The Absolute Configuration of the Tris-*l*-propylenediaminecopper(II) Ion, $(-)_{589}$-$[Cu(l\text{-}pn)_3]^{2+}$

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(Received April, 1, 1970)

Few investigations have been made of the absolute configurations of metal complexes other than those of cobalt(III). Fortunately, we have succeeded in preparing a copper(II) complex, $(-)_{589}$-$[Cu(l\text{-}pn)_3]Br_2\cdot 2H_2O$,[*1] and in determining its crystal structure. We wish here to report on its conformational features and on the absolute configuration of the complex cation.

Crystal data: monoclinic, space group $P2_1$; $a=10.71$, $b=8.93$, $c=10.88$ Å, $\beta=107.2°$; $Z=2$, $D_c=1.56$, $D_m=1.56\ \mathrm{g\cdot cm^{-3}}$, $\mu=66.9\ \mathrm{cm^{-1}}$ (for Cu$K\alpha$). The intensity data were recorded on multiple-film, equi-inclination Weissenberg photographs taken about the *a*- and *b*-axes; they were visually estimated. Absorption corrections were applied. The determination of the crystal structure was carried out by means of the three-dimensional Fourier techniques. The least-squares refinement led to the *R* value of 0.102 for 1437 reflections. In deciding the absolute configuration of the $(-)_{589}$-$[Cu(l\text{-}pn)_3]^{2+}$ ion, that of *l*-propylenediamine was cautiously referred to.

Figure 1 shows a perspective of the complex ion, viewed along the *b*-axis, the ion has an approximately three-fold axis. The *l*-propylenediamine molecules are linked to the Cu(II) atom in the "*lel*" form, every C–CH_3 bond lying in an approximately equatorial plane of the five-membered ring, as is the case with $(-)_{589}$-$[Co(l\text{-}pn)_3]^{3+}$[1] and *trans*-$[CoCl_2(l\text{-}pn)_2]^{+}$[2]; the absolute configuration of $(-)_{589}$-$[Cu(l\text{-}pn)_3]^{2+}$ can be denoted as $\Delta(\lambda\lambda\lambda)$. The average value of the longer two of the Co–N bond lengths is 2.31 Å, and that of the other four, 2.09 Å. All the bond distances and angles within the N–C–C–N skeleton of the *l*-propylenediamine are quite normal.

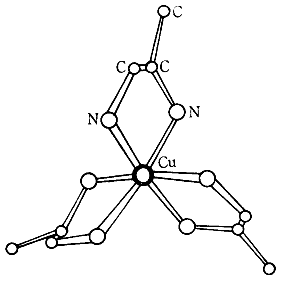

Fig. 1. A perspective of the complex ion viewed along the *b* axis.

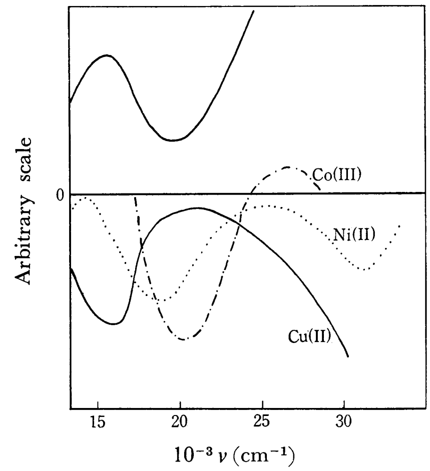

Fig. 2. The CD Spectra of tris-*l*-propylenediamine complexes and the absorption spectrum—of $(-)_{589}$-$[Cu(l\text{-}pn)_3]^{2+}$

Figure 2 depicts the CD curves of the tris-*l*-propylenediamine complexes of Co(III), Cu(II),[*2] and Ni(II)[*3] as well as the absorption spectrum of the Cu(II) complex.[*2] In the first absorption-band region, a large negative CD peak can be seen for each of these three complexes; two of these have been confirmed to have the same absolute configuration. So far as this fact is concerned, it may be presumed that complexes of the same absolute configuration possess CD peaks of the same sign in the first band region, regardless of the kind of central metal atom.

[*1] *l*-pn=*l*-propylenediamine.

1) H. Iwasaki and Y. Saito, This Bulletin, **39**, 92 (1966).

2) Y. Saito and H. Iwasaki, *ibid.*, **35**, 1131 (1962).

[*2] The CD curve and the absorption spectrum of $(-)_{589}$-$[Cu(l\text{-}pn)_3]^{2+}$ in the bromide crystals were obtained by the present authors, but qualitatively.

[*3] The CD curve of $(-)_{589}$-$[Ni(l\text{-}pn)_3]^{2+}$ was measured in a solution of its perchlorate. Crystal structure analysis of the complex is now in progress.