conformation with C(41) displaced by 0.44 Å with respect to the plane through the other four atoms O(2), C(42), C(43), and C(44).

(39) V. Kocman, J. C. Rucklidge, R. J. O'Brien, and W. Santo, *Chem. Commun.*, 1340 (1971).

(40) G. Fachinetti, C. Floriani, F. Marchetti, and M. Mellini, *J. Chem. Soc., Dalton Trans.*, in press.

(41) T. Herskovitz and L. J. Guggenberger, *J. Am. Chem. Soc.*, **98**, 1615 (1976).

(42) J. Browning, H. D. Empsall, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 381 (1973), and references therein.

(43) S. Cenini and G. La Monica, *Inorg. Chim. Acta*, **18**, 279 (1976).

(44) S. D. Ittel, *Inorg. Chem.*, **16**, 2589 (1977); J. Burgess, J. G. Chambers, D. A. Clarke, and D. W. Kemmitt, *J. Chem. Soc., Dalton Trans.*, 1906 (1977); Von D. Walther, *Z. Anorg. Allg. Chem.*, **431**, 17 (1977).

(45) The lattice constants of the triclinic cell reduced to a standard "type I" cell are as follows: $a = 9.990$ (1) Å, $b = 11.058$ (2) Å, $c = 10.820$ (2) Å, $\alpha = 73.86$ (2)°, $\beta = 85.02$ (2)°, $\gamma = 81.15$ (1)°.

(46) The unit cell parameters, reduced to the standard setting $C2/c$ (No. 15), are $a = 30.358$ (5) Å, $b = 11.327$ (2) Å, $c = 20.370$ (3) Å, and $\beta = 126.46$ (3)°. The transformation matrix from the $I2/a$ to $C2/c$ orientation is $(101//0\bar{1}0//00\bar{1})$. Coordinates of equivalent positions for the nonstandard $I2/a$ setting are $(0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2)$ +; x, y, z; $\bar{x}, \bar{y}, \bar{z}$; ${}^1/_2 - x, y, \bar{z}$; ${}^1/_2 + x, \bar{y}, z$.

(47) Absorption corrections were not applied in view of the rather low absorbance ($\mu\bar{r}$ ca. 0.5) and the irregular shape of the sample examined.

(48) Supplementary material.

Contribution from the Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy, and Cattedra di Cristallografia, Università di Perugia, 06100 Perugia, Italy

Isolation of the Ion Pair $NaCo(CO)_4$ Promoted by an Inorganic Ligand: Structure and Properties of $[(Co(salen))_2NaCo(CO)_4THF]$

GIUSEPPE FACHINETTI,[1a] CARLO FLORIANI,*[1a] PIER FRANCESCO ZANAZZI,[1b]
and ANNA ROSA ZANZARI[1b]

Received June 21, 1978

A THF (tetrahydrofuran) solution of sodium *N,N'*-ethylenebis(salicylideniminato)cobaltate(I), Co(salen)Na, reacts reversibly with carbon monoxide giving a monocarbonylic species, Co(salen)NaCO, rapidly evolving under a CO atmosphere to a compound containing $NaCo(CO)_4$ as a complexed ion pair, $[(Co(salen))_2NaCo(CO)_4THF]$ (III). The structure of III has been solved by single-crystal X-ray diffraction methods. Crystallographic details for III are as follows: space group $P\bar{1}$ (triclinic), $a = 12.356$ (3) Å, $b = 13.207$ (3), Å, $c = 17.576$ (4) Å, $\alpha = 92.83$ (2)°, $\beta = 121.55$ (2)°, $\gamma = 116.69$ (2)°, $V = 2025.8$ Å^3, and $Z = 2$. The final R factor is 4.9% for 2849 observed reflections. The most interesting feature of the structure is the fact that III is a complex of Na^+ octahedrally surrounded by six oxygen atoms provided by two Co(salen) groups, acting as bidentate chelating ligands, THF, and $Co(CO)_4^-$ bonded to Na^+ through one of the carbonylic oxygens. The $Co(CO)_4^-$ has essentially an undistorted tetrahedral symmetry. The IR spectrum in the solid state (Nujol) showed well-resolved bands at 2003, 1917, 1890, and 1867 cm^{-1}.

Introduction

Ion-pairing effects on chemical reactivity of transition-metal organic anions have received very limited attention. Recently, Collman delineated the importance of ion pairing on the reactivity of $Na_2Fe(CO)_4$,[2] whose solid-state X-ray analysis showed the existence of a solvent-separated ion pair and a contact ion pair.[3,4]

While the usual reaction of cobalt(I) square-planar complexes with carbon monoxide gives rise to the corresponding stable monocaronyl derivatives,[5] the reaction with sodium *N,N'*-ethylenebis(salicylideniminato)cobaltate(I), Co(salen)Na (I),[6-8] allows the isolation of the polynuclear system $[(Co(salen))_2NaCo(CO)_4THF]$ (III), containing the complexed ion pair $NaCo(CO)_4$. Moreover, while it is very well-known that crown ethers complex ion pairs,[9] using "inorganic ligands", such as a set of bicovalent oxygens bonded to a transition metal, it is possible to achieve parallel results.[10-15] Thus ion-pair units may be encapsulated in a cage formed by the oxygen atoms of different coordination compounds.[10-15] These complexes represent structural models for polynuclear and/or polyfunctional systems, whose utilization in molecular activation processes might be important.[16] $NaCo(CO)_4$ was shown by Edgell et al. to consist of an equilibrium of solvent-separated and contact ion pairs, such as $(CO)_3CoCo^-\cdots Na^+$ in THF.[17] We report in this study the genesis and the X-ray analysis of III showing the $(CO)_3CoCONa$ ion pair sequestered by the inorganic ligand *N,N'*-ethylenebis(salicylideniminato)cobalt(II), Co(salen).

Experimental section

All the reactions were carried out under an atmosphere of purified nitrogen or carbon monoxide. Solvents were purified by standard methods. Infrared spectra were recorded on Perkin-Elmer 282 and 337 spectrometers. Absorption or evolution of carbon monoxide was measured volumetrically. The magnetic measurements were carried out with a Gouy balance. *N,N'*-Ethylenebis(salicylideniminato)cobalt(II), Co(salen),[18] and sodium *N,N'*-ethylenebis(salicylideniminato)cobaltate(I), Co(salen)Na,[5] were prepared as previously described.

Carbonylation of Sodium *N,N'*-Ethylenebis(salicylideniminato)cobaltate(I), Co(salen)Na. A THF (400 mL) suspension of Co(salen) (13.5 g, 41.5 mmol) was reacted with sodium sand (1.028 g, 44.7 mmol). The suspension gave, on stirring, in 3 h, a deep green solution. The presence of small amounts of solid was eliminated by filtration. The green solution was stirred under CO for another 13 h at atmospheric pressure and room temperature. The color changed slowly from green to red-maroon. The volume of the solution was reduced to 150 mL and, by addition of toluene (200 mL), a red crystalline solid was obtained. This was recrystallized from THF/toluene. Heating must be avoided, because the solid can release free Co(salen). The solid contained small amounts of toluene, which could be found on heating at 180 °C and determined by GLC (ca. 3.7%). This gave rise to the observed differences in the analytical data. Anal. Calcd for $[(Co(salen))_2NaCo(CO)_4]$, $C_{36}H_{28}N_4O_8Co_3Na$: C, 51.18; H, 3.31; N, 6.63. Found: C, 51.81; H, 3.78; N, 5.88. The IR spectrum (Nujol) shows bands at 2003 (vw) and 1920 (m–s) cm^{-1} and a large rather unresolved band at 1880–1860 cm^{-1}. $\mu_{eff}(293\ K) = 2.55\ \mu_B$ per Co(salen) unit. By addition of Et_2O to the deep red solution, suitable crystals for X-ray analysis of $[(Co(salen))_2NaCo(CO)_4THF]$ were obtained. Anal. Calcd for $[(Co(salen))_2NaCo(CO)_4THF]$, $C_{40}H_{36}H_4O_9Co_3Na$: C, 52.40; H, 3.93; N, 6.11. Found: C, 52.30; H, 4.01; N, 6.01. The IR spectrum (Nujol) shows four well-resolved bands at 2003 (w), 1917 (m–s), 1890 (s), and 1867 (s) cm^{-1}. The solid, decomposed with a pyridine solution of I_2, gave 3.68 mol of CO/mol of complex.

Preparation of $[(Co(salen))_2NaCo(CO)_4]$ from $NaCo(CO)_4$. $Co_2(CO)_8$ (1.05 g, 3.07 mmol) was dissolved in toluene and reacted with sodium sand (0.195 g, 8.4 mmol) and Hg (1 mL). In 3 h a gray powder was formed. The solvent was evaporated to dryness and the Hg eliminated when the solid was dissolved in THF (100 mL). Co(salen) (5.8 g, 17.8 mmol) in excess was added to the solution on stirring for 20 min. The excess of Co(salen) was filtered out and the solution gave, by addition of toluene (200 mL), a deep red crystalline

0020-1669/78/1317-3002$01.00/0

Table I. Crystal data for [(Co(salen))$_2$NaCo(CO)$_4$THF]

$C_{40}H_{36}N_4O_9Co_3Na$
mol wt = 916
triclinic, $P\bar{1}$
$a = 12.356$ (3) Å
$b = 13.207$ (3) Å
$c = 17.576$ (4) Å
$\alpha = 92.83$ (2)°
$\beta = 121.55$ (2)°
$\gamma = 116.69$ (2)°
$V = 2025.8$ Å^3
μ(Mo Kα) = 12.84 cm^{-1}
$Z = 2$, $d_{\text{calcd}} = 1.446$ g cm^{-3}

solid (2.7 g, ca. 55%). The solid, heated in the solid state at 180 °C, was shown to contain toluene. The IR spectrum in Nujol was found to be superimposable on that of the product derived from the direct carbonylation of Co(salen)Na. By addition of Et_2O to the red solution, [(Co(salen))$_2$NaCo(CO)$_4$THF], as described above, was obtained.

Reaction of [(Co(salen))$_2$NaCo(CO)$_4$] with NaI. [(Co(salen))$_2$NaCo(CO)$_4$] (1.53 g, 1.75 mmol) was dissolved in THF (100 mL). The addition of NaI (0.53 g, 3.53 mmol) caused the immediate crystallization of a light orange solid. After 4 h, on stirring, the solid was collected and washed several times with THF (ca. 93%). Anal. Calcd for Co(salen)NaI, $C_{16}H_{14}N_2O_2INaCo$: C, 40.42; H, 2.94; N, 5.89; I, 26.73. Found: C, 41.43; H, 3.52; N, 5.43; I, 26.0. This sample contains, as shown by heating, only traces of THF (GLC determined). The mother liquor was concentrated to 50 mL and toluene (500 mL) was added. Reducing the volume of the solution to 30–50 mL and cooling at −80 °C, we obtained a red oil and a colorless overfloating solvent. The solvent was separated from the oil, and the addition of heptane gave white-gray crystals of NaCo(CO)$_4$ (ca. 72%).[19]

X-ray Data Collection. Crystals of [(Co(salen))$_2$NaCo(CO)$_4$THF] are triclinic. Lattice dimensions according to the Delaunay reduced cell were determined at 20 ± 2 °C with a least-squares procedure using the values of the setting angles of 25 reflections measured on a Philips PW 1100 four-circle diffractometer with Mo Kα radiation. The space group $P\bar{1}$, assumed on the basis of the results of intensity distribution statistics, was later confirmed by structural analysis. The crystal data are listed in Table I.

A single crystal of prismatic shape with dimensions 0.08 × 0.10 × 0.29 mm was used for intensity measurements, employing graphite-monchromatized Mo Kα radiation. The θ–2θ scan technique to a limit of $2\theta = 50°$ was adopted. Each reflection was measured with a scan width of 1.0° and a scan speed of 0.06° s^{-1} and two background measurements for 8 s on each side of the reflection. Three reflections were monitored after every 180 min. A total decay of 6% in intensity was detected. A total of 6102 independent reflections were collected; 3253 reflections with intensity I less than $3\sigma(I)$[20] were considered unobserved. Corrections were applied to the data for Lorentz and polarization effects, as well as for the variation of the monitored intensities. Absorption correction was deemed unnecessary.

Solution and Refinement of the Structure. The structure was solved by the direct multisolution method with MULTAN.[21] A total of 350 $|E|$ values ($|E| \geq 1.85$) and the 2000 best triple relations among them were used to generate eight trial phase sets. The E map for the solution with the best figure of merit showed the positions of the three Co atoms of the asymmetric unit. With the phases from these Co atoms, an α synthesis[22] showed the positions of the planar squares of oxygen and nitrogen around Co(1) and Co(2). At this stage an electron density map showed part of the N,N'-ethylenebis(salicylidenimine) ligand around Co(2), the Na ion, and its coordination octahedron. The whole structure was revealed by successive Fourier syntheses. Two cycles of full-matrix least squares with individual isotropic thermal parameters reduced $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ to 0.11. Anisotropic refinement was performed with alternate cycles of blocked least squares; owing to the large number of parameters, anisotropic thermal parameters were allowed to refine only for half of the atoms at the time. The R index converged at 0.058. At this stage hydrogen atoms were introduced at their calculated positions (1.075 Å from C atoms) and with isotropic thermal parameters equal to those of carbon atoms to which they are bonded. Their contribution reduced R to 0.053. A final pair of cycles for nonhydrogen atoms yielded the final R value of 0.049 for 2849 observed reflections. R_w, defined as $R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$, was 0.059. The function minimized during all least-squares refinement was $\sum w(F_o - F_c)^2$, where the weighting factor w equals $4F_o^2/\sigma(F_o)^2$. The scattering factors from ref 23 were used for neutral Co, Na, O, N, C, and H. Anomalous scattering corrections were included for Co and Na atoms.[24] Tables of observed and calculated structure factors are available as supplementary material. Atomic coordinate parameters and anisotropic thermal vibration parameters for nonhydrogen atoms are presented in Table II. A list of calculated hydrogen atom coordinates is available as supplementary material, as well as the complete information concerning 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. A selection of bond lengths and angles is given in Table III.

Results

Sodium N,N'-ethylenebis(salicylideniminato)cobaltate(I), Co(salen)Na, in tetrahydrofuran, THF, solution very rapidly absorbs carbon monoxide at room temperature and atmospheric pressure, as monitored by gas-volumetric measurements and IR spectra. This absorption was found reversible over many vacuum–CO cycles and can be followed by a strong band at 1885 cm^{-1}.

$$\underset{\text{I}}{\text{Co(salen)Na}} + \text{CO} \rightleftarrows \underset{\text{II}}{\text{Co(salen)NaCO}} \tag{1}$$

The first fast absorption of CO is followed by a second much slower step, while the CO band stays unchanged and centered around 1885 cm^{-1}. At this point, the absorption of CO, reaching the maximum CO/Co ratio of 1.25, is no further reversible. The color of the solution remains green during the first step and drastically changes to red at the end of the second one. The rate of the second irreversible step depends strongly on the nature of the tetradentate ligand.[7] Thus, the starting deep green solution of Co(salen)Na is converted in a deep red one, from which, by addition of Et_2O, a red crystalline solid is obtained, analyzing as [(Co(salen))$_2$NaCo(CO)$_4$THF] (III). The overall reaction producing III can be described as

$$\underset{\text{I}}{3\text{Co(salen)Na}} + 4\text{CO} \xrightarrow[\text{Et}_2\text{O}]{\text{THF}} \underset{\text{III}}{[(\text{Co(salen)})_2\text{NaCo(CO)}_4\text{THF}]} + \text{salenNa}_2{}^{25} \tag{2}$$

The solution from which III is recovered, when heated at 50 °C, releases, partially, Co(salen) and, when treated with a THF solution of NaI,[14] allows the separation of all Co(salen) as Co(salen)NaI, while NaCo(CO)$_4$ can be subsequentially isolated from the solution in quantitative yield (see Experimental Section). III can also be synthetized from its components. Co(salen), which is practically insoluble in THF, dissolves in the presence of NaCo(CO)$_4$, giving a deep red solution from which III is recovered by addition of Et_2O. By addition of toluene to the red solution, instead of III, [(Co(salen))$_2$NaCo(CO)$_4$] (IV), is obtained. While the deep red THF solution shows a strong band of complex envelope at about 1885 cm^{-1},[17] the IR spectrum of III in Nujol shows four easily distinguishable bands at 2003 (vw), 1920 (ms), 1885 (s), and 1860 (s) cm^{-1}. Although very poorly resolved, the IR spectrum of IV, in the carbonyl region, is similar to that of III, with bands at 2003 and 1920 cm^{-1} and a large rather unresolved band at 1880–1860 cm^{-1}.

Description of the Structure of III. The crystal structure is built up by the neutral unit [(Co(salen))$_2$NaCo(CO)$_4$THF], held together by van der Waals interactions, the intermolecular distances being regular. The basic unit can be described as a sodium cation complex, in which Co(CO)$_4^-$, THF, and two Co(salen) groups provide the six oxygens for the coordination sphere. The molecular structure and the numbering scheme are given in Figures 1 and 2.

The Co(CO)$_4^-$ Anion. Co(CO)$_4^-$ is not significantly distorted from the idealized tetrahedral symmetry, with C–Co–C angles ranging from 110.1 (5) to 112.0 (5)°. The four independent Co–C and C–O distances are essentially identical varying from 1.736 (11) to 1.752 (9) Å and from 1.150 (14) to 1.181 (15) Å, respectively. The CO–Na interaction affects neither the related C–O and Co–C bond distances nor the Co–C(37)–O(6) angle, 178.8 (9)°. The four Co–C–O units are nearly linear (Figure 3). The angle around the oxygen of the bridging CO is 142.1 (6)°.

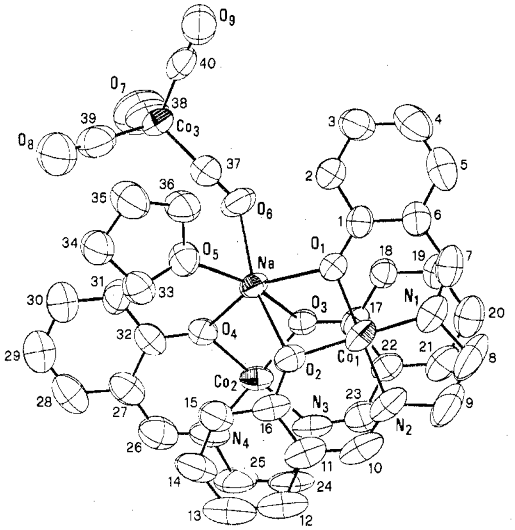

Figure 1. An ORTEP[35] drawing of the structure of [(Co(salen))$_2$NaCo(CO)$_4$THF] showing the numbering scheme. The thermal ellipsoids are drawn for 50% probability.

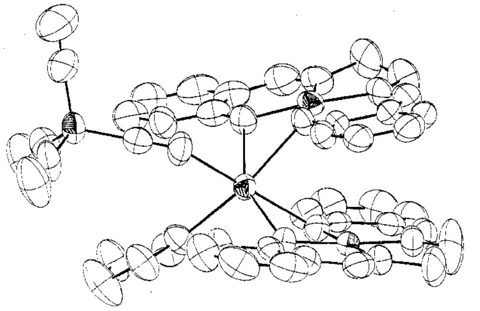

Figure 2. Another perspective view of [(Co(salen))$_2$NaCo(CO)$_4$THF] drawn by ORTEP.[35]

The Coordination Sphere of Na$^+$. Na$^+$ is coordinated to two Co(salen) units acting as bidentate chelating ligands, and the approximatively octahedral coordination is completed by a THF molecule and a Co(CO)$_4$$^-$ unit (Figure 3). The coordination environment of Na$^+$ is very similar to that in [Co(salen)$_2$NaTHF$_2$]$^+$ (V),[14] as concerns bond distances and angles (Table III). The Na–O distances range from 2.378 (7) to 2.464 (7) Å in III vs. 2.350 (11) to 2.482 (9) Å in V. A quite similar angle pattern is observed for the two complexes. The different chemical origin of the oxygens does not significantly affect these parameters. The main distortion in the sodium octahedron is due to the O–O bite of the two (Co(salen) ligands, which imposes angles O–Na–O of 64.8 (2) and 63.6 (2)°.

The Co(salen) Structure. The Co(salen) unit is nearly planar. There is close agreement between bond lengths and angles in the two chemically equivalent halves of the Co(salen) complex and the values are similar to those reported for V[14] and other tetracoordinate Co(salen) complexes.[26] The coordination around the cobalt atom is nearly planar, the deviations of the four donor atoms and of cobalt from the least-squares planes passing through O and N atoms being in the range 0.01–0.07 Å. The ethylene bridges have a nearly gauche conformation.

The THF Molecule. The THF molecule, although coordinated to sodium, undergoes a significant thermal motion in agreement with a pseudorotation of the ring similar to that of cyclopentane. The angles around O(5) are 109.4, 129.7, and 120.6°.

Discussion

The result reported in reaction 2 is completely unexpected, since the addition of CO to a wide number of Co(I) d^8 square-planar macrocyclic complexes resulted in the formation of the corresponding stable monocarbonyls.[5] We noticed, on the contrary, that the monocarbonylic species Co(salen)NaCO is formed in our case only as labile and elusive species. Further irreversible evolution of this species in carbon monoxide atmosphere corresponds to a partial disengagement of the cobalt from the rigid tetradentate ligand, producing NaCo(CO)$_4$, reaction 2. It is rather difficult to identify the property of I inducing this kind of reactivity, in comparison with other cobalt(I) complexes.[5] This notwithstanding, it could be interesting to notice the difference between Co(salen)Na-like complexes and the usual cobalt(I) complexes. While the latter contain the basic d^8 cobalt(I) site as the only reactive center, Co(salen)Na could be better described as a bimetallic or bifunctional complex containing both an acid (Na$^+$) and a basic center (Co). This hypothesis on the nature of Co(salen)Na is based on the knowledge of its structure in the solid state[7] and on the very well-documented ability of the salen's oxygens to act as bidentate chelating ligands toward alkali cations.[10-15] In addition, the bifunctional nature of Co(salen)Na seems to play a prominent role in the reaction occurring between I and carbon dioxide.[27]

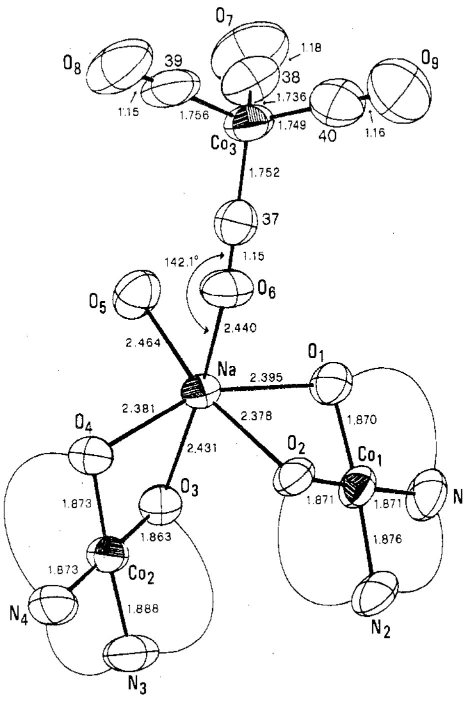

Figure 3. A partial view of the molecule, showing a selection of bond distances involving mainly Na and Co atoms.

The nature of III can be indirectly proved through synthesis from its components. As the THF solution of NaCo(CO)$_4$ increases abnormally the Co(salen) solubility, so the same effect was observed using a THF solution of NaBPh$_4$.[13] This reaction led to the isolation of the solvent-separated complexed ion pair NaBPh$_4$, as [(Co(salen))$_2$NaTHF$_2$]BPh$_4$ (V).[13-15] It must be noticed that the cobalt chelate solubility induced by sodium salts can be assumed as a proof of the interaction occurring in solution between Na$^+$ and the "inorganic ligand" Co(salen). This suggests that it will be possible to use the appropriate sodium salts as complex carriers both in water as well as in nonaqueous solvents.[28] This is a very interesting aspect in this chemistry, which must be taken into account for realizing polyfunctional systems suitable for molecular activation studies.

The structural relationship between III, IV, and V can be easily identified describing them as Na$^+$ complexes. Thus

Table II. Fractional Atomic Coordinates and Thermal Parameters[a] for Nonhydrogen Atoms[b]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq}[c]
Co(1)	0.6396 (1)	0.9898 (1)	0.0923 (1)	119 (2)	104 (1)	71 (1)	62 (1)	56 (1)	51 (1)	4.7
Co(2)	0.9044 (1)	1.0441 (1)	0.4068 (1)	118 (2)	70 (1)	50 (1)	40 (1)	28 (1)	11 (1)	4.5
Co(3)	0.3548 (2)	0.4303 (1)	0.2543 (1)	162 (2)	81 (1)	79 (1)	41 (2)	73 (1)	29 (1)	5.3
Na	0.5677 (3)	0.8382 (3)	0.2187 (2)	121 (5)	66 (3)	50 (2)	33 (3)	44 (3)	21 (2)	4.0
O(1)	0.5125 (6)	0.8242 (5)	0.0646 (4)	147 (10)	81 (6)	60 (4)	55 (7)	63 (6)	29 (4)	4.3
O(2)	0.6187 (6)	1.0209 (5)	0.1873 (4)	150 (10)	83 (6)	57 (4)	51 (7)	51 (6)	27 (4)	4.7
O(3)	0.8390 (6)	0.9291 (5)	0.3008 (4)	110 (9)	74 (6)	49 (4)	26 (6)	42 (5)	9 (4)	4.2
O(4)	0.7292 (6)	0.9228 (5)	0.3900 (4)	150 (10)	85 (6)	51 (4)	44 (7)	51 (5)	13 (4)	4.7
O(5)	0.3158 (7)	0.7639 (6)	0.1796 (5)	140 (10)	130 (8)	72 (5)	63 (8)	61 (6)	2 (5)	5.7
O(6)	0.5217 (7)	0.6390 (6)	0.2221 (5)	205 (13)	85 (7)	91 (5)	57 (8)	88 (7)	43 (5)	6.0
O(7)	0.5687 (11)	0.3913 (8)	0.4095 (7)	394 (23)	210 (13)	154 (9)	188 (14)	131 (12)	103 (9)	11.3
O(8)	0.2002 (11)	0.4780 (8)	0.3166 (7)	306 (19)	212 (3)	172 (9)	113 (13)	169 (11)	30 (9)	10.8
O(9)	0.1402 (9)	0.2246 (8)	0.0716 (6)	257 (16)	189 (12)	102 (7)	−5 (11)	113 (9)	−19 (7)	10.6
N(1)	0.6591 (9)	0.9608 (8)	−0.0038 (6)	157 (14)	143 (11)	84 (7)	80 (11)	81 (9)	60 (7)	5.8
N(2)	0.7787 (9)	1.1557 (8)	0.1267 (7)	150 (14)	112 (10)	119 (8)	72 (10)	91 (9)	71 (7)	6.2
N(3)	1.0692 (8)	1.1694 (6)	0.4145 (6)	131 (13)	56 (7)	79 (6)	22 (8)	41 (7)	11 (6)	5.5
N(4)	0.9773 (9)	1.1557 (7)	0.5185 (6)	179 (15)	83 (8)	45 (6)	47 (10)	21 (7)	−7 (6)	5.9
C(1)	0.4634 (9)	0.7286 (8)	−0.0016 (7)	113 (14)	118 (11)	60 (7)	73 (11)	54 (9)	36 (7)	4.3
C(2)	0.3667 (11)	0.6095 (9)	−0.0105 (7)	172 (17)	109 (12)	84 (8)	60 (12)	86 (10)	32 (8)	5.6
C(3)	0.3132 (12)	0.5049 (10)	−0.0786 (9)	212 (21)	115 (12)	99 (9)	69 (14)	93 (12)	13 (9)	6.9
C(4)	0.3564 (14)	0.5177 (13)	−0.1392 (8)	192 (21)	171 (15)	74 (8)	94 (15)	53 (11)	−4 (9)	7.5
C(5)	0.4491 (14)	0.6321 (15)	−0.1319 (8)	206 (21)	221 (18)	59 (8)	137 (17)	70 (11)	37 (10)	6.9
C(6)	0.5038 (11)	0.7387 (11)	−0.0646 (7)	162 (18)	145 (13)	58 (7)	82 (13)	62 (10)	31 (8)	5.5
C(7)	0.6005 (12)	0.8566 (12)	−0.0612 (7)	185 (20)	198 (16)	79 (8)	138 (16)	89 (11)	77 (10)	6.0
C(8)	0.7543 (14)	1.0725 (14)	−0.0108 (9)	224 (23)	225 (19)	93 (10)	37 (18)	99 (13)	80 (11)	9.7
C(9)	0.8403 (19)	1.1750 (13)	0.0729 (14)	425 (37)	179 (18)	248 (19)	124 (22)	293 (25)	108 (15)	11.4
C(10)	0.8256 (12)	1.2487 (10)	0.1925 (10)	143 (18)	94 (12)	131 (11)	62 (12)	73 (12)	65 (10)	6.9
C(11)	0.7828 (11)	1.2417 (10)	0.2533 (8)	129 (17)	100 (12)	78 (8)	61 (12)	33 (9)	40 (8)	5.9
C(12)	0.8443 (14)	1.3544 (11)	0.3208 (11)	197 (21)	80 (11)	103 (10)	59 (13)	38 (12)	24 (9)	7.8
C(13)	0.8049 (17)	1.3521 (12)	0.3791 (11)	274 (27)	92 (13)	123 (12)	77 (16)	68 (15)	6 (10)	9.2
C(14)	0.7045 (15)	1.2424 (12)	0.3751 (8)	303 (26)	111 (13)	89 (9)	98 (16)	90 (13)	9 (9)	7.8
C(15)	0.6417 (12)	1.1312 (9)	0.3108 (8)	218 (20)	111 (12)	68 (8)	88 (13)	70 (11)	30 (8)	5.9
C(16)	0.6800 (10)	1.1283 (8)	0.2486 (7)	112 (15)	73 (10)	55 (7)	46 (10)	19 (8)	27 (7)	4.7
C(17)	0.9011 (9)	0.9426 (8)	0.2567 (6)	95 (13)	83 (10)	52 (6)	36 (10)	38 (8)	27 (6)	4.0
C(18)	0.8396 (10)	0.8415 (8)	0.1812 (7)	132 (15)	98 (10)	61 (7)	57 (11)	60 (9)	24 (7)	4.5
C(19)	0.8979 (12)	0.8525 (10)	0.1313 (7)	177 (18)	135 (13)	76 (7)	101 (13)	77 (10)	47 (8)	5.4
C(20)	1.0259 (14)	0.9634 (13)	0.1563 (9)	224 (21)	182 (16)	90 (9)	141 (16)	106 (12)	80 (10)	6.3
C(21)	1.0900 (11)	1.0627 (10)	0.2308 (9)	166 (18)	129 (13)	97 (9)	92 (13)	87 (11)	72 (9)	5.8
C(22)	1.0314 (11)	1.0549 (9)	0.2817 (7)	140 (16)	83 (10)	58 (7)	64 (11)	46 (9)	32 (7)	4.5
C(23)	1.1057 (11)	1.1613 (9)	0.3591 (8)	121 (16)	101 (11)	92 (9)	47 (11)	59 (10)	49 (8)	5.8
C(24)	1.1536 (12)	1.2887 (9)	0.4926 (9)	193 (21)	68 (11)	114 (10)	9 (12)	52 (12)	−12 (9)	8.5
C(25)	1.1289 (13)	1.2671 (9)	0.5640 (8)	233 (23)	92 (12)	84 (9)	6 (14)	56 (12)	−18 (8)	8.6
C(26)	0.9123 (14)	1.1387 (11)	0.5596 (8)	277 (24)	130 (13)	46 (7)	111 (15)	46 (11)	1 (8)	7.0
C(27)	0.7728 (13)	1.0297 (11)	0.5287 (8)	221 (21)	120 (12)	63 (7)	103 (14)	67 (11)	27 (8)	5.7
C(28)	0.7210 (16)	1.0250 (12)	0.5855 (8)	287 (24)	168 (15)	57 (7)	139 (17)	72 (12)	23 (9)	7.1
C(29)	0.5968 (16)	0.9198 (14)	0.5628 (10)	298 (27)	222 (19)	90 (9)	159 (20)	125 (14)	61 (11)	7.9
C(30)	0.5160 (13)	0.8148 (12)	0.4835 (9)	236 (22)	175 (15)	88 (9)	112 (16)	103 (12)	50 (10)	7.1
C(31)	0.5636 (12)	0.8182 (10)	0.4275 (7)	174 (18)	117 (12)	68 (7)	62 (12)	73 (10)	24 (8)	5.6
C(32)	0.6895 (12)	0.9243 (10)	0.4472 (7)	188 (18)	117 (12)	48 (6)	97 (13)	54 (9)	26 (7)	4.9
C(33)	0.2753 (12)	0.8180 (9)	0.2235 (7)	226 (21)	130 (13)	84 (8)	113 (14)	81 (11)	39 (8)	6.3
C(34)	0.1404 (13)	0.7147 (11)	0.2106 (9)	214 (22)	159 (15)	130 (11)	63 (15)	123 (14)	5 (10)	8.4
C(35)	0.0621 (13)	0.6174 (11)	0.1174 (10)	229 (24)	186 (17)	167 (13)	32 (17)	131 (16)	−42 (12)	11.4
C(36)	0.1848 (12)	0.6447 (9)	0.1087 (7)	186 (19)	134 (13)	88 (8)	62 (14)	80 (11)	11 (9)	6.9
C(37)	0.4559 (10)	0.5570 (8)	0.2357 (6)	149 (16)	101 (11)	59 (6)	72 (12)	53 (9)	28 (7)	4.7
C(38)	0.4802 (13)	0.4045 (9)	0.3455 (8)	250 (24)	104 (12)	123 (11)	91 (15)	106 (14)	64 (9)	7.4
C(39)	0.2620 (12)	0.4588 (9)	0.2927 (8)	214 (22)	99 (12)	111 (10)	54 (14)	93 (13)	24 (9)	7.3
C(40)	0.2235 (12)	0.3065 (10)	0.1445 (8)	202 (21)	126 (13)	105 (10)	22 (14)	116 (13)	32 (9)	7.3

[a] Estimated standard deviations in parentheses refer to the last digit. The form of the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \times 10^{-4}]$. [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.[34]

$(Co(salen))_2Na^+$ has two open coordination sites, which are occupied by two THF molecules in V, by one THF and one oxygen of the $Co(CO)_4^-$ unit in III and by the oxygen atoms of $Co(CO)_4^-$ in IV. However, for lack of an X-ray analysis, any attempt to prepare suitable crystals being unsuccessful, nothing can be inferred about the molecular complexity of IV.

Ion-pairing between metal carbonylate anions and alkali metal cations has long been described to exist in low coordinating solvents.[17,29,30] The solid-state state X-ray structures of metal carbonylates show that this interaction concerns the carbonylic oxygen interacting with the counterion. This was mainly observed in the structure of $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2Mg(C_5H_5N)_4$,[31] where two octahedral sites around Mg are occupied by the carbonyl oxygens of two $[\eta^5\text{-}C_5H_5Mo(CO)_3]^-$ units. More recently, the X-ray structure on $Na_2Fe(CO)_4{\cdot}1.5C_4H_8O_2$[3] showed two kinds of contact interaction between Na^+ and $Fe(CO)_4^{2-}$, one of them being a short-range O–Na interaction. As concerns this interaction, all the carbonylic oxygens are involved in the interaction with Na^+ giving to a three-dimensional polymeric network in which each $Fe(CO)_4^{2-}$ anion is coordinated to four Na^+ ions. The pioneering work by Edgell and co-workers on solution of $NaCo(CO)_4$ showed, on the basis of the spectroscopic data, the existence in solution of contact ion pair, solvent-separated ion pair, and free ions depending on the nature of the solvent.[17] Moreover, different bonding modes of $Co(CO)_4^-$ toward Na^+

Table III. Selected Bond Lengths (Å) and Angles (deg) in $[(Co(salen))_2NaCo(CO)_4THF]$[a]

Na-O(1)	2.395 (6)	Co(2)-O(4)	1.873 (6)
Na-O(2)	2.378 (7)	Co(2)-N(3)	1.888 (7)
Na-O(3)	2.431 (6)	Co(2)-N(4)	1.873 (8)
Na-O(4)	2.381 (6)	Co(3)-C(37)	1.752 (9)
Na-O(5)	2.464 (7)	Co(3)-C(38)	1.736 (11)
Na-O(6)	2.440 (7)	Co(3)-C(39)	1.756 (11)
Co(1)-O(1)	1.870 (6)	Co(3)-C(40)	1.749 (11)
Co(1)-O(2)	1.871 (6)	O(6)-C(37)	1.153 (11)
Co(1)-N(1)	1.871 (9)	O(7)-C(38)	1.181 (15)
Co(1)-N(2)	1.876 (9)	O(8)-C(39)	1.150 (14)
Co(2)-O(3)	1.863 (5)	O(9)-C(40)	1.163 (14)
O(1)-Na-O(2)	64.8 (2)	O(2)-Co(1)-N(2)	93.4 (4)
O(1)-Na-O(3)	93.2 (2)	N(1)-Co(1)-N(2)	85.9 (4)
O(1)-Na-O(4)	154.1 (2)	O(3)-Co(2)-O(4)	85.6 (2)
O(1)-Na-O(5)	101.6 (2)	O(3)-Co(2)-N(3)	93.5 (3)
O(1)-Na-O(6)	102.6 (2)	O(3)-Co(2)-N(4)	176.2 (3)
O(2)-Na-O(3)	84.1 (2)	O(4)-Co(2)-N(3)	174.7 (3)
O(2)-Na-O(4)	99.5 (2)	O(4)-Co(2)-N(4)	94.4 (3)
O(2)-Na-O(5)	99.0 (2)	N(3)-Co(2)-N(4)	86.8 (4)
O(2)-Na-O(6)	166.5 (3)	C(37)-Co(3)-C(38)	110.2 (5)
O(3)-Na-O(4)	63.6 (2)	C(37)-Co(3)-C(39)	110.1 (5)
O(3)-Na-O(5)	164.7 (2)	C(37)-Co(3)-C(40)	106.6 (5)
O(3)-Na-O(6)	91.9 (2)	C(38)-Co(3)-C(39)	106.5 (5)
O(4)-Na-O(5)	101.1 (2)	C(38)-Co(3)-C(40)	112.0 (5)
O(4)-Na-O(6)	90.3 (2)	C(39)-Co(3)-C(40)	111.4 (5)
O(5)-Na-O(6)	88.2 (2)	Na-O(6)-C(37)	142.1 (6)
O(1)-Co(1)-O(2)	86.3 (3)	O(6)-C(37)-Co(3)	178.8 (9)
O(1)-Co(1)-N(1)	94.4 (3)	O(7)-C(38)-Co(3)	177.6 (9)
O(1)-Co(1)-N(2)	176.0 (3)	O(8)-C(39)-Co(3)	178.9 (10)
O(2)-Co(1)-N(1)	178.8 (4)	O(9)-C(40)-Co(3)	177.7 (9)

[a] Estimated standard deviations refer to the last digit.

were suggested. The solid-state structures of different $MCo(CO)_4$ [M = Tl^+, $(PPh_3)_2N^+$, $Mg(THF)_6^{2+}$][32] show the presence of symmetrical or non-cation-perturbed anions only. The geometry of $Co(CO)_4^-$ is only slightly dependent on the nature of the counterion, the higher distortion being for $TlCo(CO)_4$.[33] The addition of Co(salen) to THF solutions of $NaCo(CO)_4$ made it possible to freeze two, III and IV, of the forseen Na–$Co(CO)_4$ interacting modes. It must be pointed out that these solid-state results are not directly related to the structure of $NaCo(CO)_4$ in solution when Co(salen) is present. Even in the absence of Co(salen) Edgell observed, by the IR spectrum in THF solution of $NaCo(CO)_4$, the predominant presence of the contact ion pair Na···$OCCo(CO)_3$ with a C_{3v} symmetry.[17]

The structure of III shows the presence of this moiety, whose existence was inferred in solution only. The CO–Na interaction has no significant influence on the geometrical parameters of $Co(CO)_4^-$. The independent Co–C and C–O bond distances (averaging to 1.75 and 1.16 Å) and C–Co–C angles are essentially identical, and no deviation from the linearity was observed for the Co–C–O units (Table III). Although the CO–Na interaction does not significantly perturb the anion, the angle around carbonylic oxygen interacting with Na^+, 142.1 (6)°, is very similar to that found in cation-perturbed anions, such as $[\eta^5\text{-}C_5H_5Mo(CO)_3]^-$.[32] On the contrary, the geometry of $Fe(CO)_4^{2-}$ is greatly distorted from idealized tetrahedral symmetry, as a consequence of a multiple Na–$Fe(CO)_4$ interaction. This is reflected mainly on the C–Fe–C and Fe–C–O angles.[3]

It would be highly attractive, at this point, to compare the IR spectrum of III in the solid state with that of $NaCo(CO)_4$ in THF solution, in the region 2100–1800 cm⁻¹. It must be, however, pointed out that this comparison should be carefully done, since the IR spectrum in the solid state may bear some "solid-state effect". This could introduce the nonequivalence of the CO nonbonded to Na^+ or reducing further the $NaOCCo(CO)_3$ symmetry. III shows, indeed, four well-separated IR bands in the CO region (Figure 4) as it is forseen for a local symmetry lower than the observed C_{3v}.[17]

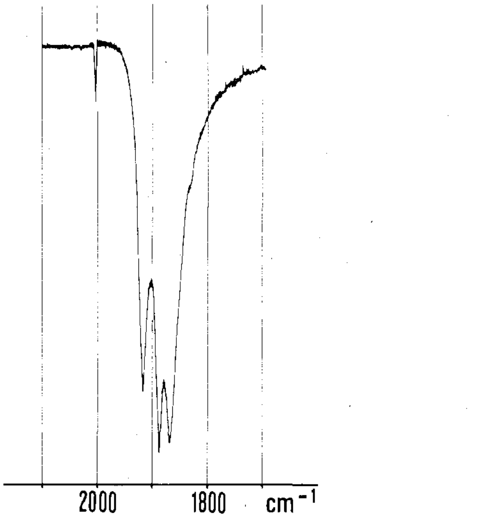

Figure 4. IR spectrum (Nujol) of $[(Co(salen))_2NaCo(CO)_4THF]$.

The spectroscopic identification of an isolated ion pair such as this is doubtfully done by the IR spectrum in the solid state. The more relevant result stays on the isolation of a previously supposed ion pair promoted by this new kind of ligand. Coordination compounds containing a set of bicovalent oxygen atoms can be used as "inorganic sequestering agents" for alkali cations, ion pairs, etc. These species act as templating agents in bridging two or more metal atoms close together in the same molecular structure. Complexes like III represent structural models in which different metal centers Co^{2+}, Co^-, and Na^+ are assembled together. This may be a rough approach to the synthesis of bi- and polyfunctional complexes, whose importance for catalytic studies is increasing.

Registry No. I, 15053-51-7; II, 67542-39-6; Co(salen)NaI, 67530-50-1; $Co_2(CO)_8$, 10210-68-1; Co(salen), 14167-18-1; CO, 630-08-0; NaI, 7681-82-5.

Supplementary Material Available: Least-squares planes in Co(salen) groups, bond lengths and angles, atomic coordinates for H atoms, and structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Università di Pisa. (b) Università di Perugia.
(2) J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 2515 (1977).
(3) H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, **98**, 2434 (1976).
(4) R. G. Teller, R. G. Finke, J. P. Collman, H. B. Chin, and R. Bau, *J. Am. Chem. Soc.*, **99**, 1104 (1977).
(5) G. Costa, G. Mestroni, and G. Tauzher, *J. Chem. Soc., Dalton Trans.*, 450 (1972); G. N. Schrauzer, J. H. Weber, and T. M. Beckman, *J. Am. Chem. Soc.*, **92**, 7078 (1970); V. L. Goedken and S. M. Peng, *J. Chem. Soc., Chem. Commun.*, 914 (1974), and references therein.
(6) C. Floriani, M. Puppis, and F. Calderazzo, *J. Organomet. Chem.*, **12**, 209 (1968); C. Floriani and F. Calderazzo, *Coord. Chem. Rev.*, **8**, 57 (1972).
(7) G. Fachinetti, C. Floriani, P. F. Zanazzi, and A. R. Zanzari, unpublished results.
(8) C. Floriani and G. Fachinetti, *Transition Met. Chem.*, **1**, 50 (1976); a short account on the carbonylation of Co(salen)Na-like complexes is given.
(9) M. R. Truter, *Struct. Bonding (Berlin)*, **16**, 71 (1973).
(10) E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 391 (1969).
(11) G. H. W. Milburn, M. R. Truter, and B. L. Vichery, *Chem. Commun.*, 1188 (1968); *J. Chem. Soc., Dalton Trans.*, 841 (1974).
(12) L. G. Armstrong, H. C. Lip, L. F. Lindoy, M. McPartlin, and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, 1771 (1977).
(13) C. Floriani, F. Calderazzo, and L. Randaccio, *J. Chem. Soc., Chem. Commun.*, 384 (1973).
(14) L. Randaccio, *Gazz. Chim. Ital.*, **104**, 991 (1974).
(15) N. Bresciani-Pahor, M. Calligaris, P. Delise, G. Nardin, L. Randaccio, E. Zotti, G. Fachinetti, and C. Floriani, *J. Chem. Soc., Dalton Trans.*, 2310 (1976).
(16) R. S. Drago and J. H. Elias, *J. Am. Chem. Soc.*, **99**, 6570 (1977).
(17) W. F. Edgell and J. Lyford, *J. Am. Chem. Soc.*, **93**, 6407 (1971), and references therein.
(18) C. Floriani and F. Caladerazzo, *J. Chem. Soc. A*, 946 (1969).

(19) W. F. Edgell and J. Lyford, *Inorg. Chem.*, **9**, 1932 (1970).

(20) Standard deviations on intensities were computed as $\sigma(I) = [P + 0.25(T_P/T_B)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$, 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 time T_B, and I is the intensity equal to $P - 0.5(T_P/T_B)(B_1 + B_2)$.

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

(22) S. Raman, *Acta Crystallogr.*, **14**, 148 (1961).

(23) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

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

(25) Not identified.

(26) M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, **7**, 385 (1972), and references therein.

(27) C. Floriani and G. Fachinetti, *J. Chem. Soc., Chem. Commun.*, 615 (1974).

(28) C. Floriani, unpublished results.

(29) M. Y. Darensbourg, D. J. Darensbourg, D. Burns, and D. A. Drew, *J. Am. Chem. Soc.*, **98**, 3127 (1976); M. Darensbourg, H. Barros, and C. Borman, *J. Am. Chem. Soc.*, **99**, 1647 (1977), and references therein.

(30) C. D. Pribula and T. L. Brown, *J. Organomet. Chem.*, **71**, 415 (1974).

(31) S. W. Ulmer, P. M. Skarstad, J. M. Burlitch, and R. E. Hughes, *J. Am. Chem. Soc.*, **95**, 4469 (1973).

(32) Data taken from ref 3.

(33) D. P. Schlussler, W. R. Robinson, and W. F. Edgell, *Inorg. Chem.*, **13**, 153 (1974).

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

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

Contribution from the Departments of Chemistry, Delft University of Technology, 2600 CA Delft, The Netherlands,
and The University of North Carolina, Chapel Hill, North Carolina 27514

Synthesis and Structural Characterization of *cis*-Dichlorobis(*N*-methylimidazole)platinum(II) and *cis*-Dibromobis(*N*-methylimidazole)platinum(II)

BRADFORD J. GRAVES,[1a] DEREK J. HODGSON,*[1a] CORNELIS G. VAN KRALINGEN,[1b] and JAN REEDIJK*[1b]

Received March 21, 1978

The synthesis and spectroscopic properties of *cis*-dichloro- and *cis*-dibromobis(*N*-methylimidazole)platinum(II), $Pt(C_4H_6N_2)_2Cl_2$ and $Pt(C_4H_6N_2)_2Br_2$, are described. The dichloro complex crystallizes in four distinct crystal modifications, all containing the *cis*-$Pt(C_4H_6N_2)_2Cl_2$ unit as deduced from far-IR spectra, conductivity measurements, and (high-temperature) X-ray powder patterns. The dibromo complex crystallizes in two forms, each of which is isomorphous with one of the forms of the dichloro complex. The crystal structure of one of the forms of the dichloro complex has been determined from three-dimensional single-crystal X-ray data obtained by counter methods. The complex crystallizes in space group *Fddd* of the orthorhombic system with 16 formula units in a cell of dimensions $a = 12.586$ (6), $b = 30.431$ (16), and $c = 12.920$ (5) Å. The observed and calculated densities are 2.29 (2) and 2.309 g cm^{-3}, respectively. The structure has been refined by full-matrix least-squares methods to a value of the conventional R factor (on F) of 0.046 using 1701 independent data. The platinum(II) center lies on a crystallographic twofold axis and is coordinated to two cis chloride ions at 2.296 (2) Å and to two imine nitrogen atoms at 2.015 (6) Å. The geometry at platinum is approximately square planar, with cis bond angles in the range 89.2–91.6°. There is no evidence for hydrogen bonding or strong intermolecular interactions in the crystal. This apparent absence of strong intermolecular forces may be the reason for the existence of multiple crystalline forms.

Introduction

As a part of a study on the structure–activity relationships of platinum complexes with antitumor activity[2] we are currently investigating a number of platinum complexes with imidazoles and pyrazoles as ligands. A preliminary report about the synthesis of Pt(II) and Pd(II) complexes with imidazole has appeared.[3] It has been found that the complex *cis*-$Pt(Iz)_2Cl_2$ (Iz = imidazole) shows cytostatic activity in mice bearing the tumour L1210 leukemia.[4] There is good evidence in the literature that hydrogen bonding is an important factor in determining the activity of the complex.[5] In order to study the possible influence of the hydrogen bonding capacity of the complex on the activity we have synthesized the *cis*-dichloro complex of Pt(II) with *N*-methylimidazole as the ligand. The synthesis and characterization of a number of other compounds with this ligand like the trans compounds and compounds containing four *N*-methylimidazole ligands coordinated to Pt(II) are described elsewhere.[6] The complex *cis*-$Pt(NMIz)_2Cl_2$ (NMIz = *N*-methylimidazole), however, was found to exist in four different crystal forms with slightly different spectroscopic properties. The *cis*-dibromo analogue exists in at least two different crystal forms which are isomorphous with two of the four crystal forms of the *cis*-dichloro complex. In order to understand these properties we determined the crystal and molecular structure of one of the crystal forms of *cis*-$Pt(NMIz)_2Cl_2$. The present paper reports the synthesis and spectroscopic properties of all four crystal forms and the X-ray structure of one crystal form.

Experimental Section

Starting Materials. Commercially available *N*-methylimidazole (abbreviated as NMIz) (Merck) was used without further purification. Platinum was commercially available as the tetrachloroplatinite, K_2PtCl_4 (Drijfhout, Amsterdam).

Synthesis of the Compounds. The compound *cis*-$Pt(NMIz)_2I_2$ was used as a starting material. This compound was synthesized by an improved procedure according to the method of Dhara.[7] A total of 415 mg (1 mmol) of K_2PtCl_4 was dissolved in 20 mL of water, and 4 g (about 24 mmol) of KI was added to yield a solution of 0.05 M PtI_4^{2-} and 1 M I^-. To this solution 164 mg (2 mmol) of the ligand was added. The cis compound precipitated immediately and was filtered, washed with ethanol and dry diethyl ether, and dried in vacuo at room temperature. A total of 613 mg (1 mmol) of the *cis*-diiodo compound was suspended in water, and a solution of 340 mg (2 mmol) of $AgNO_3$ in water was added. The suspension was stirred for 1 h and the precipitate of AgI was filtered. The filtrate presumably contains the *cis*-diaquo species. After addition of a 20-fold excess of NaCl or NaBr respectively, the *cis*-dichloro or the *cis*-dibromo compound precipitated. The product was filtered, washed with ethanol and dry diethyl ether, and dried in vacuo at room temperature. The *cis*-dichloro compound could be recrystallized from 2 N HCl or by dissolving the compound in DMF (minimum amount) and adding a fivefold excess (by volume) of 2 N HCl. The *cis*-dibromo compound

0020-1669/78/1317-3007$01.00/0 © 1978 American Chemical Society