The Structure of Dinitrito-(*NNN'N'*-tetramethylethylenediamine)nickel(II)

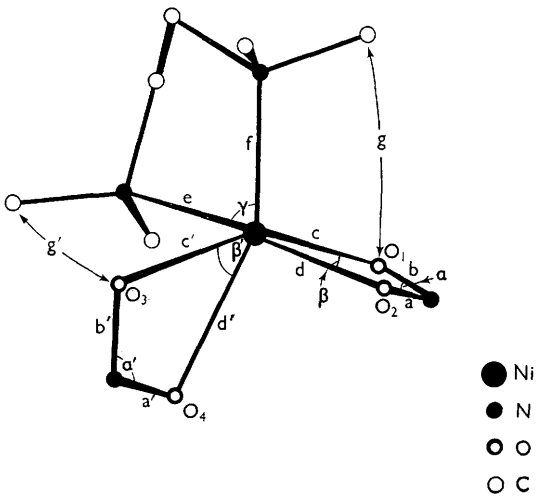
By M. G. B. DREW and D. ROGERS
(*Chemistry Department, Imperial College, London, S.W.*7)

THE compounds $NiL_2(NO_2)_2$ (L = quinoline, or α-picoline) and $Ni(Me_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2)(NO_2)_2$ were recently prepared in this laboratory, and studies of their spectra suggested that the nitrite ions were present as chelating ligands.[1]

In order to confirm this and to obtain

[1] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1965, **4**, 721.

details of the molecular geometry a three-dimensional *X*-ray study has been carried out of $Ni(Me_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2)(NO_2)_2$. The crystals are green, monoclinic prisms with $a = 7{\cdot}669$, $b = 12{\cdot}285$, $c = 12{\cdot}449$Å, $\beta = 92{\cdot}43°$, $Z = 4$, space group $P2_1/n$. The structure, based on 1408 independent visually estimated reflexions, has been refined to $R = 0{\cdot}115$. Although the molecule occupies a general position, it approximates to 2-fold (C_2) symmetry: deviations are slight but significant and due presumably to asymmetric intermolecular contacts. The principal features of the molecule are shown in the Figure and accompanying Table. Both nitrites act as chelating groups, and introduce considerable distortion of the octahedral co-ordination around the nickel atom. Thus each nitrite subtends about 60° at the nickel atom, and this is achieved by angular distortions of all four Ni–O bonds. The two that ought to occur perpendicular to the Me_2N–Ni–NMe_2 plane (O_1, O_3) have moved nearly symmetrically away from the ethylenediamine ligand and subtend 158·8° at the nickel. The other two (O_2, O_4) remain almost exactly 90° apart, but the O–Ni–O plane makes an angle of 19·2° with the plane N–Ni–N, the tilt being opposite to that of the C–C bond in the ethylenediamine. Both nitrite groups are in close contact with the ethylenediamine ring, but it seems likely that two of the O–Me contacts (3·07, 3·11Å) control the orientations of the four-membered rings. Despite this each is flat to within 0·02 Å. The O–N–O angles in each nitrite group agree well with each other (111·24°, 112·45°), but are a little smaller than in the free ion (115·4°),[2] and the nickel–oxygen bonded nitrite (115·0°),[3] though the difference is scarcely significant at this stage of refinement.



[100] *Projection of molecule.*

A recent report of the structure of potassium tetranitritomercurate(II)nitrate,[4] which contains chelating nitrites, laid stress on the fact that the four Hg–N vectors are arranged in a good approximation to a tetrahedron. In the present structure, the angle subtended by the two nitrite nitrogens at the nickel is 109·54°, but those in the ethylenediamine subtend 85·6° (in good agreement with another study[3]), and the two N–Ni–N planes are far from perpendicular. It seems better, therefore, to regard the nickel atom here as having a distorted octahedral, rather than a distorted tetrahedral, co-ordination.

Bond lengths (Å), *Angles* (°)

(*Standard deviations from block-diagonal least-squares calculations*)

a	1·259 ± 0·015	a′	1·218 ± 0·014
b	1·245 ± 0·016	b′	1·326 ± 0·014
c	2·066 ± 0·009	c′	2·059 ± 0·009
d	2·150 ± 0·009	d′	2·117 ± 0·008
α	111·65 ± 1·69	α′	111·69 ± 1·38
β	58·83 ± 0·51	β′	60·57 ± 0·51
γ	85·55 ± 0·34		
e	2·087 ± 0·009		
f	2·086 ± 0·009		
g	3·109 ± 0·016	g′	3·066 ± 0·016

(*Received, August 13th*, 1965; *Com.* 505.)

[2] G. B. Carpenter, *Acta Cryst.*, 1955, **8**, 852.
[3] M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Proc. Chem. Soc.*, 1964, 363.
[4] D. Hall and R. V. Holland, *Proc. Chem. Soc.*, 1963, 204.