A Low-spin Trigonal-bipyramidal Nickel(II) Complex Containing an Asymmetric Trigonal Field

By M. MATHEW and G. J. PALENIK*
(*Department of Chemistry, University of Florida, Gainesville, Florida* 32601)
and G. DYER and D. W. MEEK
(*Department of Chemistry, The Ohio State University, Columbus, Ohio* 43210)

Summary The first structural study of a low-spin trigonal-bipyramidal nickel(II) complex containing an asymmetric trigonal field is reported together with a discussion of the effect of the asymmetry on the lowest electronic transitions.

THE five-co-ordinate complexes [M(QAS)X]$^+$ClO$_4^-$ and [M(QP)X]$^+$ClO$_4^-$ (M = Pd, Pt and X = Cl, Br, I, CN)† show a pronounced shoulder on the low energy side of the lowest electronic absorption band.[1] The two closely-spaced transitions were thought to result from the distortions from C_{3v} symmetry observed in the structure of [Pt(QAS)I$^+$ClO$_4^-$.[2] In contrast, the corresponding nickel complexes displayed symmetric absorption bands, implying a less distorted structure. However, an asymmetric ligand field normal to the three-fold axis could also cause a splitting in the *e* levels and hence an asymmetric absorption spectrum. Therefore, a tetradentate ligand was synthesized which would favour the formation of trigonal-bipyramidal complexes but would create an asymmetric ligand field by having two different donor atoms in the trigonal plane. Our results represent the first structural data on a low-spin trigonal-bipyramidal nickel(II) complex of this type.

The ligand As[o-C$_6$H$_4$AsPh$_2$]$_2$[o-C$_6$H$_4$SMe] was synthesized from o-bromophenyldiphenylarsine and (o-methylthiophenyl)dichloroarsine. A series of intensely blue, five-co-ordinate [Ni(SAs$_3$)X]ClO$_4$ complexes (X = Cl, Br, I, NCS, CN) can be prepared. The electronic spectra of all the nickel(II) complexes were interpreted in terms of a low-spin trigonal-bipyramidal structure. A single crystal *X*-ray study was undertaken to confirm these results and to determine the distortions from C_{3v} symmetry present in the ion.

Crystal data: NiC$_{43}$H$_{35}$O$_4$As$_3$BrClS·C$_6$H$_5$Cl, M = 1159·2, monoclinic crystals from chlorobenzene, space group $P2_1/c$ (No. 14); a = 11·315 (12), b = 20·890 (24), c = 20·343 (10) Å, β = 107·62 (4)°, U = 4583.0 Å^3, D_m = 1·68 g cm^{-3}, Z = 4, D_c = 1·680 g cm^{-3}.

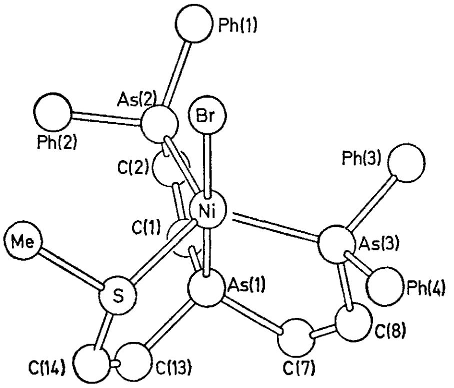

FIGURE. *A view of the* Ni^{II}[As(o-C$_6$H$_4$AsPh$_2$)$_2$(o-C$_6$H$_4$SMe)Br]† *cation indicating the molecular geometry and atomic numbering. Pertinent distances are* Ni–Br *of* 2·341(2), Ni–As(1) *of* 2·218(2), Ni–As(2) *of* 2·325(2), Ni–As(3) *of* 2·329(2), *and* Ni–S of 2·336(3) Å. *The angles in the equatorial plane are* S–Ni–As(2) *of* 115·93(10), S–Ni–As(3) *of* 114·39(10), *and* As(2)–Ni–As(3) *of* 128·56(8)°.

The intensities of 5761 (4421 non-zero) independent

---

† Abbreviations: QAS is As[o-C$_6$H$_4$AsPh$_2$]$_3$, QP is P[o-C$_6$H$_4$PPh$_2$]$_3$ TSP is P[o-C$_6$H$_4$SMe]$_3$, and SAs$_3$ is As[o-C$_6$H$_4$AsPh$_2$]$_2$[o-C$_6$H$_4$SMe].

reflections ($2\theta \leqslant 110°$ for Cu-K_α radiation) were measured with a Syntex $P\bar{1}$ diffractometer using the θ-2θ scan technique. The structure was solved by the heavy atom method and refined by least-squares methods. The R value, $R = \Sigma\|F_o| - |F_c\|/|F_o|$, was 0·100 after 2 cycles of refinement with isotropic thermal parameters and 0·063 after 6 cycles using anisotropic thermal parameters. The atomic numbering and the geometry about the Ni^{II} atom are given in the Figure.

The Ni^{II} atom is 0·142 Å out of the plane defined by the S and two As atoms and is displaced toward the Br atom. Similar effects have been reported in other trigonal bipyramidal nickel complexes involving five-membered chelate rings.[3] The Ni–As (equatorial) bonds average 2·327(2) Å compared to 2·218(2) Å for Ni–As (apical). The shortening of the apical bond is a characteristic feature of low-spin pentaco-ordinated Ni^{II} complexes whereas in high spin cases, the apical bond is frequently equal to or longer than the equatorial bond. The Ni–S distance of 2·336(2) Å is longer than the value of 2·267(7) Å in $Ni(TSP)Cl^+$ cation,[4] which suggests little or no π-interaction between the Ni and S atoms. A final point of interest is that the As and S atoms are all displaced by varying amounts from their respective benzene ring; As(1) by −0·041, As(3) by 0·006 Å, As(1) by −0·078, As(2) by +0·200 Å, As(1) by −0·034, and S by −0·138 Å. These displacements tend to produce a better fit of the tripod ligand and suggest that the assumption of planarity[3] is not valid.

The electronic spectra of the $[Ni(SAs_3)X]ClO_4$ complexes are of interest because of the two different donors in the equatorial plane; consequently, the complexes have C_s rather than approximately C_{3v} symmetry. The lowest energy band, ν_1, of the $[Ni(SAs_3)X]ClO_4$ complexes in solution or in the solid state at *ca.* 300 K are more symmetrical than anticipated for C_s symmetry. However, at 77 K the spectra of the solid halide complexes display a broadened band in the ν_1 region. In fact, the solid state spectrum of $[Ni(SAs_3I)]ClO_4$ at 77 K shows two distinct peaks at *ca.* 15,400 and *ca.* 16,800 cm^{-1}. Since pressure affects the spectrum of the solid $[Ni(SAs_3)I]ClO_4$ and $[Ni(SAs_3)Br]ClO_4$ about equally ($d\nu/dp$ ratios of 40 to 41 cm^{-1}/kbar, respectively[5]) and since the structure of the bromide complex is not distorted appreciably from a trigonal bipyramid, the two peaks in the iodide case may be attributed to the asymmetric ligand field resulting from the SAs_2 donor set in the trigonal plane. Thus, a splitting of the *e* energy level has been produced by electronic effects arising from two different types of donor atoms in the trigonal plane rather than by a static structural distortion.

We are grateful for a Department of Chemistry Postdoctoral Fellowship (to M.M.), a grant of computer time from the Computing Center (to G.J.P.), and the National Science Foundation for financial support (to G.D. and D.W.M.).

(*Received*, 17*th January* 1972; *Com.* 069.)

---

[1] G. Dyer and L. M. Venanzi, *J. Chem. Soc.*, 1965, 2771.

[2] G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 1961, 170.

[3] J. W. Dawson, B. C. Lane, R. J. Mynott, and L. M. Venanzi, *Inorg. Chim. Acta*, 1971, 5, 25, has reviewed the structura data available on tripod-like ligands.

[4] L. P. Haugen and R. Eisenberg, *Inorg. Chem.*, 1969, 8, 1072.

[5] J. R. Ferraro, D. W. Meek, E. C. Siwiec, and A. Quattrochi, *J. Amer. Chem. Soc.*, 1971, 93, 3862.