The Crystal and Molecular Structure of the Five-co-ordinated Complex of Nickel(II) Perchlorate with the Ligand *NN*-Bis-(2-diethylaminoethyl)-2-hydroxyethylamine

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THE tripod-like tetradentate ligand *NN*-bis-(2-diethylaminoethyl)-2-hydroxyethylamine $[Et_2N{\cdot}CH_2]_2N{\cdot}[CH_2]_2{\cdot}OH$ (bdhe) has been studied. With nickel perchlorate a complex is formed of empirical formula Ni bdhe ClO_4, in which the ethanol group is obviously deprotonated.[1] The reflectance spectrum of the compound is diagnostic of a five-co-ordinate high-spin nickel(II) complex. This suggests that one oxygen atom from the perchlorate ion is co-ordinated as well as the four donor atoms of the ligand molecule, as in other five-co-ordinate complexes.[2] However, the similarity between the reflectance spectrum and the absorption spectrum in nitromethane, in which the complex is completely dissociated, shows that the perchlorate ion is not part of the chromophore.[1] A three-dimensional *X*-ray analysis has now been carried out to resolve this point.

Crystal data: space group *Pbca*, $a = 15{\cdot}772 \pm 0{\cdot}020$, $b = 19{\cdot}281 \pm 0{\cdot}016$, $c = 12{\cdot}396 \pm 0{\cdot}008$ Å, $Z = 8$, $D_m = 1{\cdot}45$, $D_c = 1{\cdot}45$. The 1177 independent reflections observed were measured on integrated Weissemberg films, using Cu-K_α radiation. The structure determination was carried out with Patterson and two three-dimensional Fourier syntheses, and refined by full-matrix least-squares, with anisotropic temperature factors for all the atoms, to R 8·2%.

The structure consists of dimers possessing a centre of symmetry, formed by two ligand oxygen atoms bridging the nickel atom (Figure), Ni · · · Ni′ distance 3·09 Å. The nickel atoms are five-co-ordinate, linked to three nitrogen and two oxygen atoms. Two perchlorate ions act as counter-ions, the lowest Cl · · · Ni distance being 6·30 Å. The co-ordination geometry can better be described as a distorted trigonal bipyramid with O, N(2), and N(3) forming the equatorial plane and N(1) and O′ in the axial positions. The angles in the plane are: O–Ni–N(2) 123·7, O–Ni–N(3) 121·8, N(2)–Ni–N(3) 112·1°; the N(1)–Ni–O′ angle is 160·6° (all σ 0·5°). Bond lengths about the nickel atom are: Ni–O 1·97, Ni–O′ 1·97, Ni–N(1) 2·09, Ni–N(2) 2·16, Ni–N(3) 2·18 Å (all σ 0·01 Å). The metal atom is displaced by 0·19 Å from the equatorial plane toward O′.

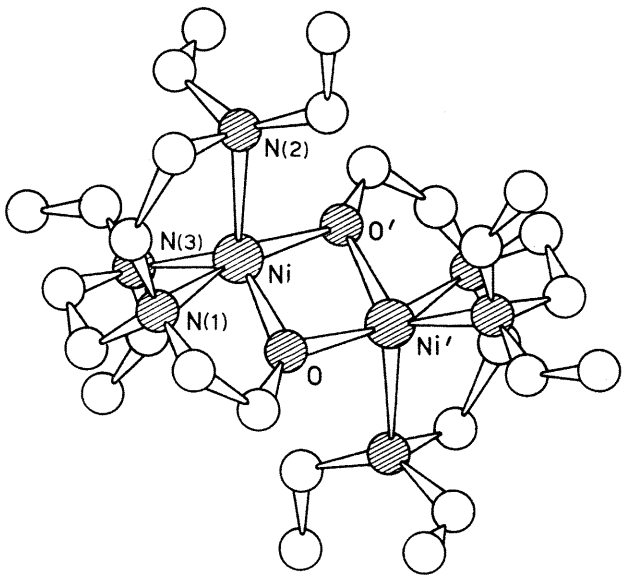

FIGURE. *A perspective view of the configuration of the complex cation* $[Ni_2(bdhe)_2]^{2+}$.

The complex compound must then be assigned the formula $[Ni_2\ bdhe_2](ClO_4)_2$, which is in agreement with the conductivity values in nitroethane and methyl alcohol, for a 1 : 2 electrolyte.

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[1] R. Morassi and L. Sacconi, to be published.
[2] J. Lewis, R. S. Nyholm, and G. A. Rodley, *Nature*, 1965, **207**, 72; P. Pauling, G. B. Robertson, and G. A. Rodley, *ibid.*, p. 73.