Table II. Bond Lengths (Å) and Angles (deg) within the Coordination Polyhedron of $[Fe_2(\mu\text{-}SH)_3(ppp)_2]ClO_4\cdot CO(CH_3)_2$[a]

	Distances		
Fe1–P1	2.232 (4)	Fe2–P4	2.253 (3)
Fe1–P2	2.204 (4)	Fe2–P5	2.230 (5)
Fe1–P3	2.234 (4)	Fe2–P6	2.236 (3)
Fe1–S1	2.362 (4)	Fe2–S1	2.343 (3)
Fe1–S2	2.345 (5)	Fe2–S2	2.332 (3)
Fe1–S3	2.334 (3)	Fe2–S3	2.324 (5)
	Angles		
P1–Fe1–P2	84.6 (1)	P4–Fe2–P5	84.8 (1)
P1–Fe1–P3	96.4 (2)	P4–Fe2–P6	96.3 (1)
P2–Fe1–P3	85.3 (1)	P5–Fe2–P6	84.3 (2)
P1–Fe1–S1	96.2 (1)	P4–Fe2–S1	92.2 (1)
P1–Fe1–S2	169.9 (2)	P4–Fe2–S2	166.1 (1)
P1–Fe1–S3	100.9 (2)	P4–Fe2–S3	93.9 (2)
P2–Fe1–S1	99.2 (2)	P5–Fe2–S1	94.4 (2)
P2–Fe1–S2	94.7 (2)	P5–Fe2–S2	100.0 (2)
P2–Fe1–S3	174.4 (3)	P5–Fe2–S3	175.6 (2)
P3–Fe1–S1	167.0 (2)	P6–Fe2–S1	171.2 (2)
P3–Fe1–S2	93.6 (1)	P6–Fe2–S2	97.1 (1)
P3–Fe1–S3	93.6 (1)	P6–Fe2–S3	100.0 (2)
S1–Fe1–S2	73.9 (1)	S1–Fe2–S2	74.5 (1)
S1–Fe1–S3	80.8 (1)	S1–Fe2–S3	81.4 (1)
S2–Fe1–S3	79.9 (1)	S2–Fe2–S3	80.4 (1)
Fe1–S1–Fe2	85.4 (1)	Fe1–S3–Fe2	84.5 (2)
Fe1–S2–Fe2	86.1 (1)		

[a] Estimated standard deviations are in parentheses.

the cluster of the metal and donor atoms, preventing its further growth.

Acknowledgment. We are indebted to Professor V. I. Nefedov for the ESCA measurements on one of the compounds. Thanks are expressed to Mr. F. Cecconi annd Mr. D. Masi for technical assistance and to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalysis.

Registry No. $[Fe_2(\mu\text{-}SH)_3(ppp)_2](ClO_4)\cdot(CH_3)_2CO$, 71393-26-5; $[Fe_2(\mu\text{-}SH)_3(ppp)_2](BF_4)$, 71425-17-7.

Supplementary Material Available: A listing of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 3: Di Vaira, M.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1978**, *17*, 816.
(2) Di Vaira, M.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1977**, *16*, 1518. Mealli, C.; Midollini, S.; Sacconi, L. *Ibid.* **1978**, *17*, 632.
(3) Sacconi, L.; Morassi, R. *J. Chem. Soc. A* **1968**, 2997; Sacconi, L.; Bertini, I.; Mani, F. *Inorg. Chem.* **1968**, *7*, 1417.
(4) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.
(5) *Chem. Soc., Spec. Publ.* **1965**, *No. 18*.
(6) Cromer, D. T.; Waber, J. A. *Acta Crystallogr.* **1965**, *18*, 104.
(7) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(8) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(9) The two models are essentially indistinguishable and results are quoted from that one of the alternative refinements which gave a slightly lower spread in the values of chemically equivalent bond distances and angles.
(10) Supplementary material.
(11) Coucouvanis, D.; Lippard, S. J; Zubieta, J. A. *Inorg. Chem.* **1970**, *9*, 2775.
(12) Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7472.
(13) Dapporto, P; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 1643.
(14) Bacci, M.; Ghilardi, C. A. *Inorg. Chem.* **1974**, *13*, 2398.
(15) Lever, A. B. P. "Inorganic Electron Spectroscopy"; Elsevier: Amsterdam, 1968.
(16) After this work had been submitted for publication, ESCA measurements were performed on the compound $[Fe_2(\mu\text{-}SH)_3(ppp)_2]ClO_4$ by Professor V. I. Nefedov at the Kurnakov Institute of General and Inorganic Chemistry of the Academy of Science of the USSR, in Moscow. The results indicate unambiguously that the compound contains SH groups and that there are no bridging unsubstituted sulfur atoms. The alternative formulation of the compound, as $[Fe_2(\mu\text{-}SH)(\mu\text{-}S)_2]ClO_4$, according to which spin pairing would be attained through strong antiferromagnetic coupling, may be therefore ruled out.

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Bifunctional Model Complexes Active in Carbon Dioxide Fixation: Synthesis and X-ray Structure of Bimetallic Cobalt(I)–Alkali Cation–Schiff Base Complexes

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Received March 16, 1979

Reduction of (*N,N'*-ethylenebis(salicylideniminato))cobalt(II), Co(salen), with lithium and sodium metals in tetrahydrofuran, THF, affords the bimetallic systems, which are active in carbon dioxide fixation, [(Co(salen))NaTHF] and $[(Co(salen))Li(THF)_{1.5}]$. The structures of these complexes have been solved by single-crystal X-ray diffraction methods. Both of them contain a diamagnetic cobalt(I) in a slightly distorted square-planar coordination geometry due to a salen ligand which coordinates the alkali cation through the oxygen atoms. [(Co(salen))NaTHF] crystallizes in the orthorhombic space group $P2_12_12$ with lattice parameters a = 7.416 (2) Å, b = 21.848 (9) Å, c = 11.639 (5) Å, and Z = 4. The structure has been solved by using 1579 observed reflections and refined to R = 0.030. The crystal structure consists of infinite chains, whose monomeric unit is $[(Co(salen))_2Na_2(THF)_2]$. They can be described by distorted octahedra around Na^+ sharing the opposite faces. Both THF and Co(salen) act, through the oxygen atoms, as bridging ligands between two adjacent sodium cations. $[(Co(salen))Li(THF)_{1.5}]$ is triclinic, space group $P\bar{1}$, with lattice parameters a = 16.892 (3) Å, b = 14.310 (3) Å, c = 10.899 (3) Å, α = 94.6 (2)°, β = 99.5 (2)°, γ = 122.3 (2)°, and Z = 2. The structure has been solved by direct methods and refined by least-squares methods to R = 0.089, for 2680 reflections. In the structure of $[(Co(salen))Li(THF)_{1.5}]$ there are two different molecular complexes, $[(Co(salen))Li(THF)_2]$ and $[(Co(salen))_2Li_2(THF)_2]$, in a 2:1 ratio. In both complexes, Li^+ is in a distorted tetrahedral coordination. In the first complex, the four oxygens for the lithium coordination are provided by Co(salen), acting as a bidentate chelating ligand, and two THF molecules. In the centrosymmetric tetranuclear complex $[(Co(salen))_2Li_2(THF)_2]$ one of the THF oxygens of $[(Co(salen))Li(THF)_2]$ is replaced by a Co(salen) oxygen atom which bridges two lithium cations.

Introduction

Metal basicity has proved valuable in rationalizing reactivity patterns in organometallic and coordination compounds, especially in terms of the binding and activation of small gas molecules.[1] Particularly effective have been the d^8 and d^{10} metal complexes with tertiary phosphine type ligands,[1] but a second type includes macrocyclic ligand systems with harder N and O donors in which the metal has been reduced to a low

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Table I. Crystal Data for [(Co(salen))NaTHF] and [(Co(salen))Li(THF)$_{1.5}$]

(Co(salen))NaTHF	(Co(salen))Li(THF)$_{1.5}$
$C_{20}H_{22}O_3N_2CoNa$, mol wt 420	$C_{44}H_{52}O_7N_4Co_2Li_2$, mol wt 881
orthorhombic, $P2_12_12$	triclinic, $P\bar{1}$
$a = 7.416$ (2) Å	$a = 16.892$ (3) Å
$b = 21.848$ (9) Å	$b = 14.310$ (3) Å
$c = 11.639$ (5) Å	$c = 10.899$ (3) Å
$V = 1886$ Å^3	$\alpha = 94.6$ (2)°
$Z = 4$, $D_{\text{calcd}} = 1.478$ g cm^{-3}	$\beta = 99.5$ (2)°
μ(Mo Kα) = 9.92 cm^{-1}	$\gamma = 122.3$ (2)°
	$V = 2151$ Å^3
	$Z = 2$, $D_{\text{calcd}} = 1.360$ g cm^{-3}
	μ(Mo Kα) = 8.59 cm^{-1}

valence state by electrochemical means[2,4,5] or chemical means using borohydride[3] or alkali metals.[6,7] Use of the alkali metal reduction with O-donor ligand systems can lead to subsequent complexation of the alkali metal cation, and the systems are effectively acting as "sequestering agents" for the alkali cations.[8,9] Such bimetallic complexes formed from (*N,N'*-ethylenebis(salicylideniminato))cobalt(II), Co(salen), and alkali metals were then found to be bifunctional, serving as acid–base sites for binding of CO_2.[10-12] Such acid–base bifunctional catalysis is well established in heterogeneous (e.g., metal oxide)[13] and enzyme systems.[12]

This paper reports on the structure of the bimetallic bifunctional cobalt(I)–alkali cation–Schiff base complexes.

Experimental Section

The syntheses were carried out under an atmosphere of purified nitrogen or argon. Solvents were carefully purified and dried by standard methods. IR spectra were recorded on a Perkin-Elmer 282 spectrometer. The magnetic measurements were carried out with a Faraday balance. (*N,N'*-Ethylenebis(salicylideniminato))cobalt(II), Co(salen), was prepared as previously described.[14]

Preparations. Sodium (*N,N'*-Ethylenebis(salicylideniminato))cobaltate(I), [(Co(salen))NaTHF]. Co(salen) (10 g, 30.78 mmol) was suspended in THF (200 mL) and reacted with sodium sand (0.73 g, 31.75 mmol). After 24 h of stirring, a deep green solution was obtained, from which, by addition of $(C_2H_5)_2O$ (200 mL), deep green crystals of [(Co(salen))NaTHF] were obtained (ca. 80%). Anal. Calcd for [(Co(salen))NaTHF], $C_{20}H_{22}N_2O_3CoNa$: C, 57.14; H, 5.24; N, 6.67. Found: C, 57.01; H, 5.38; N, 6.30. The magnetic measurement gave a $\chi_M^{\text{cor}} = 432 \times 10^{-6}$ cgsu at 293 K. The solid is highly soluble in THF or pyridine and highly reactive toward oxygen and moisture.

Lithium (*N,N'*-Ethylenebis(salicylideniminato))cobaltate(I), [(Co(salen))Li(THF)$_{1.5}$]. Co(salen) (10 g, 30.7 mmol) was suspended in THF (200 mL) and reacted with metallic lithium (0.23 g, 3.31 mmol) under argon. After 12 h of stirring, a deep green solution was obtained, which was evaporated to dryness. The solid was dissolved in toluene (80 mL) and a small amount of solid was filtered out. By adding hexane (200 mL) to the toluene solution and allowing the mixture to stand for 24 h, we obtained deep green crystals of [(Co(salen))Li(THF)$_{1.5}$]. The solid is soluble in THF and partially so in Et_2O, from which it could be recrystallized (ca. 80%). The complex is highly reactive toward oxygen and moisture and must be handled under a carefully controlled inert atmosphere. Anal. Calcd for [(Co(salen))Li(THF)$_{1.5}$], $C_{22}H_{26}N_2O_{3.5}CoLi$: C, 60.02; H, 5.91; N, 6.36. Found: C, 60.47; H, 6.0; N, 6.37. The magnetic measurement gave $\chi_M^{\text{cor}} = 180.5 \times 10^{-6}$ cgsu at 293 K. Crystals of III and IV appear deep green or bright violet, depending on their dimensions.

X-ray Data Collection of [(Co(salen))NaTHF]. A crystal of [(Co(salen))NaTHF], approximately 0.1 × 0.5 × 0.7 mm, enclosed in a capillary glass tube, was used for X-ray data collection on a Philips PW 1100 four-circle diffractometer. The crystal data are given in Table I. The cell parameters were determined with graphite-monochromatized Mo Kα radiation by a least-squares fit of 25 reflections in the range 20° < 2θ < 29° at 18 ± 2 °C. The orthorhombic space group $P2_12_12$ was uniquely assigned from systematic extinctions. Intensities for the independent reflections with 2θ less than 50° were measured with the θ–2θ scan mode at a 2θ rate of 0.05 s^{-1} with a scan width of 1.2° and background counts of 10 s on either side of the peak. To check crystal stability, we measured the intensities of three reflections after every 180 min during the data collection. A total variation of 5% in intensity was observed.

The intensities were corrected for the Lorentz and polarization factors and for the decay of the crystal. A total of 1732 reflections were measured and, of these, 1579 reflections with $I > 3\sigma(I)$[15] were considered observed and used for the structure determination.

Solution and Refinement of the Structure of [(Co(salen))NaTHF]. The structure was solved by the usual combination of Patterson, Fourier, and least-squares methods. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor w equals $4F_o^2/\sigma^2(F_o^2)$. Refinement of the positional and isotropic thermal parameters of the nonhydrogen atoms gave $R = 0.089$. Positional parameters of the H atoms were calculated and included in the subsequent refinement in the fixed positions with constant isotropic thermal parameters equal to 6 Å^2. Three cycles of full-matrix least-squares refinement were carried out with anisotropic thermal parameters for the nonhydrogen atoms.

The atomic scattering factors for neutral atoms used were from ref 16.

The corrections for the real and imaginary components of the anomalous dispersion for the Co and Na atoms[17] were included in the last steps of the refinement.

The final values of R and R_w were 0.030 and 0.039, respectively.

$$R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|} \qquad R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2}$$

To determine the absolute configuration of the structure, we refined the inverted structure, yielding $R = 0.038$ and $R_w = 0.050$. The positional and thermal parameters of the nonhydrogen atoms are given in Table II. Lists of structure factors, H atom parameters, all interatomic distances and angles, and the equations of least-squares planes through some groups of atoms and the deviations of these atoms from the planes are available as supplementary material. A selection of bond lengths and angles is given in Table III.

X-ray Data Collection of [(Co(salen))Li(THF)$_{1.5}$]. Crystals of the compound were sealed in capillary glass tubes under nitrogen and mounted on a Philips PW 1100 four-circle diffractometer equipped with graphite monochromator and Mo radiation. Crystals were found to be triclinic and the unit-cell dimensions were refined by a least-squares technique to give the best fit between calculated and observed settings χ, φ, and 2θ measured at 16 °C for 25 reflections (in the range 2θ = 26–32°) centered on the diffractometer. The refinement yielded the lattice parameters listed with other crystal data in Table I. The space group $P\bar{1}$ was assumed on the basis of intensity distribution statistics.

The three-dimensional X-ray data were obtained from a crystal with dimensions 0.4 × 0.2 × 0.2 mm. Intensities were measured with the same procedure as described for [(Co(salen))NaTHF]. During the course of the experiment, the intensity of the three reference reflections regularly decreased about 15%. A renormalization of the intensities was consequently performed. Data were corrected in the usual way for Lorentz and polarization effects. No absorption correction was applied. Out of 7394 independent reflections collected in a sphere of radius 2θ = 50°, 2680 with $I \geq 3\sigma(I)$[15] were retained for successive computations.

Solution and Refinement of the Structure of [(Co(salen))Li(THF)$_{1.5}$]. In an E map based on the most probable sign set for 200 E values (MULTAN[18]) the two Co atoms of the asymmetric unit were located. The other nonhydrogen atoms were found by Fourier methods. The structure was refined by the least-squares method, with the same computational procedure above described for [(Co(salen))NaTHF]. Two cycles of full-matrix least squares with individual isotropic thermal parameters reduced R to 0.14. Owing to the large number of parameters, anisotropic refinement was performed with alternate cycles of blocked least squares for all atoms with the exception of the carbon atoms of the tetrahydrofuran groups, for which the isotropic refinement yielded very high values of thermal parameters. The reason for this was ascribed to positional disorder or dynamical disorder of tetrahydrofuran groups as for pseudorotation in the ring. The contribution of H atoms of salen groups at fixed positions, and with isotropic thermal parameters equal to 6 Å^2, was taken into account in the last cycles of refinement. The final R value is 0.089, R_w being 0.10. This rather high figure is probably due to the poor quality of data, because of the deterioration of the crystals and the above-mentioned disorder. The scattering factors from ref 16 were used for neutral Co, Li, O,

Table II. Fractional Atomic Coordinates and Thermal Parameters[a] for Nonhydrogen Atoms[b] in [(Co(salen))NaTHF]

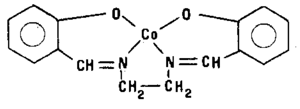
atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}[c]
Co	0.2614 (1)	0.0975 (1)	0.0312 (1)	36 (1)	29 (1)	47 (1)	−1 (1)	−2 (1)	4 (1)	3.0
Na(1)	0.	0.	0.1432 (2)	64 (2)	50 (2)	46 (2)	−28 (1)	0	0	4.3
Na(2)	0.5	0.	0.1393 (3)	46 (2)	43 (2)	54 (2)	−3 (1)	0	0	3.9
O(1)	0.2091 (4)	0.0766 (1)	0.1858 (2)	51 (2)	28 (2)	43 (1)	−8 (2)	−3 (1)	−3 (1)	3.3
O(2)	0.2367 (5)	0.0117 (1)	0.0074 (2)	47 (2)	33 (2)	42 (1)	−3 (2)	0 (2)	−2 (1)	3.3
O(3)	0.3080 (6)	−0.0721 (2)	0.2488 (3)	148 (4)	47 (2)	69 (2)	−6 (2)	36 (3)	12 (1)	7.2
N(1)	0.2735 (5)	0.1791 (1)	0.0565 (3)	39 (2)	31 (2)	69 (2)	3 (2)	−6 (2)	10 (1)	3.7
N(2)	0.3264 (5)	0.1138 (2)	−0.1175 (3)	43 (2)	46 (2)	58 (2)	0 (2)	7 (2)	9 (1)	4.0
C(1)	0.2004 (5)	0.1154 (2)	0.2737 (3)	38 (2)	33 (2)	49 (2)	−1 (2)	−1 (2)	−8 (1)	3.2
C(2)	0.1686 (6)	0.0924 (2)	0.3843 (4)	47 (2)	48 (2)	53 (3)	−4 (2)	−1 (2)	−5 (2)	4.0
C(3)	0.1570 (7)	0.1301 (2)	0.4794 (4)	55 (3)	69 (2)	55 (3)	4 (2)	5 (3)	−16 (2)	4.8
C(4)	0.1742 (7)	0.1930 (2)	0.4674 (5)	68 (3)	58 (2)	70 (3)	4 (2)	−3 (3)	−31 (2)	5.3
C(5)	0.2042 (7)	0.2172 (2)	0.3599 (4)	62 (3)	42 (2)	76 (3)	8 (2)	−9 (3)	−25 (2)	4.8
C(6)	0.2197 (6)	0.1804 (2)	0.2612 (4)	35 (2)	33 (2)	63 (3)	0 (2)	−10 (2)	−7 (1)	3.5
C(7)	0.2523 (8)	0.2087 (2)	0.1538 (4)	48 (2)	25 (2)	72 (3)	−3 (2)	−11 (3)	−1 (1)	3.9
C(8)	0.2997 (7)	0.2162 (2)	−0.0485 (4)	67 (3)	41 (2)	70 (3)	3 (2)	3 (3)	19 (2)	4.8
C(9)	0.3964 (8)	0.1764 (2)	−0.1342 (5)	68 (3)	51 (2)	80 (3)	−4 (2)	16 (3)	26 (2)	5.4
C(10)	0.3287 (6)	0.0768 (2)	−0.2045 (4)	48 (2)	60 (2)	48 (3)	5 (2)	10 (2)	9 (2)	4.2
C(11)	0.2685 (7)	0.0140 (2)	−0.2001 (3)	38 (2)	61 (2)	45 (2)	8 (2)	3 (3)	−3 (2)	3.9
C(12)	0.2570 (9)	−0.0190 (2)	−0.3030 (3)	60 (3)	81 (3)	45 (2)	11 (4)	2 (3)	−7 (2)	5.0
C(13)	0.1978 (7)	−0.0792 (3)	−0.3051 (4)	68 (4)	75 (2)	52 (3)	21 (3)	−9 (3)	−25 (2)	5.3
C(14)	0.1492 (7)	−0.1075 (2)	−0.2042 (4)	55 (2)	52 (2)	63 (3)	10 (2)	−8 (3)	−18 (2)	4.6
C(15)	0.1653 (6)	−0.0766 (2)	−0.1001 (4)	49 (2)	39 (2)	50 (3)	6 (2)	−5 (2)	−10 (2)	3.7
C(16)	0.2266 (7)	−0.0158 (2)	−0.0949 (3)	36 (2)	41 (2)	43 (2)	9 (2)	−4 (2)	−5 (1)	3.2
C(17)	0.2829 (7)	−0.1304 (2)	0.1986 (4)	65 (3)	55 (2)	56 (3)	4 (2)	7 (3)	3 (2)	4.8
C(18)	0.2906 (7)	−0.1777 (2)	0.2922 (4)	57 (3)	46 (2)	68 (3)	0 (2)	0 (3)	3 (2)	4.6
C(19)	0.3415 (8)	−0.1439 (2)	0.4001 (4)	67 (3)	51 (2)	66 (3)	4 (2)	6 (3)	−2 (2)	5.0
C(20)	0.3227 (8)	−0.0771 (2)	0.3694 (5)	74 (4)	56 (2)	64 (3)	−1 (3)	0 (3)	−13 (2)	5.3

[a] Estimated standard deviations in parentheses refer to the last digit. The form of the anisotropic thermal parameters is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}) \times 10^{-3}]$. [b] A list of calculated hydrogen positions is available as supplementary material. [c] B_{eq} (Å^2) are the equivalent isotropic temperature factors according to Hamilton.[31]

N, C, and H. Anomalous scattering corrections were included for Co atoms.[17] Tables of observed and calculated structure factors are available as supplementary material. Atomic coordinates and thermal parameters are listed in Table IV. A selection of bond lengths and angles is given in Table V. A list of calculated hydrogen atom coordinates, the complete information about all interatomic distances and angles, and the equations of some important least-squares planes with the deviations of atoms from these planes are available as supplementary material.

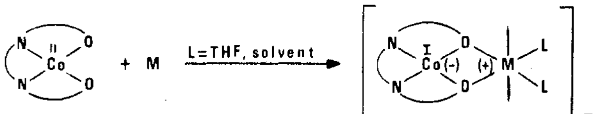
Results

THF suspensions of Co(salen) (I) react with lithium or



Co(salen) (I)

sodium metals (M) to give a deep green solution, from which crystals of [(Co(salen))M(THF)$_n$] (II), [(Co(salen))NaTHF] (III) and [(Co(salen))Li(THF)$_{1.5}$] (IV), are isolated (see Experimental Section).



(1)

Co(salen) (I)

[(Co(salen))ML$_n$]$_m$ (II)

M = Li, Na

The degree of solvation of complex II depends on the nature of the alkali cation, the solvents used, and the crystallization rate. The M/Co ratio must be carefully controlled, since cobalt, over a much longer time and with a higher M/Co ratio, can be further reduced,[6] while a M/Co ratio lower than 1 gives mixed-valence Co(I)–Co(II) polynuclear complexes.[19] Their very low solubility, however, prevents a possible contamination of the final cobalt(I) complexes. The diamagnetism,[20] as well as the rigidity of the salen ligand, suggests square-planar coordination for II.

Table III. Selected Bond Lengths (Å) and Angles (deg) in [(Co(salen))NaTHF]$_2$[a]

Co–O(1)	1.896 (3)	Na(1)–O(1)	2.334 (3) (×2)
Co–O(2)	1.903 (3)	Na(1)–O(2)	2.375 (3) (×2)
Co–N(1)	1.809 (3)	Na(1)–O(3)	3.034 (4) (×2)
Co–N(2)	1.831 (4)	Na(2)–O(1) (×2)	2.783 (3) (×2)
		Na(2)–O(2) (×2)	2.496 (3) (×2)
		Na(2)–O(3) (×2)	2.476 (4) (×2)
O(1)–Co–O(2)	83.2 (1)	Na(1)–O(1)–C(1)	126.0 (3)
O(1)–Co–N(1)	95.3 (1)	Na(2)–O(1)–C(1)	124.8 (3)
O(1)–Co–N(2)	175.7 (2)	Na(1)–O(2)–C(16)	120.2 (3)
O(2)–Co–N(1)	177.2 (2)	Na(2)–O(2)–C(16)	123.1 (3)
O(2)–Co–N(2)	94.5 (2)		
N(1)–Co–N(2)	87.1 (2)		
O(1)–Na(1)–O(1′)	155.5 (1)	O(1)–Na(2)–O(1′)	157.6 (1)
O(1)–Na(1)–O(2)	64.8 (1)	O(1)–Na(2)–O(2)	56.8 (1)
O(1)–Na(1)–O(2′)	135.2 (1)	O(1)–Na(2)–O(2′)	141.9 (1)
O(1)–Na(1)–O(3)	77.7 (1)	O(1)–Na(2)–O(3)	80.6 (1)
O(1)–Na(1)–O(3′)	92.4 (1)	O(1)–Na(2)–O(3′)	87.9 (1)
O(2)–Na(1)–O(2′)	96.6 (1)	O(2)–Na(2)–O(2′)	104.1 (1)
O(2)–Na(1)–O(3)	76.7 (1)	O(2)–Na(2)–O(3)	86.1 (1)
O(2)–Na(1)–O(3′)	140.3 (1)	O(2)–Na(2)–O(3′)	134.5 (1)
O(3)–Na(1)–O(3′)	132.2 (1)	O(3)–Na(2)–O(3′)	118.1 (1)

[a] Estimated standard deviations refer to the last digit, and primes denote atoms generated by the twofold axis.

The IR spectra (Nujol) of III and IV look very similar, and comparison with the Cosalen spectrum shows the loss in the reduced species of the ν(C=N) at 1605 and 1625 cm^{-1}.[6,21]

The bimetallic nature and structure of the complexes and the factors affecting the extent of the polymerization of the bimetallic unit in the solid state are revealed by the X-ray analysis of III and IV.

Structure of [(Co(salen))NaTHF] (III). The structure of III consists of Na$^+$ ions at special positions on twofold axes surrounded by six oxygen atoms provided by Co(salen) and THF molecules. These distorted octahedra share opposite

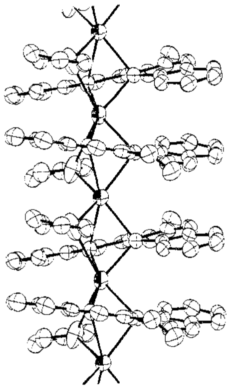


Figure 1. An ORTEP[32] perspective view of the polymeric $[(Co(salen))NaTHF]_n$. The thermal ellipsoids are drawn for 50% probability.

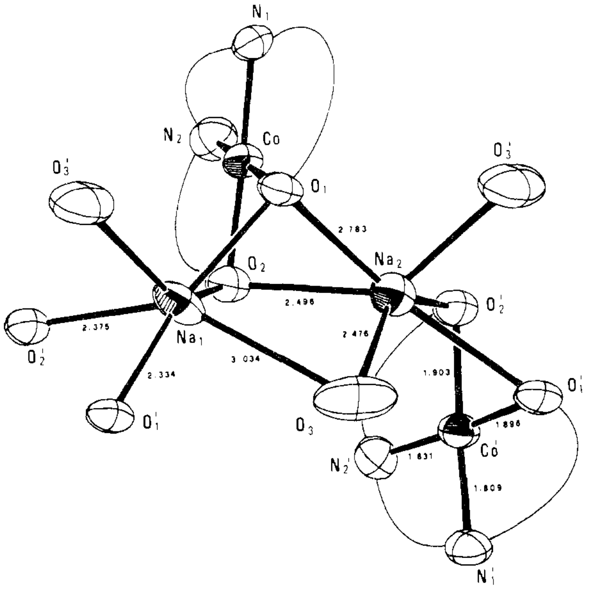


Figure 2. A drawing of the repetitive unit, $[(Co(salen))_2Na_2(THF)_2]$ of complex III, showing bond distances of the coordination polyhedra around Co and Na. The organic parts of the ligands have been omitted for clarity.

faces to form infinite chains running along the *a* direction (Figure 1). The repetitive unit, $[(Co(salen))_2Na_2(THF)_2]$, of this polymeric structure is shown in Figure 2. Both Co(salen) and THF molecules bridge contiguous Na^+ ions. The overall structure of III can be described in terms of Co(salen) layers, the interlayer distance being about $^1/_2a$, i.e., 3.7 Å, with Na^+ cations interposed between. The more relevant bond distances and angles concerning the coordination spheres of cobalt and sodium are reported in Table III, while the numbering scheme is shown in Figure 2.

Structure of Co(salen) in Complex III. The salen coordination around cobalt(I) is nearly planar, the deviation of the cobalt atom from the least-squares plane passing through the four donor atoms being −0.099 Å. Two factors could have influence on the structural parameters, the +1 oxidation state of the cobalt and the sharing of the salen's oxygens between two Na^+ ions. While this latter factor does lead to a significant lengthening of the Co–O bond distances, there is an unusual shortening of the Co–N bond distances (1.809 (3) and 1.831 (4) Å) on comparison with a mean value of 1.91 Å observed for several Co(salen) derivatives.[23] The imino (C=N) bond distances fall in the usual range, 1.313 (6) and 1.295 (6) Å, and thus the shorter Co–N distances are ascribed mainly to the low oxidation state of the transition metal rather than to the special bonding mode of the salen in the polymeric structure.

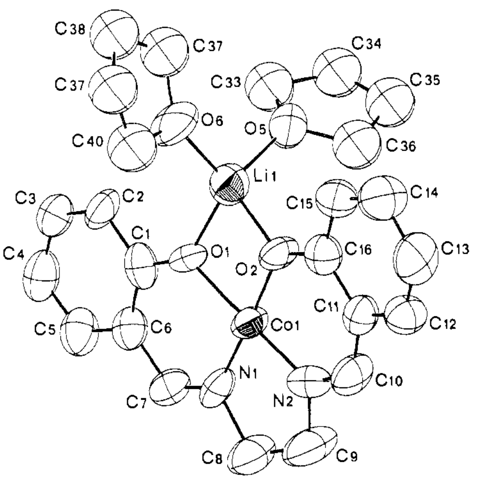


Figure 3. An ORTEP[32] view of the bimetallic unit $[(Co(salen))Li(THF)_2]$ present in $[(Co(salen))Li(THF)_{1.5}]$ crystals. The thermal ellipsoids are drawn at the 50% probability level. The size of carbon atoms of THF is reduced for clarity.

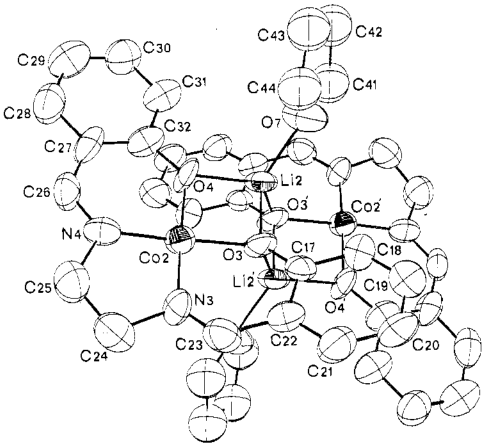


Figure 4. A view of the tetranuclear unit $[(Co(salen))_2Li_2(THF)_2]$ present in $[(Co(salen))Li(THF)_{1.5}]$, showing the labeling scheme.

The geometry of the organic part of the salen unit and the coordination polyhedron angles agree well with those reported for other tetracoordinate Co(salen) complexes.[8,9,22,23]

Coordination of Sodium Cations in Complex III. Both crystallographically nonequivalent Na^+ ions are surrounded by six oxygens, four from two Co(salen) units and two from THF molecules (Figure 2). All the oxygens are tetracoordinated, with Co(salen) and THF bridging two Na^+ ions. Both Na^+ ions have four shorter and two longer Na–O distances (Table III and Figure 2). The longest distances (Na(1)–O(3) = 3.034 (4) Å and Na(2)–O(1) = 2.783 (3) Å) are very different than those usually found in this type of complex (2.35–2.50 Å).[8,9,23] The Na–O and O–Na–O bond distances and angles (Table III) show that the coordination polyhedra around the Na^+ ion do not approximate either to an octahedron or to a tetragonal prism. The anchoring mode of the Na^+ to the salen's oxygens brings the Na^+ acid center close to the basic cobalt(I), but the main distortion around the Na^+ ions is probably due to the O–O bite of the Co(salen) ligand, which imposes the following angles: O(1)–Na(1)–O(2) = 64.8 (1)° and O(1)–Na(2)–O(2) = 56.8 (1)°.[8,9,22] The THF molecule bridges two Na^+ ions at nonequivalent distances (2.476 (4) and 3.034 (4) Å).

Structure of $[(Co(salen))Li(THF)_{1.5}]$ (IV). In IV, there are two different molecular complexes, $[(Co(salen))Li(THF)_2]$ (V) (Figure 3) and $[(Co(salen))_2Li_2(THF)_2]$ (VI) (Figure 4), present in a 2:1 molar ratio. Figure 5 shows the molecular packing. In V, the Li^+ coordinates four oxygens provided by

Table IV. Fractional Atomic Coordinates and Thermal Parameters[a] for Nonhydrogen Atoms in $[(Co(salen))Li(THF)_{1.5}]$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li(1)	0.0503 (21)	0.2592 (24)	−0.1413 (26)	80 (15)	77 (16)	71 (18)	51 (14)	15 (13)	14 (13)
Li(2)	0.4621 (19)	0.9135 (22)	−0.0842 (24)	73 (14)	50 (14)	39 (16)	39 (12)	−12 (11)	−11 (11)
Co(1)	0.2168 (2)	0.4065 (2)	0.0543 (2)	63 (2)	57 (1)	43 (2)	33 (2)	−2 (1)	−4 (1)
Co(2)	0.5723 (2)	0.8811 (2)	0.1107 (2)	64 (2)	55 (1)	45 (2)	40 (2)	4 (1)	6 (1)
O(1)	0.1861 (7)	0.3485 (9)	−0.1219 (9)	53 (7)	72 (8)	39 (7)	29 (6)	−8 (6)	−11 (6)
O(2)	0.0849 (8)	0.2956 (9)	0.0406 (9)	64 (8)	72 (8)	33 (7)	30 (15)	6 (6)	2 (5)
O(3)	0.4831 (8)	0.9259 (9)	0.0962 (8)	80 (8)	75 (8)	23 (7)	52 (6)	12 (5)	4 (5)
O(4)	0.5456 (8)	0.8619 (9)	−0.0660 (10)	93 (9)	81 (8)	69 (9)	77 (7)	30 (7)	17 (6)
O(5)	−0.0249 (9)	0.3183 (11)	−0.2126 (13)	108 (10)	120 (11)	76 (10)	84 (9)	8 (7)	−5 (6)
O(6)	−0.0212 (10)	0.1077 (12)	−0.2325 (14)	127 (12)	70 (10)	105 (11)	57 (9)	−19 (8)	−33 (9)
O(7)	0.3344 (10)	0.7953 (12)	−0.1870 (14)	106 (11)	66 (8)	79 (10)	42 (8)	−18 (8)	−3 (6)
N(1)	0.3424 (10)	0.5069 (11)	0.0623 (12)	87 (11)	66 (9)	33 (10)	45 (9)	15 (7)	3 (7)
N(2)	0.2396 (10)	0.4573 (11)	0.2224 (13)	54 (10)	56 (9)	61 (11)	24 (8)	−3 (8)	10 (8)
N(3)	0.5912 (10)	0.8942 (10)	0.2812 (12)	69 (11)	56 (8)	66 (11)	49 (8)	20 (8)	20 (7)
N(4)	0.6535 (10)	0.8366 (11)	0.1192 (12)	70 (10)	68 (11)	35 (10)	36 (8)	7 (7)	6 (7)
C(1)	0.2463 (15)	0.3817 (15)	−0.1991 (16)	80 (15)	58 (14)	75 (16)	53 (12)	36 (13)	32 (11)
C(2)	0.2068 (14)	0.3300 (15)	−0.3301 (15)	91 (16)	80 (15)	37 (11)	55 (12)	9 (10)	−5 (9)
C(3)	0.2646 (16)	0.3617 (17)	−0.4101 (17)	82 (16)	87 (15)	50 (16)	49 (14)	24 (13)	9 (11)
C(4)	0.3632 (18)	0.4434 (19)	−0.3703 (20)	110 (19)	92 (15)	67 (20)	67 (16)	45 (14)	24 (13)
C(5)	0.4034 (15)	0.4963 (16)	−0.2434 (20)	78 (18)	68 (15)	93 (18)	36 (14)	41 (15)	16 (13)
C(6)	0.3465 (13)	0.4661 (14)	−0.1540 (18)	69 (14)	46 (11)	73 (16)	34 (14)	26 (12)	16 (10)
C(7)	0.3894 (13)	0.5256 (14)	−0.0226 (17)	66 (15)	47 (12)	60 (14)	23 (12)	6 (12)	3 (10)
C(8)	0.4028 (15)	0.5771 (16)	0.1940 (17)	80 (15)	74 (15)	73 (16)	23 (12)	5 (12)	−11 (11)
C(9)	0.3390 (13)	0.5587 (17)	0.2758 (19)	74 (13)	110 (15)	70 (17)	6 (12)	11 (12)	−23 (12)
C(10)	0.1824 (15)	0.4194 (17)	0.2973 (16)	81 (15)	82 (15)	45 (16)	34 (13)	23 (12)	8 (5)
C(11)	0.0840 (15)	0.3269 (16)	0.2589 (17)	74 (15)	68 (14)	53 (16)	42 (12)	19 (12)	11 (10)
C(12)	0.0327 (15)	0.2934 (17)	0.3482 (18)	64 (15)	68 (15)	68 (18)	30 (13)	16 (13)	13 (13)
C(13)	−0.0629 (19)	0.2043 (21)	0.3177 (21)	121 (19)	142 (20)	62 (19)	82 (17)	47 (15)	37 (14)
C(14)	−0.1119 (14)	0.1480 (17)	0.1911 (20)	77 (16)	103 (16)	80 (18)	36 (14)	26 (13)	21 (13)
C(15)	−0.0590 (13)	0.1823 (15)	0.1001 (18)	55 (11)	65 (14)	78 (19)	25 (9)	13 (11)	7 (11)
C(16)	0.0377 (15)	0.2691 (16)	0.1278 (17)	72 (16)	64 (14)	66 (17)	44 (14)	20 (13)	19 (11)
C(17)	0.4252 (12)	0.9049 (12)	0.1756 (15)	49 (12)	38 (11)	51 (13)	21 (9)	−2 (9)	−6 (8)
C(18)	0.3396 (13)	0.8993 (15)	0.1372 (18)	63 (13)	88 (15)	75 (18)	45 (12)	22 (12)	8 (11)
C(19)	0.2819 (15)	0.8865 (17)	0.2193 (21)	64 (15)	113 (15)	93 (20)	41 (13)	9 (14)	−17 (13)
C(20)	0.3099 (16)	0.8823 (17)	0.3495 (19)	90 (16)	123 (18)	53 (17)	58 (14)	34 (14)	0 (12)
C(21)	0.3929 (15)	0.8856 (15)	0.3849 (16)	76 (15)	74 (14)	67 (17)	40 (13)	28 (12)	6 (10)
C(22)	0.4539 (13)	0.8989 (13)	0.3051 (16)	73 (14)	49 (11)	55 (15)	33 (11)	14 (11)	3 (9)
C(23)	0.5397 (13)	0.8989 (15)	0.3517 (16)	64 (13)	81 (15)	50 (15)	37 (12)	9 (11)	12 (10)
C(24)	0.6767 (14)	0.8990 (18)	0.3414 (19)	82 (15)	96 (18)	87 (18)	52 (14)	−5 (12)	0 (13)
C(25)	0.6936 (14)	0.8346 (18)	0.2531 (17)	90 (16)	110 (18)	76 (15)	71 (9)	14 (11)	21 (12)
C(26)	0.6790 (11)	0.8000 (15)	0.0326 (19)	44 (12)	74 (14)	84 (17)	38 (11)	20 (14)	15 (11)
C(27)	0.6425 (13)	0.7903 (14)	−0.0996 (19)	81 (15)	51 (13)	99 (18)	49 (12)	38 (13)	16 (11)
C(28)	0.6703 (14)	0.7447 (15)	−0.1888 (23)	64 (15)	76 (14)	127 (22)	44 (12)	32 (14)	15 (13)
C(29)	0.6308 (17)	0.7254 (17)	−0.3203 (22)	121 (19)	91 (15)	87 (22)	63 (15)	44 (16)	17 (13)
C(30)	0.5698 (15)	0.7584 (17)	−0.3630 (18)	76 (15)	81 (15)	80 (19)	40 (13)	34 (13)	16 (13)
C(31)	0.5403 (14)	0.8056 (15)	−0.2758 (19)	102 (16)	77 (15)	79 (18)	52 (12)	30 (14)	4 (12)
C(32)	0.5797 (14)	0.8231 (14)	−0.1400 (18)	87 (15)	51 (13)	70 (17)	39 (12)	26 (12)	10 (10)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(33)	−0.0333 (16)	0.3440 (19)	−0.3350 (21)	8.6 (6)	C(39)	−0.0771 (38)	−0.0733 (45)	−0.2576 (49)	22.9 (18)
C(34)	−0.0683 (21)	0.4244 (25)	−0.3216 (30)	13.0 (9)	C(40)	0.0044 (20)	0.0356 (26)	−0.1951 (25)	11.2 (8)
C(35)	−0.0795 (23)	0.4382 (26)	−0.1959 (31)	13.6 (9)	C(41)	0.2883 (22)	0.7952 (26)	−0.2975 (30)	12.2 (8)
C(36)	−0.0371 (17)	0.3858 (20)	−0.1239 (22)	9.2 (7)	C(42)	0.2267 (41)	0.6757 (59)	−0.3643 (53)	22.4 (22)
C(37)	−0.0998 (20)	0.0526 (25)	−0.3461 (26)	11.1 (8)	C(43)	0.2399 (36)	0.6140 (44)	−0.2796 (53)	22.4 (18)
C(38)	−0.1175 (25)	−0.0520 (32)	−0.3778 (34)	14.3 (10)	C(44)	0.2931 (26)	0.6805 (33)	−0.1608 (36)	15.3 (12)

[a] Estimated standard deviations in parentheses refer to the last digit. For the form of the anisotropic thermal parameters see the footnote *a* of Table II.

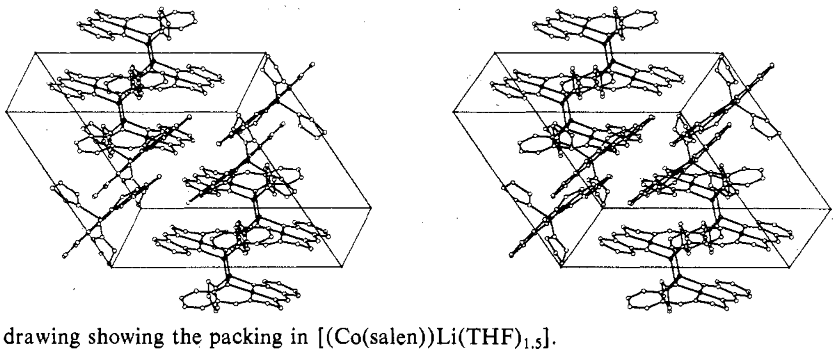


Figure 5. A stereoscopic drawing showing the packing in $[(Co(salen))Li(THF)_{1.5}]$.

a Co(salen) group and two THF molecules, while complex VI is a dimer of the cobalt–lithium bimetallic unit. In VI, Li^+ coordinates the oxygen atom of one THF molecule and two oxygens from Co(salen), while the fourth oxygen provided by the Co(salen) group is related to the first one through an inversion center. The more relevant bond distances and angles

Table V. Selected Bond Lengths (Å) and Angles (deg) in $[Co(salen)Li(THF)_{1.5}]$[a]

Li(1)-O(1)	1.90 (3)	Co(1)-O(1)	1.898 (10)
Li(1)-O(2)	1.92 (3)	Co(1)-O(2)	1.891 (11)
Li(1)-O(5)	1.96 (3)	Co(1)-N(1)	1.798 (13)
Li(1)-O(6)	1.90 (3)	Co(1)-N(2)	1.811 (12)
Li(2)-O(3)	1.92 (3)	Co(2)-O(3)	1.917 (13)
Li(2)-O(3')	1.99 (3)	Co(2)-O(4)	1.867 (11)
Li(2)-O(4)	1.90 (3)	Co(2)-N(3)	1.810 (13)
Li(2)-O(7)	1.94 (3)	Co(2)-N(4)	1.788 (14)

O(1)-Li(1)-O(2)	83.6 (12)	O(1)-Co(1)-O(2)	84.2 (4)
O(1)-Li(1)-O(5)	118.2 (15)	O(1)-Co(1)-N(1)	93.6 (5)
O(1)-Li(1)-O(6)	118.4 (16)	O(1)-Co(1)-N(2)	177.0 (5)
O(2)-Li(1)-O(5)	111.2 (15)	O(2)-Co(1)-N(1)	177.2 (5)
O(2)-Li(1)-O(6)	121.8 (16)	O(2)-Co(1)-N(2)	92.8 (5)
O(5)-Li(1)-O(6)	103.7 (14)	N(1)-Co(1)-N(2)	89.3 (6)
O(3)-Li(2)-O(3')	100.5 (14)	O(3)-Co(2)-O(4)	84.5 (4)
O(3)-Li(2)-O(4)	83.6 (11)	O(3)-Co(2)-N(3)	93.9 (5)
O(3)-Li(2)-O(7)	117.2 (14)	O(3)-Co(2)-N(4)	178.2 (4)
O(3')-Li(2)-O(4)	118.8 (11)	O(4)-Co(2)-N(3)	176.9 (5)
O(3')-Li(2)-O(7)	120.1 (14)	O(4)-Co(2)-N(4)	93.9 (5)
O(4)-Li(2)-O(7)	110.6 (14)	N(3)-Co(2)-N(4)	87.7 (6)

[a] Estimated standard deviations refer to the last digit. The apex indicates atoms generated by the inversion center.

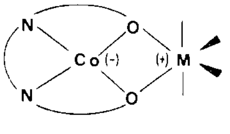
concerning the coordination geometries of cobalt and lithium are given in Table V, and the numbering scheme is given in Figure 6.

Co(salen) Structure in V and VI. Less constraint in the structures of both lithium complexes gives rise to a better square-planar arrangement of the salen ligand around cobalt, the deviation of the cobalt from the least-squares plane passing through the four donor atoms being 0.004 Å for Co(1) and 0.027 Å for Co(2). A significant shortening of the Co–N bond distances parallels that observed for complex III (Co(1)–N(1) = 1.798 (13) Å, Co(1)–N(2) = 1.811 (12) Å, Co(2)–N(3) = 1.810 (13) Å, Co(1)–N(4) = 1.788 (14) Å) (Figure 6). Again this strongly suggests that the +1 cobalt oxidation state affects the Co–N bond distances. All the other bond distances and angles, both for the organic part of the salen and for the coordination polyhedron around cobalt, are very close to those observed for many other Co(salen) complexes[8,9,23] including III.

Coordination Sphere of Lithium Cation in V and VI. The coordination sphere around Li(1) and Li(2) is nearly tetrahedral, the main distortion being due to the O–O bite of the Co(salen), which imposes an O–Li–O angle of 83.6°. All the Li–O distances are found in the range 1.90 (3)–1.99 (3) Å (Figure 6). The structural parameters of the two lithium complexes are very close.

Discussion

The solid-state structures of complexes III and IV are built up by the basic bimetallic unit [(Co(salen))M], where the open coordination sites around the alkali cation are filled by the oxygen atoms of another Co(salen) unit or by solvent molecules. While the relative arrangement of the two metallic centers is mainly imposed by the rigidity of the tetradentate salen ligand, the molecular complexity of the complexes mainly depends on the ionic radius of the alkali cation. The largest alkali cation, Na^+ vs. Li^+, allows an extension of the polymerization, since the rather hindered salen oxygens can act as bridging donor atoms. The coordination around cobalt(I) is only slightly distorted from square planar, and so these complexes fall in the wide class of transition metal(I)–d^8 square-planar systems.[1,26] The stabilization of this oxidation state for cobalt depends on the ability of the unsaturated ligand to form π bonding with the metal. A significant observation, in this context, is the shift of the ν(C=N) from the usual 1605–1625-cm^{-1} region to a lower unidentified position,[6,21] suggesting that the C=N groups could be involved in back-donation by the metal. This is further suggested by the unusually short Co–N bond distances in all of these complexes compared to complexes in which cobalt has a +2 or +3 oxidation state.[22] The closeness of the basic cobalt(I) to the Li^+ (Na^+) acid center in these complexes is of interest in that they model such adjacent acid and base centers likely present in certain enzyme systems.[12] The ion-pair nature of complex II is also highly reminiscent of the same solid-state nature of carbonylmetalate anion–alkali cation systems. The ion-pair nature of $Na_2Fe(CO)_4$[25] and $NaCo(CO)_4$[9] in the solid state is well documented and it likely pertains in solution.[26] The solution behavior of our cobalt(I) systems is likely dependent on the chemistry of the alkali cation center, especially since V and VI come from the same solution (e.g., eq 2). Complex VII maintaining the bimetallic unit would be a structural model for the complexes in solution. Some data support the existence of such an entity in solution. We observed an abnormal solubility of Me(salen) complexes in THF in the presence of some sodium salts ($NaBPh_4$, $NaCo(CO)_4$, etc.),[8,9] Na^+ apparently operating as a complex carrier. Very recently, Collman's group delineated



Co(salen)M

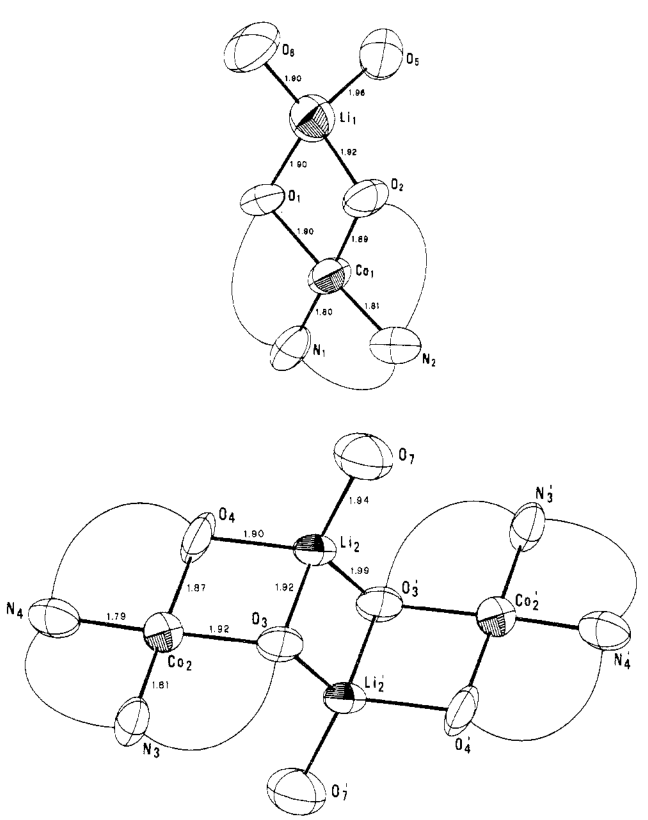
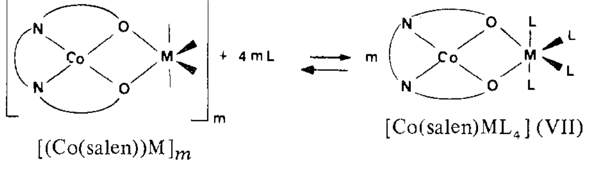


Figure 6. A partial drawing of the dinuclear $[(Co(salen))Li(THF)_2]$ (top) and tetranuclear $[(Co(salen))_2Li_2(THF)_2]$ (bottom) complexes, showing bond distances for the coordination polyhedra around Li and Co.



(2)

$[(Co(salen))M]_m$ $[Co(salen)ML_4]$ (VII)

L = THF

the importance of the ion pairing on the reactivity of $Na_2Fe(CO)_4$,[27] and we have found that the solution reactivity of complex II can be interpreted in terms of the existence of the ion pair such as VII.[28] While the reaction of carbon monoxide with cobalt(I) complexes, that do not allow the ion pairing,[29] produces a stable monocarbonyl species, reaction of II with CO is a multistep process giving finally $[(Co(salen))_2NaCo(CO)_4THF]$.[9,30] Moreover, complex II reacts in solution with CO_2, giving isolable adducts.[10,11,28]

The X-ray structural determination carried out on one of these CO_2 complexes showed that both metal centers are involved in fixing the CO_2, which is C bonded to the cobalt and O bonded to the alkali cation. The fixation likely involves concerted attack of the nucleophilic cobalt(I) on the electrophilic carbon of the CO_2, while the acid M^+ partner of the bifunctional system interacts with the basic oxygens.[10,11]

The potential of such bifunctional complexes for activating other small molecules is being studied.

Acknowledgment. We thank the CNR (Rome) for financial support, Dr. G. Dell'Amico for some magnetic measurements, and Professor B. R. James for assistance with the manuscript.

Registry No. (Co(salen))NaTHF, 71369-90-9; (Co(salen))Li(THF)$_{1.5}$, 71316-78-4; Co(salen), 14167-18-1.

Supplementary Material Available: Bond lengths and angles within salen and THF ligands for complexes III and IV (Tables SI and SII), least-squares planes for complexes III and IV (Tables SIII and SIV), calculated positional parameters for hydrogen atoms for III and IV (Tables SV and SVI), and structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231. Halpern, J. *Adv. Chem. Ser.* **1968**, *No. 70*, 1. Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.

(2) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109 and references cited therein. Takvoryan, N.; Farmery, K.; Katovic, V.; Lovecchio, F. V.; Gore, E. S.; Anderson, L. B.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 731.

(3) Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97 and references cited therein. Schrauzer, G. N.; Weber, J. H.; Beckman, T. M. *J. Am. Chem. Soc.* **1970**, *92*, 7078. Schrauzer, G. N. *Inorg. Synth.*, **1968**, *11*, 65.

(4) Rillema, D. P.; Endicott, J. F.; Papaconstantinou, E. *Inorg. Chem.* **1971**, *10*, 1739.

(5) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1969**, *8*, 1611; **1971**, *10*, 463.

(6) Floriani, C.; Puppis, M.; Calderazzo, F. *J. Organomet. Chem.* **1968**, *12*, 209. Calderazzo, F.; Floriani, C. *Chem. Commun.*, **1968**, 417.

(7) Costa, G.; Mestroni, G.; Pellizer, G. *J. Organomet. Chem.* **1968**, *11*, 333. Costa, G.; Mestroni, G. *Ibid.* **1968**, *11*, 325.

(8) Floriani, C.; Calderazzo, F.; Randaccio, L. *J. Chem. Soc., Chem. Commun.* **1973**, 384; Bresciani-Pahor, N.; Calligaris, M.; Delise, P.; Nardin, G.; Randaccio, L.; Zotti, E.; Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 2310. Milburn, H.; Truter, M. R.; Vichêry, B. L. *Ibid.* **1974**, 841. Armstrong, L. G.; Lip, H. C.; Lindoy, L. F.; McPartlin, M.; Tasker, P. A. *Ibid.* **1977**, 1771.

(9) Fachinetti, G.; Floriani, C.; Zanazzi, P. F.; Zanzari, A. R. *Inorg. Chem.* **1978**, *17*, 3002.

(10) Floriani, C.; Fachinetti, G. *J. Chem. Soc., Chem. Commun.* **1974**, 615.

(11) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405.

(12) Dennard, A. E.; Williams, R. J. P. "Transition Metal Chemistry"; Carlin, R. L., Ed.; Marcel Dekker: New York, 1966; Vol. 2, p 122.

(13) Ugo, R. *Engelhard Techn. Bull.* **1971**, *11*, 45. Thomas, J. M. "Introduction to the Principles of Heterogeneous Catalysis"; Academic Press: New York, 1967. Bond, G. C. *Chem. Eng. (N.Y.)* **1968**, *63*, 3.

(14) Floriani, C.; Calderazzo, F. *J. Chem. Soc. A* **1969**, 946.

(15) Standard deviations on intensities were computed as $I = [P + 0.25(T_P/T_B)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$, where P is the total peak count in a scan of time T_P, B_1 and B_2 are the background counts each in a time T_B, and I is the intensity, equal to $P - 0.5(T_P/T_B)(B_1 + B_2)$.

(16) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, pp 202–205.

(17) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

(18) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368.

(19) Floriani, C., unpublished results.

(20) Notwithstanding that complexes III and IV are fundamentally diamagnetic, sometimes we found the presence of significant paramagnetism. It must be remembered that these complexes are very air sensitive. Moreover we verified that, since the samples are sealed in glass tubes, even the presence of a very small amount of burned material causes the appearance of a significant amount of paramagnetism.

(21) Teyssie, P.; Charette, J. J. *Spectrochim. Acta* **1963**, *19*, 1407.

(22) Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385.

(23) Randaccio, L. *Gazz. Chim. Ital.* **1974**, *104*, 991.

(24) Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386.

(25) Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 2434. Teller, R. G.; Finke, R. G.; Collman, J. P.; Chin, H. B.; Bau, R. *Ibid.* **1977**, *99*, 1104.

(26) Darensbourg, M. Y.; Darensbourg, D. J.; Burns, D.; Drew, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3127. Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978**, *17*, 297. Edgell, W. F.; Lyford, J. *J. Am. Chem. Soc.* **1971**, *93*, 6407 and references cited therein.

(27) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515; **1978**, *100*, 4766. Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119.

(28) Floriani, C., unpublished results.

(29) Costa, G.; Mestroni, G.; Tauzher, G. *J. Chem. Soc., Dalton Trans.* **1972**, 450. Goedken, V. L.; Peng, S. M. *J. Chem. Soc., Chem. Commun.* **1974**, 914 and references cited therein.

(30) Floriani, C.; Fachinetti, G. *Transition Met. Chem.* **1976**, *1*, 50.

(31) Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

(32) Johnson, C. K. "ORTEP", Report ORNL-3794, Oak Ridge National Laboratory: Oak Ridge, Tenn., 1965.

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Stereochemistry of Equatorial Photosubstitution Reactions. The Chromium(III)–Fluoropentaamine Case

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Received March 9, 1979

It is shown that the observed stereomobility of equatorial photosubstitution reactions can be accommodated within the framework of ligand field theory. By use of orbital and state energy correlation diagrams, electronic selection rules can be seen to be operative in governing the course of the photoreaction. Possible complications due to radiationless deactivation processes are discussed.

Introduction

The substitution photochemistry of Cr(III) complexes has been at the basis of a number of experimental rules, whose formulation has greatly stimulated inorganic photochemistry as a whole.[1–5] In a series of recent papers,[6–9] we have shown how the main facts could be rationalized within the framework of ligand field considerations. As for the stereochemistry of the Cr(III) complexes, our treatment was limited to the so-called "axial labilization". An illustrative example of this type of labilization is provided by the photoreaction[11]

$$\textit{trans}\text{-Cr(en)}_2(\text{NH}_3)\text{F}^{2+} + \text{H}_2\text{O} \xrightarrow{h\nu} \textit{cis}\text{-Cr(en)}_2(\text{H}_2\text{O})\text{F}^{2+} + \text{NH}_3$$

where the axial amine ligand is replaced by a solvent molecule

0020-1669/79/1318-3475$01.00/0