Single-crystal Structure of *cis,cis*-1,3,5-Tris(pyridine-2-aldimino)cyclohexanenickel(II) Perchlorate

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Summary A single-crystal *X*-ray study has shown the Ni^{II} complex of *cis,cis*-1,3,5-tris(pyridine-2-aldimino)-cyclohexane to have a geometry intermediate between trigonal prismatic and octahedral, with an average angle of twist from trigonal prismatic of approximately 32°.

THE geometry of the Zn^{II} complex of *cis,cis*-1,3,5-tris-(pyridine-2-aldimino)cyclohexane was previously determined to be trigonal prismatic, and it was also reported that the Ni^{II} complex was not isomorphous with the Zn^{II} complex.[1] Because of the recent interest in trigonal prismatic co-ordination of α-di-imines[2-5] and the difficulty in distinguishing spectroscopically between the two geometries,[2] we undertook a single-crystal *X*-ray study of the Ni^{II} complex.

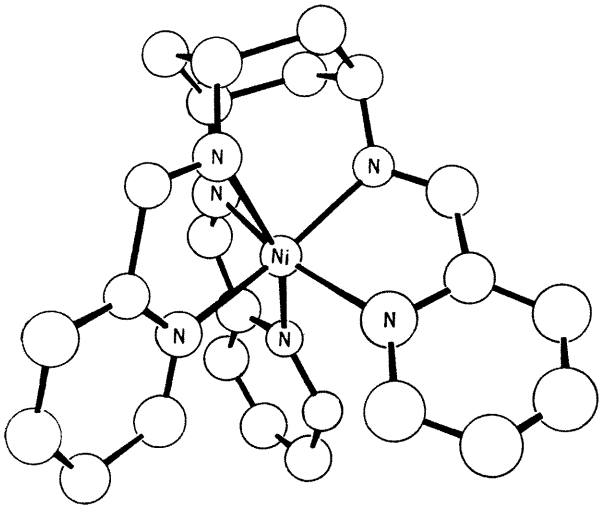

FIGURE 1. *Structure of the* cis,cis-1,3,5-*tris(pyridine-2-aldimino)-cyclohexanenickel*(II) *ion. The sizes of the circles indicate isotropic temperature factors as well as perspective. All atoms not labelled are carbon.*

The Ni^{II} perchlorate was prepared as previously reported,[2] and crystallizes from water in the monoclinic system: $a = 15{\cdot}470\ (7)$, $b = 9{\cdot}971\ (5)$, $c = 20{\cdot}503\ (10)$ Å, $\beta = 120{\cdot}88\ (2)°$, $Z = 4$, $D_c = 1{\cdot}60$ g cm^{-3}, and $D_m = 1{\cdot}62$ g cm^{-3}. Precession photographs indicated either of two space groups: $P2/c$ or Pc. Data were collected using an automated Picker diffractometer with Zr-filtered Mo-K_α radiation. A total of 2796 reflections were collected using the θ–2θ scan method and a scan rate of 1°/min, of which 1800 that were employed in the analysis were greater than $3\sigma_I$ (where σ_I is the standard error in I_{obs} based on counting statistics). An acentric distribution of *E*'s calculated using FAME indicated the space group of lower symmetry *Pc*, which has two molecules per asymmetric unit. Patterson and Fourier methods were used for solution of the structure and full-matrix isotropic least-squares refinement yielded the present *R* value of 8·7%.

Bond distances and angles for the Ni^{II} *co-ordination spheres*

	Nickel 1 bond length (Å)	σ^a	Nickel 2 bond length (Å)	σ^a
$Ni–N_{ald}$	2·00—2·12	0·03	1·96—2·08	0·03
$Ni–N_{py}$	2·08—2·15	0·03	2·09—2·16	0·03
	bond angle	σ^b	bond angle	σ^b
$N_{ald}–Ni–N_{ald}$	84—86°	1	82—87°	1
$N_{py}–Ni–N_{py}$	92–93°	1	92—94°	1
$N_{ald}–Ni–N_{py}$	77—80°	1	77—80°	1

N_{ald} = aldimino nitrogen, N_{py} = pyridine nitrogen.
[a] Estimated standard deviation in individual bond lengths.
[b] Estimated standard deviation in individual bond

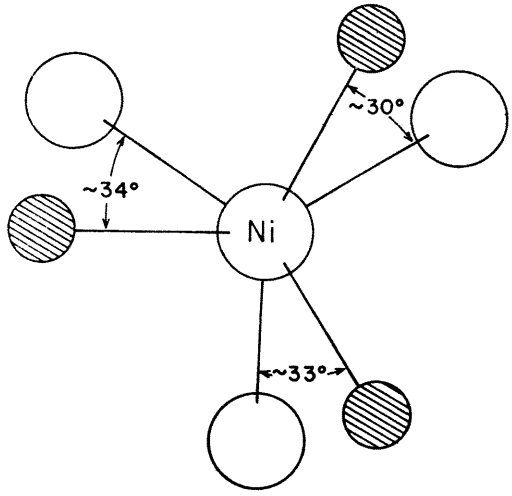

FIGURE 2. *Projection of the co-ordination sphere down the pseudo-three-fold axis showing the angles of twist from trigonal prismatic of about* 32°. *The aldimino-nitrogens are shaded.*

One of the two equivalent molecules in the asymmetric unit is shown in Figure 1. In comparison with the Zn^{II} complex, the Ni^{II} cation has significant distortion from trigonal prismatic co-ordination. Ranges for nickel–nitrogen bond distances and nitrogen–nickel–nitrogen angles are presented in the Table for both cations in the asymmetric unit.

The co-ordination sphere, as viewed down the 3-fold axis, is shown in Figure 2. The aldimino nitrogens form a triangular face of approximately 2·81 Å, while those of the pyridine moieties form a face of 3·02 Å and the "average angle of twist" between the two faces is 32°. This value compares quite closely with that for the Ni^{II} complex of 1,1,1-tris(pyridine-2-aldiminomethyl)ethane, which is isomorphous with the corresponding Zn^{II} complex that has been found to have an angle of 28°.[5,6] Such similarity for the Ni^{II} complexes is especially intriguing in view of the dissimilarity of the Zn^{II} complexes, and additional work to resolve this point is in progress.

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[6] An average angle of twist of 43° has been found for the Fe^{II} complex of 1,1,1-tris(pyridine-2-aldiminomethyl)ethane. A. E. Gebala and E. B. Fleischer, unpublished results.