Crystal and Molecular Structure of a Cationic Sodium Complex: the Sodium Tetraphenylborate Adduct of *NN'*-Ethylenebis(salicylideneiminato)cobalt(II). Cobalt(II), Nickel(II), and Copper(II) Complexes of Quadridentate Schiff Bases as Complexing Agents for Lithium, Sodium, and Ammonium Cations

By Carlo Floriani* and Fausto Calderazzo
(*Istituto di Chimica Generale ed Inorganica, University of Pisa,* 56100 *Pisa, Italy*)

and Lucio Randaccio
(*Istituto Chimico, University of Trieste,* 34127 *Trieste, Italy*)

Summary The crystal and molecular structure of a sodium complex derived from *NN'*-ethylenebis(salicylideneiminato)cobalt(II) and sodium tetraphenylborate is reported together with several other alkali metals and ammonium cations adducts.

The possibility for *NN'*-ethylenebis(salicylideneiminato)-metal(II) complexes, hereinafter abbreviated as M(salen), to co-ordinate to transition[1-4] and non-transition elements[5-8] is known.

We now report the sodium tetraphenylborate adducts of Co(salen) (red), Ni(salen) (orange) and Cu(salen) (violet-blue) of formula $[\mathrm{M(salen)}]_2\,\mathrm{NaBPh_4,2THF}$, prepared from the components in tetrahydrofuran (THF). The three sodium tetraphenylborate adducts are isomorphous.

The molecular structure of $[\mathrm{Co(salen)}]_2,\mathrm{NaBPh_4,2THF}$ has been solved by *X*-ray diffraction data analysis. The crystals are monoclinic, space group $P2_1/c$, with $a = 14{\cdot}415$, $b = 14{\cdot}329$, and $c = 27{\cdot}897$ Å and $\beta = 98{\cdot}0^\circ$, $D_m = 1{\cdot}330$ g cm^{-3} (flotation), $D_c = 1{\cdot}324$ g cm^{-3} with four units [Co-

(salen)]$_2$, Na,(THF)$_2$,BPh$_4$, $\mu = 6{\cdot}8$ cm^{-1} (for Mo-K_α). Siemens diffractometer measurements of intensities were carried out using a crystal sealed in a thin capillary.

The structure was solved from 3771 independent non-zero ($I > 4\sigma_I$) reflections with $\theta \leqslant 25°$, by Patterson and Fourier methods and refined by block-diagonal least-squares methods to the present R-value of 0·083.

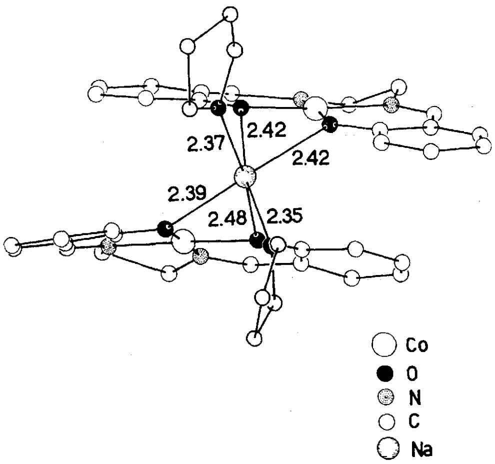

Figure. *View of the* [Co$_2$(salen)$_2$Na,(THF)$_2$]$^+$ *cation with some relevant bond distances.*

The crystals consist of discrete [Co$_2$(salen)$_2$Na,(THF)$_2$]$^+$ cations and [BPh$_4$]$^-$ anions. The tetraphenylborate anions, held together by phenyl–phenyl interactions, are arranged along planes perpendicular to the (101) planes and passing at z equal to 0 and 0·5. The complex cations are arranged in between these planes. The sodium cation has an approximately octahedral co-ordination, being surrounded by six oxygen atoms, two for each Co(salen) group [Na–O distances ranging from 2·391(9) to 2·482(9) Å] and two from the THF groups [Na–O distances 2·35(1) and 2·37(1) Å]. The THF groups are at two *cis*-positions of the distorted octahedron. The complex cation, of approximate C_2 symmetry, is shown in the Figure, where also some bond lengths of interest are indicated. The Co(salen) units are nearly planar, with a slight distortion towards an umbrella-shape of the type frequently encountered[9] in M(salen) complexes. The THF groups undergo high thermal motion (the thermal parameters of all the atoms are around 10 Å^2), in agreement with a 'pseudorotation' of the ring similar to that of cyclopentane. The five-membered rings are not planar and their atoms are within $\pm 0{\cdot}15$ Å of their mean plane. The structural parameters of the [BPh$_4$]$^-$ anion are in good agreement with those recently reported.[10] The mean B–C bond length is 1·64(1) Å, and the mean C–C bond length is 1·40(1) Å. This is the first well authenticated example of an alkali-metal cation complexed to a co-ordination compound, to be compared with both the 'complexed ion-pairs'[8] and the recently reported[11] 'cryptates'.

The following adducts were similarly prepared: [3-MeO·-Co(salen)]$_2$,NaBPh$_4$,2THF (I), [M(salen)]$_2$,NH$_4$SCN (II; M = Ni, Cu), [Co(salen)]$_2$,NH$_4$SCN,THF (III), 3-MeO·-Co(salen),NH$_4$SCN (IV), M(salen),LiX,THF (V; M=Co; X=Br,I,SCN; M=Cu; X=SCN), 3-MeO·Co(salen), LiBr (VI), and 3-MeO·Co(salen),LiSCN,THF (VII).

Satisfactory analytical results were obtained for all the compounds reported in this paper. The magnetic moment of (I) [$\mu_{\text{eff}} = 2{\cdot}31$ B.M. at 293 K] suggests no fundamental change of stereochemistry around the central metal atom. This is in agreement with a structure for (I) similar to that found for the M(salen),NaBPh$_4$ adducts.

The ammonium derivatives (II)—(V) and (VII) show C–N i.r. stretching vibrations substantially unchanged with respect to NH$_4$SCN. This suggests that the SCN group is not co-ordinated to the central metal atom. Ammonium cryptates have not been isolated[11] as yet, whereas a methylammonium 'complexed ion-pair' with NN'-ethylenebis-(acetylacetoneiminato)copper(II) and perchlorate as counter-ion is known.[13]

We feel that, in the presence of a potentially co-ordinating anion, the decision between the 'complexed ion-pair' and the co-ordination of the anion to the central metal atom may depend on very delicate energetic factors. It is worth mentioning that compound (VI) has a magnetic moment $\mu_{\text{eff}} = 3{\cdot}69$ B.M. at 293 K, substantially independent of temperature down to 120 K ($\theta = 40°$) to be compared with the magnetic moment $\mu_{\text{eff}} = 3{\cdot}70$ B.M. at 297 K found[14] for the pyridine adducts of 3-MeO-Co(salen), in which the central cobalt atom is almost certainly five-co-ordinate. In view of this, we suggest that in compound (VI) the halide is co-ordinated to cobalt.

Support from the Italian National Research Council (C.N.R., Rome) is acknowledged.

(*Received*, 16*th March* 1973; *Com.* 358.)

---

[1] D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.
[2] E. N. Baker, D. Hall, A. J. McKinnon, and T. N. Waters, *Chem. Comm.*, 1967, 134.
[3] S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, 1969, **B25**, 1671.
[4] R. DeIasi, L. S. Holt, and B. Post, *Inorg. Chem.*, 1971, **10**, 1498.
[5] M. D. Hobday and T. D. Smith, *J. Chem. Soc.* (*A*), 1971, 1453.
[6] M. D. Hobday and T. D. Smith, *J. Chem. Soc.* (*A*), 1971, 3424.
[7] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1805.
[8] G. H. W. Milburn, M. R. Truter, and B. L. Vickery, *Chem. Comm.*, 1968, 1188.
[9] M. Calligaris, G. Nardin, and L. Randaccio, *Coordination Chem. Rev.*, 1972, **7**, 385.
[10] M. Di Vaira and A. Bianchi Orlandini, *J.C.S. Dalton*, 1972, 1704.
[11] B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Letters*, 1969, 2889 and references therein.
[12] A. Earnshaw, P. C. Hewlett, E. A. King, and L. F. Larkworthy, *J. Chem. Soc.* (*A*), 1968, 241.
[13] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 396.
[14] C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1969, 946.