# Isomers of Bis[(*R*)-*N*-(aminopropyl)salicylaldiminato]-cobalt(III) and -chromium(III) Cations. Circular Dichroism and *X*-Ray Structure Analysis

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*Summary* Complexes of (*R*)-*N*-(aminopropyl)salicylaldimine with cobalt(III) and chromium(III) have been synthesised and two isomers of the cobalt complex with the same absolute configuration, (*S*), and one isomer of the chromium complex, which is a pseudo-racemate, have been isolated and characterised.

Complexes of chromium(III) and cobalt(III) with *N*-(2-aminoethyl)salicylaldimine (salH–en) have been described[1,2] and the crystal structures of [Cr(sal–en)$_2$]I[3] and [Co(sal–en)$_2$]-I$\cdot$H$_2$O[2] showed that the tridentate ligands bond to the metal ions in planes approximately at right angles to one another. These cations are dissymmetric and have been resolved into their optical isomers.[2]

When (*R*)-1,2-diaminopropane (*R*-pn) is used in place of ethylenediamine in the syntheses of such complexes, the salicylaldehyde may react with either amine group thus giving rise to the possibility of the formation of two different ligands. Hence, assuming that only the meridional arrangement is taken up by the ligands, three isomers of a complex of the type [M(sal–*R*-pn)$_2$]$^+$ are possible, each of which could exist as optical isomers.

Fractional crystallisation of the product of the reaction of cobalt(II) acetate with *R*-pn and salicylaldehyde in the presence of hydrogen peroxide, followed by the addition of sodium iodide, yielded two products with formula [Co(sal–*R*-pn)$_2$]I$\cdot$3H$_2$O in approximately equal amounts. The $^1$H n.m.r. spectrum of the less soluble isomer (I) in (CD$_3$)$_2$SO showed a pair of doublets at $\delta$ 1·22 and 1·25 (3H) and 1·62 and 1·65 (3H) (Me) and two singlets at $\delta$ 8·24 (1H) and 8·41 (1H) (CH) and that of the more soluble isomer (II) showed a doublet at $\delta$ 1·23 and 1·26 (6H) and a singlet at $\delta$ 8·41 (2H). These data indicated that the ligands in isomer (II) were identical and the methyl group was on the C atom adjacent to the terminal amino-group. In the isomer (I) one ligand was the same as those in isomer (II), while in the other ligand the methyl group was on the C atom adjacent to the azomethine group. These conclusions were confirmed by *X*-ray structure analysis which also showed the absolute configuration of the cations to be (*S*).

The perchlorate of the isomer (I), Figure (a), crystallised from aqueous ethanol as [Co(sal–*R*-pn)$_2$]ClO$_4\cdot$0·75EtOH. The crystals are monoclinic, space group $P2_1$, with $a$ = 10·682(4), $b$ = 8·672(3), $c$ = 15·565(6) Å, $\beta$ = 92·4(1)°, $Z$ = 2. The intensity data were collected on a Picker FACS-1 diffractometer using graphite crystal monochromated Cu-$K_\alpha$ radiation. The structure was solved by the heavy-atom technique and refined by least-squares methods to a final $R$ value of 0·068 for 2205 reflections with $I \geqslant 3\sigma(I)$. The presence of ethanol in the crystals was revealed by difference Fourier syntheses and confirmed by mass spectrometry. The amount of ethanol per mole of cation was determined by thermogravimetric analysis and refinement of site occupancy.

The isomer (II), Figure (b), crystallised as [Co(sal–*R*-pn)$_2$]-I$\cdot$3H$_2$O from water. The crystals are orthorhombic, space group $C222_1$, with $a$ = 10·570(3), $b$ = 16·052(3), $c$ = 15·220(7) Å, $Z$ = 4. The intensity data were collected on a Siemens diffractometer using Ni-filtered Cu-$K_\alpha$ radiation. The structure was refined to a final $R$ value of 0·102 for 621

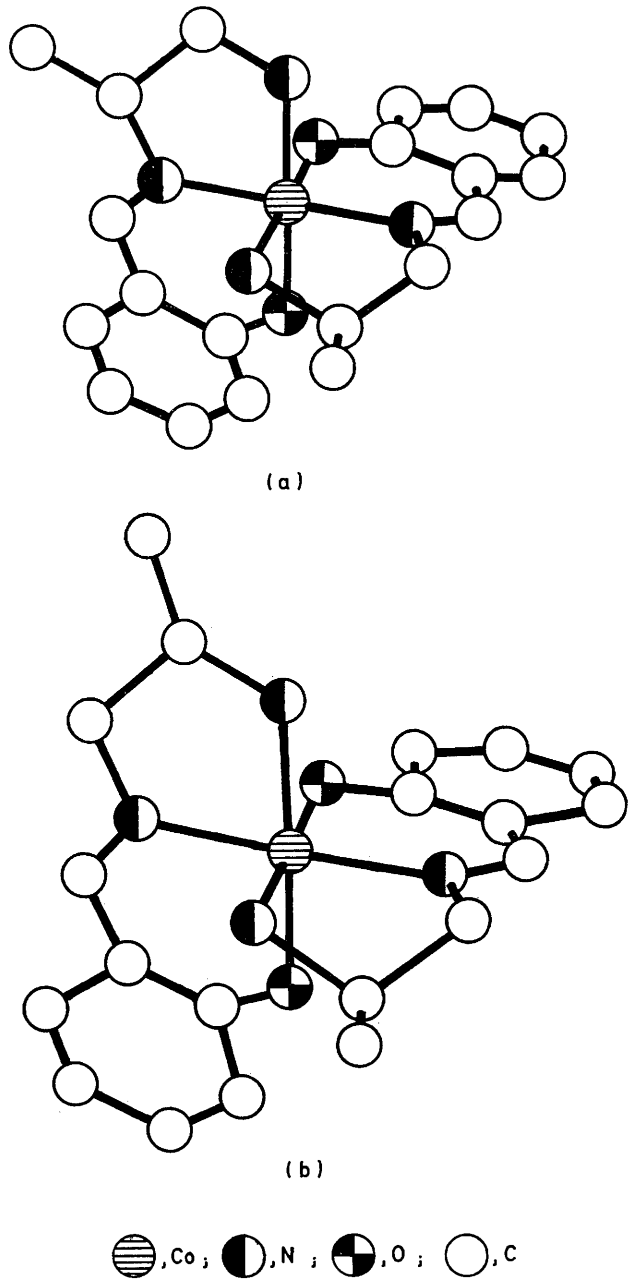

Figure. Structure of [Co(sal-*R*-pn)$_2$]$^+$: (a) isomer (I), (b) isomer (II).

reflections of which 487 had $I \geqslant 3\sigma(I)$ and 134 were given $I = 1{\cdot}5\sigma(I)$.

The electronic and c.d. spectra of the isomers in ethanol are very similar. A compound with formula $[Cr(sal\text{-}R\text{-}pn)_2]ClO_4$ was obtained from the reaction of tris(salicylaldehydato)chromium(III) with *R*-pn. The magnitude of the c.d. of this compound is considerably less than that of the c.d. of the cobalt isomers in the u.v. region where absorption bands arise from $\pi \rightarrow \pi^*$ transitions of the phenolate group of the ligands. This seemed to indicate that this compound was different from the cobalt compounds. *X*-Ray structure analysis showed that it was the pseudo-racemate corresponding to the isomer (II). Thus the c.d. spectrum showed the magnitude of the c.d. caused by the presence of the optically active ligands in the complex. The crystals of $[Cr(sal\text{–}R\text{-}pn)_2]ClO_4$ are triclinic, space group $P1$, with $a = 8{\cdot}627(1)$, $b = 12{\cdot}729(2)$, $c = 12{\cdot}580(2)$ Å, $\alpha = 113{\cdot}02(2)°$, $\beta = 105{\cdot}17(2)°$, $\gamma = 103{\cdot}16(2)°$, $Z = 2$. Intensity data were collected and the structure solved as described for the isomer (I), the final *R* value being 0·044 for 4473 reflections with $I \geqslant 3{\cdot}6\sigma(I)$.

A very small quantity of a third component has been isolated from the reaction product with cobalt(III) and $^1H$ n.m.r. and c.d. spectra indicate that it is the pseudo-racemate of the isomer (II). It is therefore apparent that there is considerable stereospecificity in the complex formation with cobalt(III) but not with chromium(III). This difference in behaviour can be explained by the fact that in the reactants the chromium(III) is already complexed with the salicylaldehyde whereas cobalt is present as solvated cobalt(II) ions.

We thank Dr. B. F. Hoskins, University of Melbourne, and Dr. G. B. Robertson, Research School of Chemistry, A.N.U., for making available the *X*-ray diffractometers, and one of us (M.S.B.) gratefully acknowledges the award of an A.N.U. Postgraduate Scholarship.

(*Received, 6th July* 1976; *Com.* 763.)

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