Structure of Pentakis(trimethylarsine oxide)nickel(II) Perchlorate

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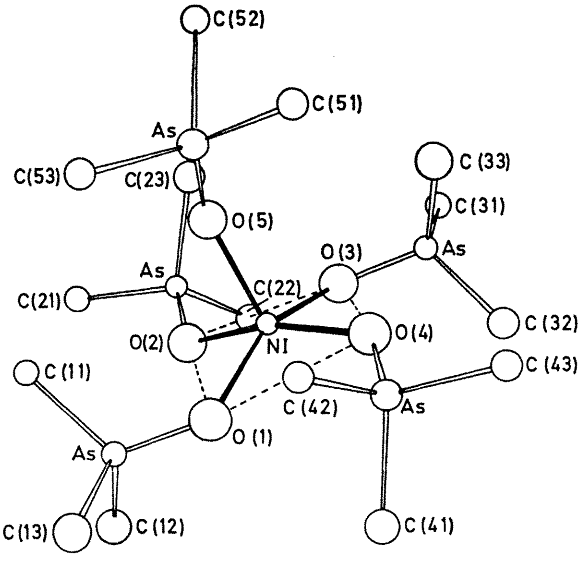
Summary The structure of pentakis(trimethylarsine oxide)-nickel(II) perchlorate has been investigated crystallographically and the co-ordination geometry shown to be approximately square pyramidal.

STRUCTURAL details of a number of high-spin five-co-ordinate complexes are now available, and it has been found that structures intermediate between trigonal bipyramidal and square pyramidal geometry are usually adopted. Steric factors are probably of prime importance and as most structures are of compounds with polydentate ligands which impose their own steric requirements, it was of interest to determine the structure of a high-spin complex with identical monodentate ligands. A series of such complexes has been prepared by Brodie *et al.*,[1] and we have determined the crystal structure of one of these. [Ni(Me$_3$AsO)$_5$](ClO$_4$)$_2$ crystallizes in the space group $P2_1/n$, with cell dimensions a = 11·208(6), b = 26·94(1), c = 11·227(3) Å, β = 90·44(3).† The density could not be accurately measured because of the extreme sensitivity of the compound to moisture, but a value of Z = 4 gave a reasonable D_c of 1·83 g./cm.^{3} The zero level and eight upper levels were collected by Weissenberg equi-inclination techniques, and 1171 reflections were estimated visually. A trial structure was obtained by symbolic addition, and this has now been refined to a conventional R-factor of 13% for the observed reflections. A diagram of the structure of the [Ni(Me$_3$AsO)$_5$]$^{2+}$ ion is shown in the Figure. Four of the oxygens closely approximate a basal square; the nickel atom is about 0·3 Å above the plane of this square.



FIGURE

The fifth AsO group, which is in the axial position of a square pyramid, behaves quite differently from the other four ligands under refinement. The temperature factors of the three methyl carbons and of the oxygen in this axial group are much larger than the corresponding values for the four basal groups. The axial group thus appears to be much less rigidly bound than the other four groups, and

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† Numbers in parentheses are estimated standard deviations of the last digit.

capable of much larger vibrations because of this. The axial oxygen is not well centred above the nickel atom; it lies at least 0·3 Å away from the axial vector of the basal plane. On the other hand, the axial arsenic atom falls practically on the axial vector, which makes the arrangement of arsenic atoms square-pyramidal also. It may be that the packing requirements of the arsenic atoms dominate this structure.

The Ni–O distances in the square pyramid range from 1·95—2·02 Å, and the axial oxygen is not at this stage of refinement significantly different from the basal four. The distances and angles in the co-ordinated AsO group appear to be normal, and the molecular structure is very similar to that of the complex $[Co(Ph_2MeAsO)_4ClO_4]^{2+}$ which has previously been investigated.[2]

The possibility that some sort of disorder is responsible for the peculiar refinement properties of the axial group has been considered and rejected. A difference map of the region around the axial group has been calculated; this shows only the five peaks of the AsO group as shown in the Figure, and no others. The peaks are more diffuse than those found in a similar plot of one of the basal AsO groups.

The perchlorate groups are both well outside the nickel co-ordination sphere. The nearest Ni–O distance to a perchlorate oxygen is greater than 6 Å. The perchlorate oxygens also have very large temperature factors, but show no evidence of disorder.

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[1] A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *Inorg. Chim. Acta*, 1968, **2**, 195.

[2] P. Pauling, G. B. Robertson, and G. A. Rodley, *Nature*, 1965, **207**, 73.