The Crystal Structure of *cis*-Dichlorobis(2,2′-dipyridyl)cobalt(III) Tetrachlorocobaltate(II), *cis*-$[Co\ Cl_2\ dip_2]_2[Co\ Cl_4]$

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In 1936 Jaeger prepared a green-colored cobalt(III) complex,[1] $[Co\ Cl_2\ dip_2]Cl$, whose cation has been believed to have a structure analogous to that of *trans*-$[Co\ Cl_2\ en_2]^+$,[2] the two dipyridyl molecules being coplanar. A coplanar disposition of dipyridyl molecules, however, has never yet been found, not even for any of the bis-dipyridyl copper(II) complexes,[3–6] in which the dipyridyl molecules are most likely to be on a plane. This is attributable to the steric interference between the two dipyridyl molecules in this arrangement. Therefore, the structure of Jaeger's green cobalt complex is of much interest with respect to the disposition of the chelating ligands.

The crystals obtained by Jaeger's method[1] were too thin for X-ray work. Vlček found another way of preparing this compound.[7] The crystals of a suitable size were obtained following the latter method. However, none of the definite formulae, such as $[Co\ Cl_2\text{-}dip_2]Cl$, were compatible with the values of elemental analyses (C, 43.31; N, 10.00; H, 3.19%).

The crystal data were as follows: monoclinic, $a=21.22$, $b=14.11$, $c=7.36$ Å, and $\beta=98.3°$; the space group was $P2/n$. Z was assumed to be four. Multiple-film equi-inclination Weissenberg photographs, *hk*0-*hk*5, were taken with Ni$K\alpha$ radiation. The intensities of 1684 reflections were estimated visually, and the usual corrections were applied. The crystal structure was determined by the conventional Patterson and Fourier techniques and refined to an R factor of 0.136 by block-diagonal least-squares method, using isotropic thermal parameters.

It was established that the green crystal does not contain the *trans*-$[Co\ Cl_2\ dip_2]^+$, but is composed of *cis*-$[Co\ Cl_2\ dip_2]^+$ and $[Co\ Cl_4]^{2-}$ in a ratio of 2:1. The results of elemental analyses are consistent with the formula of *cis*-$[Co\ Cl_2\ dip_2]_2[Co\ Cl_4]$.[8] The crystal structure is shown in the figure. The geometry around the Co(III) atom is similar to that in *cis*-$[Co\ Cl_2\ en_2]^+$[9] and in *cis*-$[Co\ Cl_2\ phen_2]^+$.[10]

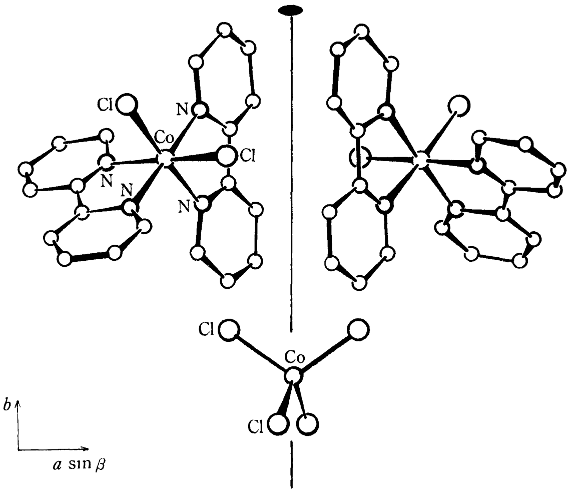

Figure. The crystal structure viewed along the c-axis.

The corresponding bond lengths and angles agree well with one another within the limits of experimental error; the values used below are averages. The Co(III)–Cl bond, 2.23 Å, compares well with those in the above complexes. In the chelate ring, ∠N–Co–N and ∠Co–N–C are 81.3° and 122.7° respectively. Both of the dipyridyl molecules are almost planar, the two pyridine rings twisting slightly to each other (~5°).

$[Co\ Cl_4]^{2-}$ is almost tetrahedral. Co(II)–Cl is 2.28 Å, which is consistent with that found in $[N(CH_3)_4]_2[Co\text{-}Cl_4]$ (2.280 Å).[11]

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[8] The Vlček's green complex has been reexamined by J. G. Gibson, R. Laird, and E. D. McKenzie (*J. Chem. Soc., A*, **1969**. 2089); they concluded that it should be denoted as *cis*-$[Co\ Cl_2\text{-}dip_2]_2\ [Co\ Cl_4]$ on the basis of the studies of magnetic property, reflectance spectra and X-ray powder diffraction pattern. However, we have been unware of their work until recently.

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