A Mixed-valence Cobalt(I)–Cobalt(II) Complex containing a Bridging Sodium Cation

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Sodium [*N,N'*-ethylenebis(salicylideneaminato)]cobaltate(I), [Co(salen)Na(thf)]$_n$ (thf = tetrahydrofuran), reacts with the cobalt(II) parent complex [Co(salen)] to form a neutral mixed-valence Co^{I}–Co^{II} complex in which two identical [Co(salen)] units act as equatorial ligands for a Na$^+$ cation completing its octahedral co-ordination sphere with two thf molecules *trans* to each other.

Reduction of complexes containing polydentate or macrocyclic ligands imposing a square planar geometry produces either metal-centred nucleophiles or ligand-centred radical anions.[1] Such a reaction is usually a stepwise process by which a definite whole number of electrons can be introduced into the structure depending on the metal : reducing agent molar ratio.[2,3] Mixed-valence complexes, or formal fractional oxidation states for metal ions cannot be obtained unless two metal ions are bridged by some ligand.[4,5] The [M(μ-X)$_n$M] fragment is the fundamental constituent of such complexes, and is responsible for electron exchange processes, which are of primary importance in chemistry.[5,6] Can this electron transfer be achieved by a completely different structural fragment and, if so, can this occur between two complexes containing polydentate ligands without involving any group bridging the two metal ions? A mixed-valence compound related to this question is reported in this paper.

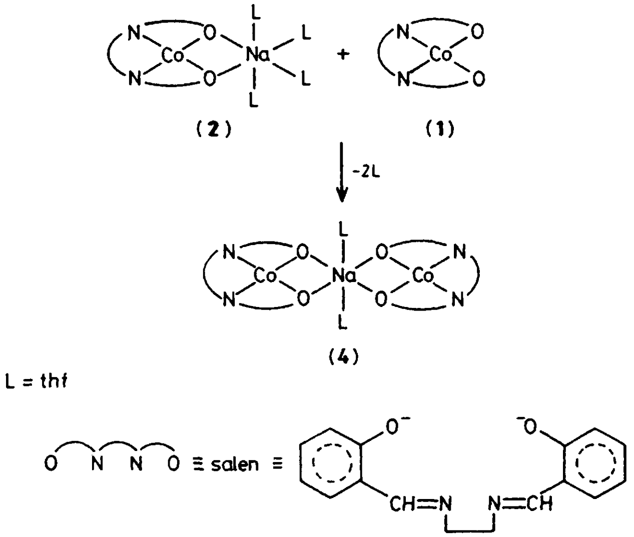
N,N'-Ethylenebis(salicylideneaminato)cobalt(II), [Co(salen)] (**1**), undergoes a stepwise reduction process to (**2**) and (**3**)[3] [equation (1)]. During reactivity studies on the bifunctional Co^{I}–Na complex (**2**), we became aware of (**4**), another derivative of (**1**) (Scheme 1).[7]

$$\underset{(\mathbf{1})}{[\mathrm{Co(salen)}]} + \mathrm{Na} \xrightarrow{\mathrm{thf}} \underset{(\mathbf{2})}{[\mathrm{Co(salen)Na(thf)}]_n} + \mathrm{Na} \xrightarrow{\mathrm{thf}} \underset{(\mathbf{3})}{[\mathrm{Co(salen)Na_2(thf)}_n]} \qquad (1)$$

A thf solution of (**2**) reacted with an equimolar amount of (**1**) to form dark-green crystals of (**4**) (*ca.* 70%),‡ which is significantly less soluble than (**2**) in thf, and is much less air-sensitive. Reduction of (**1**) with a 2 : 1 Co : Na molar ratio afforded the same result. Complex (**4**) has one unpaired electron and a magnetic moment very close to that of (**1**) (2.39 μ_B at 290 K). Complex (**2**) is a very tightly bound ion-pair complex[8] undergoing ligand substitution at the alkali metal cation by the [Co(salen)] ligand. Co-ordination of alkali cations by [M(salen)]-type ligands is a very well established reaction.[9,10] In this context complexation of Na$^+$ by (**1**) (Scheme 2) is closely analogous to Scheme 1 and an interesting structural relationship can be established between (**4**) and (**5**).[10] The structure of (**4**), determined by *X*-ray analysis,§ is shown in Figure 1 with selected bond distances and angles. Structural parameters of (**4**) should be compared with those of other Co–Na salen complexes (**2**)[3a] and (**5**)[10a,c] containing cobalt(I) and cobalt(II), respectively.

Complex (**4**) is a neutral co-ordination compound of Na$^+$ having a pseudo-octahedral geometry, with two bidentate [Co(salen)] ligands *trans* to each other, while the *trans* axial positions are filled by two thf molecules. Sodium is nearly coplanar with O(1), O(2), O(3), and O(4), being out of the plane by 0.0064 Å. The two co-ordination planes N(1),N(2),O(1),O(2) and N(3),N(4),O(3),O(4) are almost parallel, forming a dihedral angle of 2.2°, and they form dihedral angles of 37.6° and 36.7° with the O(1),O(2),O(3),O(4) plane, respectively. The neutrality of the complex requires one of the [Co(salen)] units to be formally monoanionic containing cobalt(I) and the other one neutral containing cobalt(II). The two [Co(salen)] units are, however, crystallographically identical, thus allowing (**4**) to be defined as a mixed-valence Co^{I}–Co^{II} complex. It is difficult, however, to distinguish between a genuinely delocalized ground state, or merely one in which rapid, reversible electron transfer between the two cobalt ions is occurring. Crystallographic and spectroscopic data do not allow the two possibilities to be distinguished.[5]

In fact, a change in the oxidation state of the metal only slightly affects the structural parameters,[3a] the Co–N bond



Scheme 1

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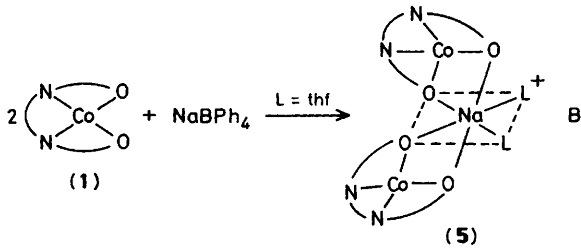
‡ Satisfactory analytical data have been obtained.

§ *Crystal data* for (**4**): $C_{40}H_{44}Co_2N_4NaO_6$, M = 816.8, triclinic, space group $P\bar{1}$, a = 15.184(3), b = 13.925(2), c = 8.707(2) Å, α = 98.75(2), β = 92.95(2), γ = 91.40(2)°, U = 1816.2 Å^3, Z = 2, D_c = 1.493 g cm^{-3}, μ(Mo-K_α) = 9.50 cm^{-1}; crystal dimensions: 0.06 × 0.10 × 0.75 mm. The structure was solved by the heavy atom method (Patterson and Fourier synthesis) and refined anisotropically by blocked full matrix least-squares. For 3170 unique observed structure amplitudes [$I > 3\sigma(I)$] collected at room temperature on a Philips PW 1100 diffractometer in the range $3 < \theta < 25°$, R = 0.052. All calculations were carried out using MULTAN and *SHELX* 76. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2

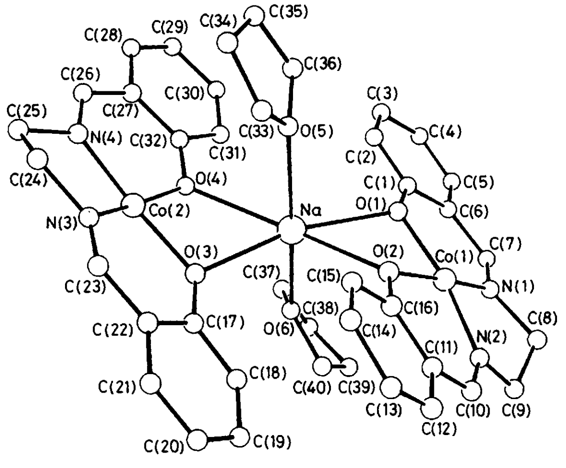


Figure 1. Complex (4), [Co(salen)]$_2$Na(thf)$_2$. Bond distances (Å): Na–O(1), 2.563(5); Na–O(2), 2.407(5); Na–O(3), 2.393(5); Na–O(4), 2.539(5); Na–O(5), 2.529(6); Na–O(6), 2.486(6); Co(1)–O(1), 1.895(4); Co(1)–O(2), 1.891(4); Co(1)–N(1), 1.845(5); Co(1)–N(2), 1.852(5); Co(2)–O(3), 1.895(4); Co(2)–O(4), 1.897(4); Co(2)–N(3), 1.845(5); Co(2)–N(4), 1.857(5); C(7)–N(1), 1.278(8); C(23)–N(3), 1.283(8); N(2)–C(10), 1.286(8); N(4)–C(26), 1.276(8).

distances being the most sensitive. All the Co–N bond distances in complex (4) are similar, averaging 1.850(5) Å. This value is similar to that found in (5) [1.858(10) Å],[10c] and significantly longer than the value [1.820(4) Å] in (2).[3a] The Co–O bond distances [Co–O$_{av.}$ 1.895(4) Å] show the reverse trend, being similar to those found in (2) [Co–O$_{av.}$ 1.899(3) Å][3a] and significantly longer than those in (5) [Co–O$_{av.}$ 1.858(8) Å].[10c] There is no significant difference in the C=N bond distances in complexes (2), (4), and (5), in spite of the fact that such a functionality is the most sensitive to electronic enrichment of the complex. The C=N stretch is, in fact, shifted from the usual 1605—1625 cm^{-1} region [complex (1)] to a lower unidentified position [complex (4)]. This result provides significant evidence for a delocalized structure. Na–O distances [Na–O$_{av.}$ 2.486(6) Å] are significantly different from those in (5) [Na–O$_{av.}$ 2.405(10) Å],[10c] while a very irregular trend is observed in (2).[3a] The most striking structural characteristic of (4) is the *trans*-arrangement of the two [Co(salen)] units, which contrasts with the *cis*-arrangement in complex (5) containing solely cobalt(II). This is probably to achieve the best electron delocalization or transfer between the two [Co(salen)] units. The present work provides the first concrete evidence for an intermediate which can be present in alkali cation-mediated electron transfer processes between transition metal complexes.[11]

Even though the structure of (4) shows a sterically accessible Co–Na unit, we did not observe any of the typical reactivity associated with the same bifunctional unit in (2); *e.g.* CO$_2$ and CO$_2$-like molecules do not react with (4).[7]

This paper shows a new synthetic route to mixed-valence compounds, in which the electron exchange or delocalization can be ensured by alkali cations. We found that the reaction in Scheme 1 could be extended to other metal ions, to the synthesis of hetero-bimetallic mixed-valence compounds by the reaction of (2) with salen derivatives of other metals, and to other alkali metal ions. All these reactions have been performed in thf; the effect of other solvents is unknown thus far.

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