Internal Strain in Five- and Six-membered Chelate Rings: Crystal Structure of Bisdi-(3-aminopropyl)aminenickel(II) Perchlorate and of Bisdi-(2-aminoethyl)aminenickel(II) Chloride Monohydrate

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COMPLEXES with saturated six-membered rings are less stable than those with five-membered rings, and the lower stability has usually been ascribed to the presence of strain. With the aim of confirming this and studying the nature of the strain, we solved the crystal structures of the title compounds, Ni dpt$_2$ (ClO$_4$)$_2$ and Ni den$_2$ Cl$_2$,H$_2$O. Both compounds crystallize from water: the first in the form of orthorombic blue prisms elongated along *a*; the second in the form of monoclinic diamond-shaped plates, with the *c* and *a* axes parallel to the diagonals. From the structure of the cations Figure) the following conclusions can be drawn.

In both compounds the donor atoms co-ordinate in an equatorial plane of an octahedron. Nonplanar terdentate ligands, such as "den" and "dpt", are also able to co-ordinate vicinally at the vertices of one face of an octahedron. This arrangement has been shown for "den" in MoO$_3$ den[1] and Mo(CO)$_3$ den;[2] no structural analysis has been reported for "dpt" complexes. The complex cation [Ni dpt$_2$]$^{2+}$ has an almost regular octahedral geometry, as shown by the average value of 91·5° for the N(primary)–Ni–N(sec.) angles; this value is close to that reported for dichloro-1,4,8,11-tetra-azacyclotetradecanenickel(II) (94·3°).[3] The corresponding value in the "den" complex is 81·7°, in agreement with the value found in Ni en$_3$(NO$_3$)$_2$ (82·3).[4] Ni–N(primary) bond lengths do not differ significantly in the two compounds and are in agreement with the values reported in ref. 5 (2·12 Å); on the other hand Ni–N(sec.) bond lengths in [Ni dpt$_2$]$^{2+}$ are approx. 0·2 Å longer than in [Ni den$_2$]$^{2+}$, whose value (2·05 Å) is in agreement with the values reported in ref. 3. This fact could account for the smaller bond energy in the "dpt" complex.

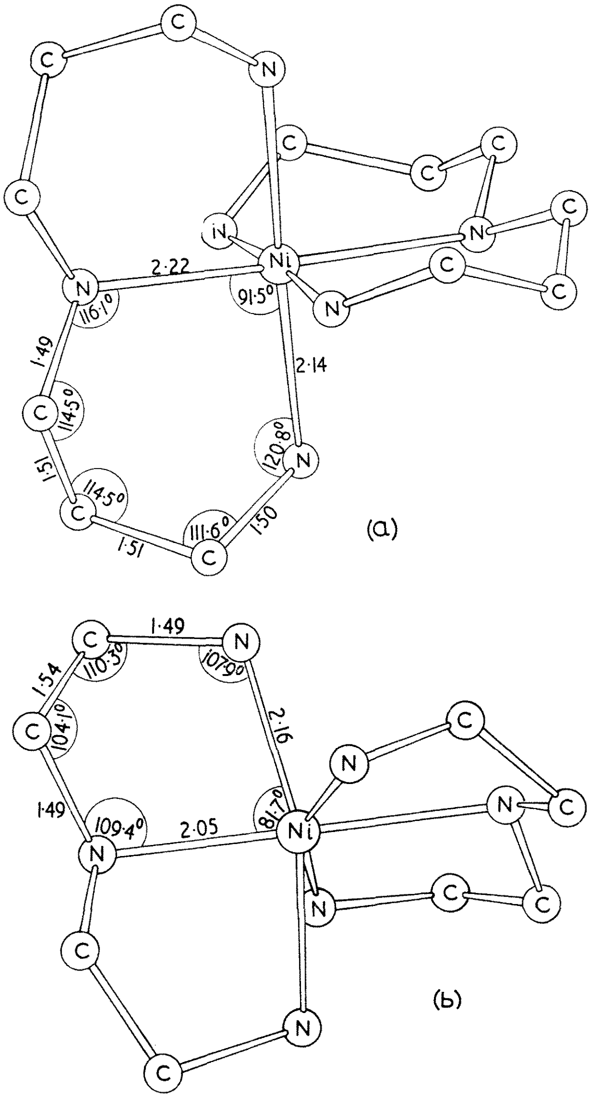

FIGURE. *Structure of* (a) Ni dpt$_2$$^{2+}$ *and* (b) Ni den$_2$$^{2+}$. *Average values of bond lengths and angles are given.*

Intramolecular distances, calculated assuming atoms in tetrahedral positions, showed H · · · H distances in general greater than 2·35 Å only a few of them being in the range 2·25—2·30 Å, which corresponds to a partly eclipsed conformation. In the [Ni dpt$_2$]$^{2+}$ cation, however, some contacts in the range 2·15—2·20 Å are present between the amino-group hydrogens of one ligand and the axial hydrogens of the other.

The conformation of the six-membered chelate rings in the "dpt" complex resembles the chair conformation of cyclohexane. The mean value of the acute angles between the planes through N(primary)–Ni–N(sec.) and the mean planes through N(primary)–C and N(sec.)–C bonds is 24°. As a result, the rings are flatter than cyclohexane, and the values of Ni–N(primary)–C and Ni–N(sec.)–C angles become larger. A ring of such a conformation should be strained, according to Corey and Bailar,[5] who report that an unstrained ring should be more sharply folded than cyclohexane. For the compound examined, on the other hand, a conformation like the one suggested by Corey and Bailar would cause still shorter H · · · H contacts between the axial hydrogens of one ligand and the amino-group hydrogens of the other. The strain in the rings could then be associated with ligand–ligand interactions, and this should be in agreement with the remarkable difference in the values of the first and second stability constants of the complex ($K_1 = 9{\cdot}19$; $K_2 = 3{\cdot}55$);[6] moreover, thermochemical studies[7] indicated that the heat of formation in the first stage ($-\Delta H^0 = 10{\cdot}56$ kcal.mole^{-1}) is higher than in the second stage ($-\Delta H^0 = 7{\cdot}08$ kcal.mole^{-1}).

Bond angles and distances in the "den" complex do not differ from normal values and, as a consequence of the deviation of N(primary)–Ni–N(sec.) angles from 90°, the octahedral co-ordination is considerably distorted from the normal d^2sp^3 configuration. This is probably not to be considered a relevant strain, since an angle of 86·2° has been calculated[5] for an hypothetical strain-free M–en ring and similar values have been found in all known structures. In Co(Et$_4$ den)Cl$_2$,[8] MoO$_3$ den,[1] and Mo(CO)$_3$ den,[2] the average N(primary)–M–N(sec.) values are respectively 80·4°, 73°, and 74°.

Crystal data for bisdi-(3-aminopropyl)aminenickel(II) perchlorate are: $a = 16{\cdot}61 \pm 0{\cdot}04$, $b = 13{\cdot}43 \pm 0{\cdot}04$, $c = 20{\cdot}15 \pm 0{\cdot}07$ Å, space group $Pbca$, $Z = 8$. The intensities of 2330 reflections were measured photometrically on integrated Weissenberg photographs. For bisdi-(2-aminoethyl)aminenickel(II) chloride monohydrate: $a = 13{\cdot}50 \pm 0{\cdot}02$, $b = 8{\cdot}69 \pm 0{\cdot}01$, $c = 14{\cdot}01 \pm 0{\cdot}02$ Å, $\beta = 102{\cdot}5 \pm 0{\cdot}4°$; space group $P2_1/c$, $Z = 4$. The intensities of 1900 reflections were measured photometrically on integrated Weissenberg photographs. The structures were solved by three-dimensional Patterson and Fourier methods, and were first refined by three-dimensional Fourier syntheses and then by full-matrix least-squares.

R factors were: 0·080 for Ni dpt$_2$(ClO$_4$)$_2$ and 0·12 (to be refined) for Ni den$_2$Cl$_2$,H$_2$O.

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[1] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1964, **3**, 397.
[2] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314.
[3] B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Comm.*, 1965, 97.
[4] L. N. Swink and M. Atoji, *Acta Cryst.*, 1960, **13**, 639.
[5] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.
[6] A. Vacca, D. Arenare, and P. Paoletti, *Inorg. Chem.*, 1966, **5**, 1384.
[7] P. Paoletti, F. Nuzzi, and A. Vacca, *J. Chem. Soc.* (*A*), 1966, 1385.
[8] Z. Dori, R. Eisenberg, and H. B. Gray, *Inorg. Chem.* 1967, **6**, 483.