

## The First X-Ray Structure of an Octahedral Transition Metal Complex containing a Strongly Chelating Bidentate Perchlorate<sup>1</sup>

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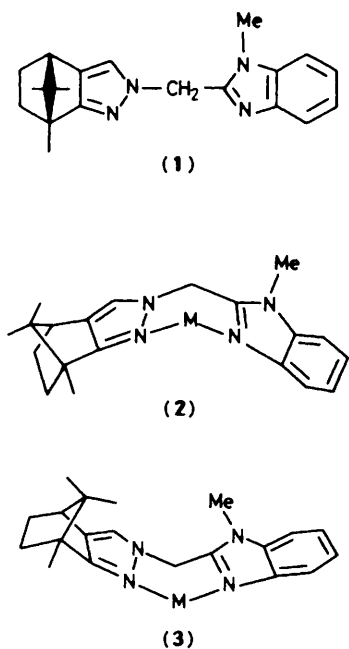
An X-ray structure determination of the complex formed by reaction of the chiral bidentate ligand L, (1), with nickel(II) perchlorate shows the presence in the asymmetric unit of two different stereoisomers of  $[\text{NiL}_2(\text{ClO}_4)]^+$ , each of which contains a strongly chelating bidentate perchlorate.

Although the perchlorate anion was once considered to be non-co-ordinating<sup>2</sup> there are now many examples known in which perchlorate acts as a monodentate or bridging bidentate ligand to a variety of metals.<sup>3</sup> In spite of the fact that a chelating bidentate mode of co-ordination by perchlorate has long been postulated to exist on the basis of i.r. spectroscopy,<sup>4</sup> only recently has this been unambiguously demonstrated by X-ray crystal structure determinations of the dodecahedral inorganic perchlorates  $\text{Zr}(\text{ClO}_4)_4$ <sup>5</sup> and  $\text{Ti}(\text{ClO}_4)_4$ .<sup>3</sup> We now report the first X-ray structure of an octahedral complex containing a chelating bidentate perchlorate.

We are currently engaged in the synthesis and study of new polydentate ligands incorporating nitrogen heterocycles fused

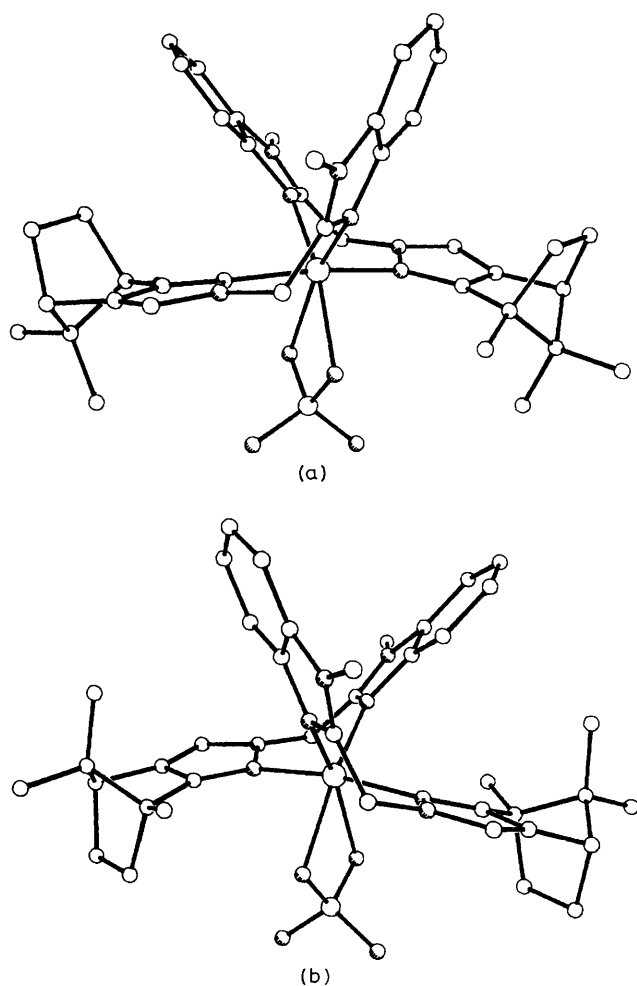
to a bornane skeleton for use as chiral auxiliaries in asymmetric organic synthesis.<sup>1,6</sup> As part of this work the chiral bidentate ligand (1) was prepared<sup>†</sup> and its co-ordination chemistry with various transition metal ions investigated. Reaction of (1) with nickel perchlorate hexahydrate in ethanol solution deposited blue crystals of stoichiometry  $\text{Ni}(\text{1})_2(\text{ClO}_4)_2(\text{EtOH})$  for which a single crystal X-ray structure determination was carried out.<sup>‡</sup>

The structure is unusual in that the asymmetric unit contains two different stereoisomers of the cation each of which possesses a strongly chelating bidentate perchlorate and the bulky bornane groups in a *trans* configuration (Figure 1). Ligands such as (1) adopt one of two boat conformations, (2)



<sup>†</sup> The ligand (1) was prepared by phase-transfer catalysed alkylation of (4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-1*H*(2*H*)-indazole<sup>7</sup> with 2-chloromethyl-1-methylbenzimidazole<sup>8</sup> in 85% yield, m.p. 118.5–119.5 °C.

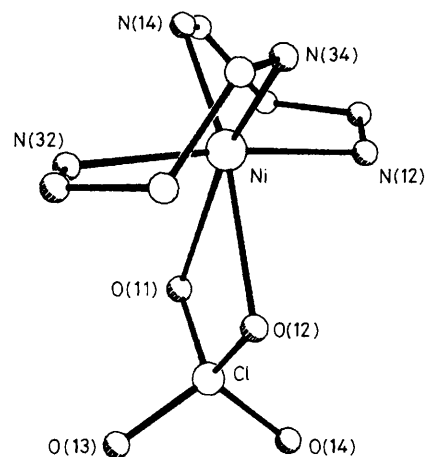
<sup>‡</sup> Crystal data:  $\text{C}_{40}\text{H}_{48}\text{N}_8\text{O}_8\text{Cl}_2\text{Ni}\cdot\text{EtOH}$ ,  $M = 944.6$ , monoclinic, space group  $P2_1$ ,  $a = 13.370(8)$ ,  $b = 21.152(13)$ ,  $c = 15.605(9)$  Å,  $\beta = 99.73(5)^\circ$ ,  $U = 4350(4)$  Å<sup>3</sup>,  $T = 140$  K,  $D_c = 1.44$  g cm<sup>-3</sup>,  $Z = 4$  (two isomers in asymmetric unit), blue crystal of dimensions  $0.72 \times 0.49 \times 0.13$  mm,  $\mu = 6.32$  cm<sup>-1</sup>. 8774 Unique reflections ( $2\theta \leq 45^\circ$ ) were measured with a Nicolet R3m four-circle diffractometer using graphite monochromated Mo- $K_\alpha$  radiation (0.71069 Å) and fixed speed  $1.4^\circ$   $\omega$ -scans. The data were corrected for Lorentz and polarization effects and an absorption correction, based on azimuthal  $\psi$  scans, applied. 7111 Reflections were judged observed [ $I > 3\sigma(I)$ ]. The structure was solved by conventional Patterson and Fourier techniques and refined by blocked-cascade least-squares procedures. The enantiomorph used was that consistent with the known absolute configuration of (+)-camphor, from which the ligand was synthesised. The asymmetric unit contains two different isomers of the cation, two ordered perchlorate anions, and two ethanol molecules, one of which has the oxygen atom disordered over two sites. Anisotropic refinement was carried out. The  $R$ -factor based on non-hydrogen atom refinement only is 0.063 for the observed data. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 1.** Perspective views of the two isomeric cations in the asymmetric unit.

and (3), for the chelate ring on co-ordination to a metal centre.<sup>1,6c</sup> The two cations in the asymmetric unit differ in that one has the ligands co-ordinated in a  $\Lambda$  configuration with the two chelate rings in boat conformation (2) (Figure 1; cation a) whilst the other has a  $\Delta$  configuration with the two chelate rings in conformation (3) (Figure 1; cation b). Inspection of molecular models shows that of the three possible geometrical isomers, only that with the bulky bornane groups in a *trans* configuration is possible for steric crowding reasons. Furthermore, owing to the chiral nature of (1) the  $\Lambda$  and  $\Delta$  forms of this geometrical isomer are not equivalent. Since each ligand can exist in two conformations, there are thus six possible isomers which have the bornane groups in a *trans* configuration. Molecular models show that in all but the two observed isomers [*viz.*  $\Lambda$ -(2),(2) and  $\Delta$ -(3),(3)] there exist destabilising steric interactions between the co-ordinated perchlorate and hydrogen atoms in the bornane fragment.

The geometry of the chelating perchlorates is shown in Figure 2. As with other co-ordinated perchlorates<sup>3,5,9</sup> the Cl-O bond lengths are shorter to the non-co-ordinating oxygens than to the co-ordination oxygens. Although the geometry at chlorine is close to tetrahedral, co-ordination



**Figure 2.** Co-ordination core of the nickel atom of cation (a). Selected bond lengths and angles [and the corresponding values of cation (b)] are: Ni-O(11), 2.334(7) [2.332(6)]; Ni-O(12), 2.207(6) [2.199(6)]; Ni-N(12), 2.071(7) [2.051(7)]; Ni-N(14), 2.011(6) [2.009(6)]; Ni-N(32), 2.105(7) [2.099(7)]; Ni-N(34), 2.024(7) [2.017(7)]; Cl-O(11), 1.458(6) [1.445(6)]; Cl-O(12), 1.445(6) [1.472(6)]; Cl-O(13), 1.418(7) [1.426(7)]; Cl-O(14), 1.431(6) [1.439(6)] Å; O(11)-Ni-O(12), 60.9(2) [61.1(2)]; O(11)-Ni-N(34), 161.9(2) [162.2(2)]; N(12)-Ni-N(14), 88.2(3) [88.6(3)]; N(12)-Ni-N(32), 173.1(3) [169.9(3)]; N(32)-Ni-N(34), 88.8(3) [89.0(3)]; O(12)-Ni-N(14), 162.7(3) [163.4(3)]; N(14)-Ni-N(34), 96.2(3) [99.6(3)]; O(11)-Cl-O(12), 105.0(4) [104.4(4)]°.

about the nickel atom deviates strongly from idealized octahedral geometry, as exemplified by the small O-Ni-O angle [61.0(2)°]. Related Co<sup>II</sup> and Ni<sup>II</sup> complexes of dipyrazolylmethanes with a chelating perchlorate have previously been proposed<sup>10</sup> to have the co-ordination geometry found here on the basis of spectroscopic data.

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