Trigonal Prismatic Co-ordination in the *cis,cis*-1,3,5-Tris(pyridine-2-carboxaldimino)cyclohexanezinc(II) Ion

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Summary A single-crystal *X*-ray diffraction study has shown the Zn^{II} complex of *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane to have trigonal prismatic co-ordination.

HERETOFORE, authenticated examples of trigonal prismatic co-ordination were limited to compounds which exclusively contain sulphur-bonded metal atoms from the second and third transition series.[1,2] Our interests in hindered ligand systems[3] has led to a three-dimensional *X*-ray study of the Zn^{II} complex of *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane, and we find, as shown in Figure 1, that trigonal prismatic co-ordination can occur with nitrogen-bonded metal atoms of the first transition series as well.

The anhydrous perchlorate crystallizes in the space group $P2_1/c$ with $a = 13{\cdot}440 \pm 0{\cdot}008$, $b = 13{\cdot}738 \pm 0{\cdot}006$, $c = 15{\cdot}279 \pm 0{\cdot}008$ Å, $\beta = 109° \; 53' \pm 1'$, $Z = 4$, $D_m = 1{\cdot}67$ g.cm.$^{-3}$, and $D_c = 1{\cdot}65$ g.cm.$^{-3}$. A fully automatic Picker diffractometer, equipped with a highly oriented graphite monochromator, was used to collect a 2-fold redundant set of data totalling 11,369 reflections using the standard θ–2θ scan technique and Mo-K_α radiation. The set of 2185 unique reflections with $I_{obs} > 2{\cdot}33\sigma_I$, (where σ_I is the standard error in I_{obs} based on counting statistics)

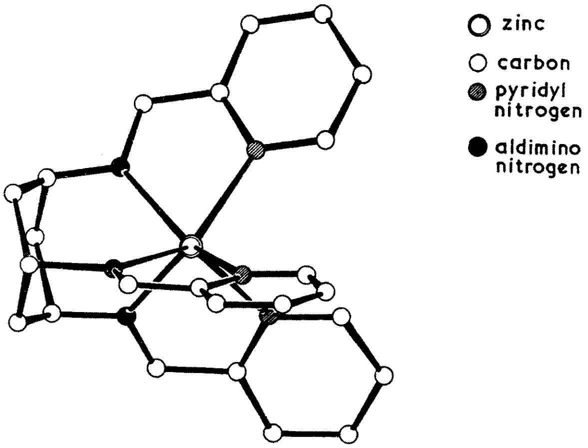

FIGURE 1. *Structure of the* cis,cis-1,3,5-*tris(pyridine-2-carboxaldimino)cyclohexanezinc*(II) *ion. The pseudo-threefold axis is horizontal and in the plane of the paper.*

was used to determine the structure. Application of the Sayre equation and Fourier methods located all non-hydrogen atoms, which have been refined anisotropically using a full-matrix least-squares treatment to the present R of 0·048.

The C–C bond lengths in the cyclohexane ring vary from 1·49 to 1·57 Å. Within the pyridine rings the C–N distances range from 1·31 to 1·36 Å while the C–C bond lengths occur between 1·37 and 1·42 Å. Within the aldimino-group the C–N distances vary from 1·24 to 1·27 Å. The aldimino N–Zn bond lengths range between 2·14 and 2·17 Å, while the pyridyl N–Zn distances occur between 2·21 and 2·27 Å. The maximum error in distances is presently estimated at ±0·02 Å. The co-ordination polyhedron is formed by the triangle of aldimino N atoms with an average edge length of 2·85 Å and the triangle of pyridyl N atoms in which the average edge length is 3·23 Å. The co-ordinating atoms then form a somewhat tapered trigonal prism whose height is approximately 2·64 Å. The structure could be described alternatively as a severely truncated trigonal pyramid, but this description is less useful. Bond angles between only aldimino N atoms and the Zn atom are about 83°, while those between only pyridyl N atoms and the metal atom are close to 90°. The average aldimino N–Zn–pyridyl N bond angle within the same pyridinecarboxaldimino-group is, however, only about 74°. In addition, the triangular faces of the prism are slightly twisted with respect to each other, and the magnitude of the twist is shown in Figure 2.

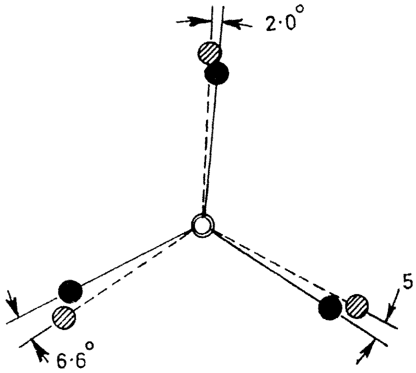

FIGURE 2. *The co-ordination polyhedron as viewed down the pseudo-threefold axis. The atoms are coded as in Figure* 1.

The presence of the metal atom forces each pyridinecarboxaldimino-group to be planar and, in the absence of other perturbing influences, the triaxial conformation of the cyclohexane ring would require that each plane which contains a pyridinecarboxaldimino-group also contains the pseudo-threefold axis of the ion. However, in this idealized structure the 6-H atoms of each pyridine ring would be directed under the ion toward the psdudo-threefold axis. The relief of the non-bonded contacts which would otherwise result is probably responsible for the enlargement of the lower base of the trigonal prism. The slight twist may be due to this cause as well, but intermolecular non-bonded contacts may also be responsible in part.

We have also found that powder patterns of the Ni^{II} and Zn^{II} compounds differ markedly. It may be that the ligand field stabilization energy is sufficient to enforce octahedral co-ordination in the Ni^{II} complex ion.

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[2] After this manuscript was submitted for publication, it became known that the trinuclear cation formed from Co and 2-aminoethanol contained Co^{II} in trigonal prismatic co-ordination with the O atoms of the ligands. J. A. Bertrand, J. A. Kelley, and E. G. Vassian, *J. Amer. Chem. Soc.*, 1969, **91**, 2394.

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