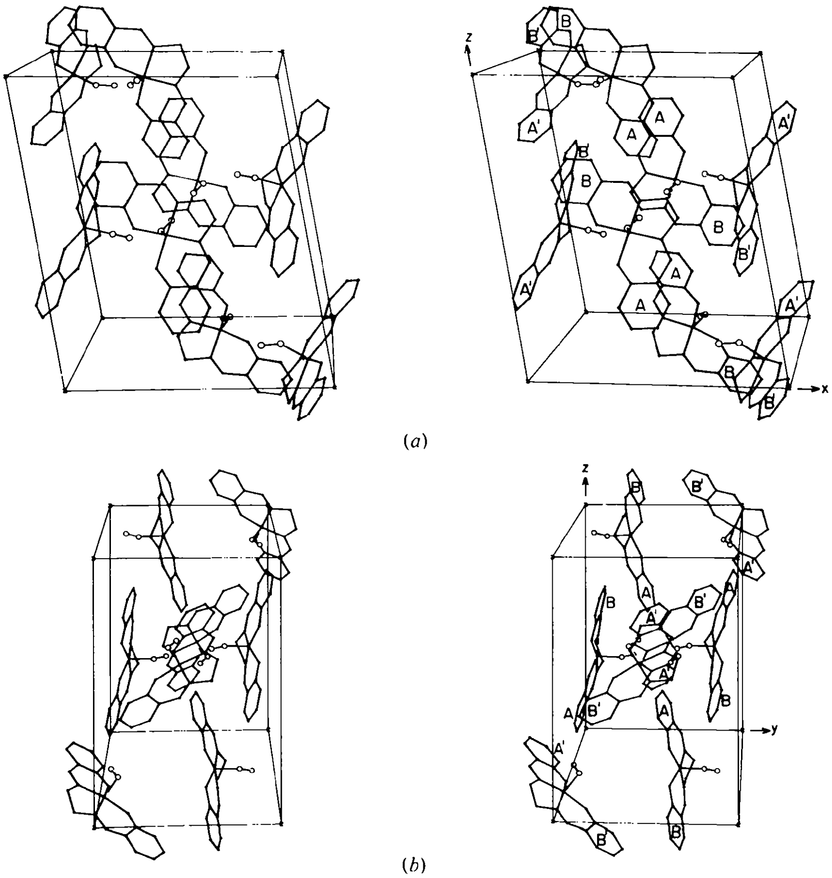
O(1)′	0·069 (4)	N(1)′	−0·068 (4)
O(2)′	−0·042 (3)	N(2)′	0·076 (5)

Table 8. *Conformational data for five-coordinate metal salen complexes (in degrees and* Å)

α, β, and γ are defined in the text; d_M, d_8, and d_9 are the displacements from the coordination plane of the metal, C(8), and C(9) respectively. NOON and NCCN are the torsional angles N(1)–O(1)–O(2)–N(2) and N(1)–C(8)–C(9)–N(2).

Complex	α	β	γ	d_M	NOON	NCCN	d_8	d_9	Reference
Co(NO)(salen) (I)	9·65	9·92	2·41	0·24	1·7	40·8	0·17	−0·43	Present work
Co(NO)(salen) (II)	5·62	2·74	8·10	0·26	5·4	36·7	0·15	−0·44	Present work
Fe(NO)(salen) (23°C)	14·49	7·64	8·21	0·46	2·1	35·8	0·12	−0·35	Johnson *et al.* (1977)
Fe(NO)(salen) (−175°C)	9·99	6·89	3·89	0·36	0·5	14·5	0·02	−0·14	Johnson *et al.* (1977)
ClFe(salen)	14·9	6·5	19·4	0·49	9·1	43·7	0·38	−0·40	Gerlock & Mabbs (1967)
Co(salen)(pyridine)	14·2	14·2	28·4	0·20	0·0	0·0	0·05	0·05	Calligaris, Minichelle, Nardin & Randaccio (1970)
Co(salbn)(pyridine)*	10·6	2·8	11·2	0·21	4·0	41·9	0·17	−0·47	Bresciani, Calligaris, Nardin & Randaccio (1974)
Co(3-MeO-salen)(H$_2$O)	13·0	13·0	26·0	0·43	0·0	53·4	0·35	−0·44	Calligaris, Nardin & Randaccio (1974)

* The complex has two crystallographically independent molecules in the unit cell. The other molecule is best described as a trigonal bipyramid. Salbn is the *N,N'*-butylenebis(salicylideneiminate) dianion.



(*a*)

(*b*)

Fig. 4. Stereoviews of the packing of Co(NO)(salen) (*a*) perpendicular to the *ac* plane, (*b*) perpendicular to the *bc* plane.

salen ligand the two ethylene C atoms would be equally disposed above and below the coordination plane of the salen ligand. This is not the case for (I). Moreover, the geometry of the ethylene linkage relative to the coordination plane is identical in the two independent Co(NO)(salen) molecules. One ethylene C atom is 0·16 Å above the coordination plane in the symmetrically stepped molecule (I) and 0·15 Å above the plane in (II). The other ethylene C atom is below the coordination plane by 0·43 Å and 0·44 Å, respectively, in (I) and (II).

Some insight into the two different conformations for

(I) and (II) is provided by the packing diagrams and the intermolecular contacts. Fig. 4 shows stereo packing diagrams oriented perpendicular to the *ac* plane (Fig. 4*a*) and perpendicular to the *bc* plane (Fig. 4*b*). Examination of the four molecules in the central region of each of these views shows that the Co–N(nitrosyl) vector for molecule I (unprimed plane labels) is nearly parallel to the *b* axis (angle ~17°) while the Co–N(nitrosyl) vector in molecule II is approximately parallel to the *a* axis (angle ~22°). Thus, the independent molecules form interleaving stacks along the *a* and *b* axes. Since the *b* axis is much shorter than the *a* axis (11·98 *vs* 14·42 Å) the molecules that pack along **b** (molecule I) tend to lie between the flat 'faces' of the molecules that pack along **a** (molecule II). Asymmetric interaction of a flat face of one salen ligand plane with the edge of another salen ligand plane would be expected to favor deformation of the former ligand skeleton rather than the latter.

The intermolecular contacts (calculated as the perpendicular distances of atoms from the ligand planes defined previously) are consistent with the above implications from the stereoviews of Fig. 4. Most of the nonbonded contacts on the bottom of each molecule come from an inversion-related molecule. The inversion-related contacts on the bottom side of the unsymmetrical molecule (II) range from 3·17 Å near C(5)′ and 3·22 Å near C(11)′ up to 3·62 Å near N(2)′. In the symmetrically stepped molecule (I) the inversion-related nonbonded contacts on the bottom side are more uniform and range from 3·30 to 3·48 Å. All other nonbonded contacts on the bottom sides of the molecules are greater than 3·45 Å, except for an O(3) contact near C(4) of 3·36 Å for molecule I. The contacts to the planes on the top side of (I) range from 3·45 to 3·52 Å. Plane *A*′ in (II) has as its principal contact on the top an interaction at 3·58 Å. The top of plane *B*′ has a close contact of 3·01 Å with C(13)′ over the region of O(1)′, C(1)′, and C(2)′ and an interaction with the edge of plane *B* [C(14) and C(15) near C(3)′ and C(4)′]. The contacts on the top of *B*′ will tend to decrease the angle between planes *B*′ and *C*′.

Several conclusions concerning the solid-state structure of Co(NO)(salen) can be drawn from the structural results discussed above. (1) The conformation of the salen ligand planes is controlled by crystal-packing effects. (2) The conformation of salen ligand planes does not affect the conformation of the ethylene C atoms. (3) The conformation of the ligand planes does not strongly perturb the geometry of the $\{\mathrm{CoNO}\}^8$ group. Finally, we note that the somewhat larger and more uniform intermolecular contacts of (I), the symmetrically stepped conformer of Co(NO)(salen), suggest that it is the more stable of the two conformers observed here.

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