# The Absolute Configuration of $(+)_D$-$[Co(CN)_2en_2]^+$

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The absolute configurations of the several cobalt(III) complexes of the type, $[Co\,\widehat{AA}_3]$ or $[Co\,\widehat{AB}_3]$,[1-3] have been established by making use of the anomalous dispersion effect of Cu$K\alpha$ radiation. However, no direct X-ray determination of the absolute configuration has been made for any complexes of the type, *cis*-$[CoX_2\widehat{AA}_2]$. We, therefore, attempted to elucidate the crystal structure of *cis*-$(+)_D$-$[Co(CN)_2en_2]Cl\cdot H_2O$ as well as the absolute configuration of the complex ion in this compound.

The crystals are light yellow and tabular, the (100) planes being well-developed. They are monoclinic, with cell dimensions of $a=8.23$, $b=11.74$, $c=6.65$ Å and $\beta=107.8°$. The space group is $P2_1$, and the unit cell contains two formula units.

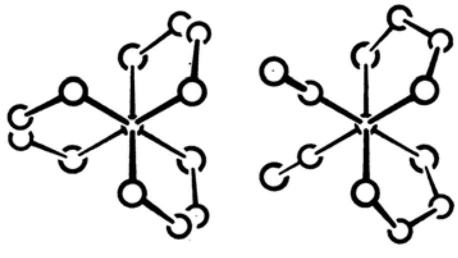
The *hk*0, *h*0*l* and 0*kl* reflection data were obtained from the Weissenberg photographs taken with Ni$K\alpha$ radiation. The Patterson maps, *P*-*(UV)*, *P(UW)* and *P(VW)*, and the minimum functions derived from these, gave the approximate coordinates of all the non-hydrogen atoms. So, the successive Fourier refinements and, then, the least-squares refinements were carried out. After three cycles of the least squares calculations, a final set of atomic parameters was obtained, discrepancy index *R* being 0.14.

Now, in order to determine the absolute configuration of the complex ion, the oscillation photographs were taken around the *y*-axis with Cu$K\alpha$ radiation. In this case, the diffraction spots corresponding to *hkl* and $\overline{hkl}$ should not be equal in intensity owing to the breakdown of Friedel's law. Actually, numerous inequality relationships were observed as listed in Table 1. Moreover, these were proved to be accounted for with the set of atomic parameters mentioned above, but not with its inversion. Thus, the absolute configuration of $(+)_D$-$[Co(CN)_2en_2]^+$, has been revealed, as illustrated in Fig. 1, in which that of $(+)_D$-$[Co\,en_3]^{3+}$ is also pictured for reference.

The complex ion has an pseudo two-fold axis passing through the cobalt atom and bisecting the C(CN)-Co-C(CN) angle; as a whole, approximate symmetry of the complex ion is $C_2$. The CN-groups are linked to the cobalt atom with their carbon atoms, and the Co-C-N bonds are almost linear. Corey and Bailar classified two possible conformations of the ethylenediamine molecules in $[Co\,en_3]^{3+}$ ion into the "lel" and "ob" forms.[4] According to their classification, both the ethylenediamine molecules in $(+)_D$-$[Co(CN)_2en_2]^+$ may be denoted as of the "ob" form. The bond lengths and bond angles within the complex ion are normal as compared to those previously established.[5,6]

TABLE 1.

| $(h1l)$ | $F_c(h1l)^2$ | obs. | $(h\bar{1}l)$ | $F_c(h\bar{1}l)^2$ |
|---|---|---|---|---|
| (212) | 73 | < | $(2\bar{1}2)$ | 218 |
| (215) | 133 | < | $(2\bar{1}5)$ | 288 |
| (211) | 1754 | > | $(2\bar{1}1)$ | 953 |
| (311) | 611 | < | $(3\bar{1}1)$ | 1290 |
| (411) | 58 | < | $(4\bar{1}1)$ | 195 |
| (314) | 435 | < | $(3\bar{1}4)$ | 509 |
| (415) | 159 | > | $(4\bar{1}5)$ | 103 |
| $(31\bar{1})$ | 756 | < | $(3\bar{1}\bar{1})$ | 1058 |
| $(41\bar{1})$ | 463 | > | $(4\bar{1}\bar{1})$ | 384 |
| $(61\bar{4})$ | 348 | < | $(6\bar{1}\bar{4})$ | 456 |
| $(61\bar{5})$ | 326 | > | $(6\bar{1}\bar{5})$ | 185 |
| $(61\bar{7})$ | 15 | < | $(6\bar{1}\bar{7})$ | 29 |
| $(71\bar{5})$ | 388 | > | $(7\bar{1}\bar{5})$ | 260 |
| $(71\bar{6})$ | 58 | < | $(7\bar{1}\bar{6})$ | 107 |



$\Delta(\lambda\lambda)$ $\Delta(\delta\delta\delta)$

Fig. 1. The absolute configurations of $(+)_D$-$[Co(CN)_2en_2]^+$ and $(+)_D$-$[Co\,en_3]^{3+}$.

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