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New Type of σ-Organocobalt Complexes; Salts of Alkyl-*mer*-[*N*-(2-aminoethyl)-7-methylsalicylideneaminato](ethylenediamine)-cobalt(III); Preparation, Characterization, and *X*-Ray Crystallographic Evidence for Structure

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Summary Representatives of a novel type of σ-organocobalt(III) complex including both a tridentate and a bidentate ligand, *viz.* salts of alkyl-*mer*-[*N*-(2-aminoethyl)-7-methylsalicylideneaminato](ethylenediamine)-cobalt(1+) have been prepared and characterized; the structure of the ethylcobalt cation being determined by an *X*-ray study of its bromide.

IT is generally accepted that both the formation and the splitting of a transition metal–carbon bond are strongly dependent on the nature of other ligands at the metal atom. Most σ-organocobalt(III) complexes obtained so far include a planar tetradentate or bis-bidentate ligand derived from a wide range of related macroheterocycles or chelating agents; other types of complex contain several specific monodentate or bidentate strong-field ligands, *i.e.* CN, C_5H_5, bipyridyl *etc.*[1] Here we report the preparation and characterization of a new series of stable cobalt(III) complexes in which the metal atom is linked to a tridentate and a bidentate ligand as well as an alkyl group.

After the attempted template synthesis of ethyl-*NN'*-ethylene-bis(7-methylsalicylideneaminato)cobalt† (**1**) by an adaptation of the procedure used by Schrauzer *et al.* for the preparation of alkylcobalt complexes with other Schiff bases[3]

$$Co^{2+} \xrightarrow[\text{MeOH, OH}^-]{\text{i, } o\text{-HOC}_6\text{H}_4\text{COMe, H}_2\text{N[CH}_2\text{]}_2\text{NH}_2\text{; ii, NaBH}_4\text{/Pd; iii, EtBr}} (\mathbf{1}) + (\mathbf{2a}) \qquad (1)$$

(reaction 1), an additional intensely coloured crystalline product (**2a**) was obtained (red prisms from aqueous methanol), its yield increasing with dilution. Photolysis of (**2a**) resulted in the formation of ethane, ethylene, and butane, *i.e.* the normal products of homolytic cleavage of ethylmetal derivatives. In contrast with normal alkylcobalt complexes with tetradentate or bis-bidentate ligands [such as (**1**)], (**2a**) decomposes readily in the presence of dilute acids, to give ethane, ethylene, and butane, as well as *o*-hydroxyacetophenone. Complex (**2a**) is most soluble, but moderately so, in the most polar organic solvents such as MeOH or Me_2SO, and somewhat less soluble in water. Treatment of (**2a**) with $AgNO_3$ in methanolic solution leads to immediate precipitation of AgBr. The solid-state i.r. spectrum of (**2a**) shows strong absorptions in the region 3100—3330 cm^{-1}, which may be assigned to stretching vibrations of co-ordinated amino-groups involving two kinds of hydrogen atoms, *viz.* those which do participate in H-bonding (more intense and broad bands at 3130 and 3225 cm^{-1}) and those which do not (sharp peaks at 3295 and 3320 cm^{-1}). There are also marked differences between the spectra of (**2a**) and (**1**) throughout the region of C–H stretching vibrations (2840—3100 cm^{-1}); the intensities of CH_2 bands compared with CH_3 as well as C(arom.)–H bands are much higher in the spectrum of (**2a**).

On the basis of these findings we suggest that (**2a**) has the formula $[RCo^{III}\{o\text{-}OC_6H_4C(Me){=}N[CH_2]_2NH_2\}\{H_2N\text{-}[CH_2]_2NH_2\}]^+X^-$ (R = Et, X = Br) which agrees with elemental analyses.

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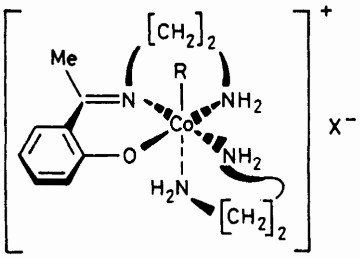
† This complex has been prepared by Costa *et al.*[2] in another manner.

Homologues of (**2a**) with R = Me (**2c**), and Bu^n (**2d**), were similarly prepared and characterized. The perchlorate (**2b**) was obtained from (**2a**) *via* anion exchange. The i.r. spectrum of (**2b**) lacks the bands in the spectrum of (**2a**) attributed to stretching vibrations of N–H bonds involving bridging hydrogens. Thus H-bonds in (**2a**) are obviously neither inter- nor intra-cationic but link the complex cations with the bromide anions.

Direct evidence for the proposed formula of compounds (**2**) as well as establishment of the geometry of the complex cations was provided by an *X*-ray single-crystal diffraction study of (**2a**).



(**2**)

a; R = Et, X = Br
b; R = Et, X = ClO_4
c; R = Me, X = Br
d; R = Bu^n, X = Br

Crystal data: monoclinic, space group $P2_1/n$, a = 14·481(7), b = 8·320(3), c = 15·382(7) Å, β = 108·65(3) °, Z = 4. 2200 reflections with $F^2 \geqslant 2\sigma$ were measured with Mo-K_α radiation, and the structure was refined to an R value of 0·068. The structure comprises distorted octahedral complex cations (Figure) and bromide anions linked by rather weak H-bonds (five N · · · · Br distances per cation in the range 3·51—3·68 Å). The tridentate ligand is meridionally co-ordinated, corresponding to its nearly planar configuration. An interesting feature of the structure is a marked asymmetry of the chelating ethylenediamine. The inequality of the two Co–N distances in the ring is evidently due to a *trans*-labilizing influence of the alkyl ligand.‡

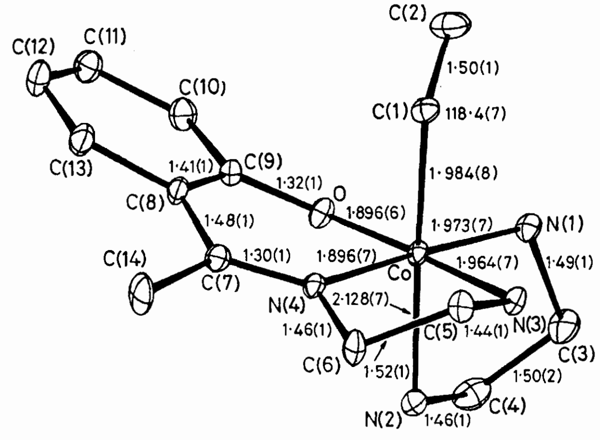


FIGURE. Structure of the cation in (**2a**).

Despite the considerable lengthening of the Co–N bond *trans* to the alkyl group, the complex cation is fairly stable towards ligand substitution. Thus it remains unaffected on addition of pyridine to a methanolic solution of (**2a**), which is indicated by the absence of any shift in the visible spectrum. It is noteworthy that alkylcobalt complexes with tetradentate ligands readily exchange Lewis base *trans* to the alkyl group.[1]

Steric and other factors favouring formation of complexes of the new type as well as the reactivity of the Co–C bond in such compounds are under investigation.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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