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The Structure of Tetrakis(methyldiphenylarsine oxide)nitratonickel(II) Nitrate

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Abstract. $[Ni(C_{13}H_{13}AsO)_4(NO_3)]^+.NO_3^-$, $M_r = 1223{\cdot}38$, tetragonal, $P4/n$, $a = 16{\cdot}006\,(3)$, $c = 10{\cdot}813\,(2)$ Å, $V = 2770{\cdot}2\,(6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}47$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 35{\cdot}77$ mm^{-1}, $F(000) = 1236$, $T = 290$ K, $R(F) = 0{\cdot}056$, $wR(F) = 0{\cdot}061$ for 1000 unique observed reflections with $F > 5\sigma(F)$. The cation coordination complex is square-based pyramidal in which the four arsine oxide ligands are related by the crystal tetrad on which lie the Ni and nitrate N atoms. The coordinated nitrate is rotationally disordered. The metal atom lies 0·37 (1) Å above the basal plane defined by the four arsine O donor atoms and 0·38 (1) Å out of the plane of the coordinated nitrate. The latter feature implies misdirected valency between the metal and the nitrate group, the consequences of which upon the paramagnetic susceptibilities and optical *d–d* spectrum, and on the electron spin resonance **g** tensor of the cobalt(II) analogue, define the subject matter of a recent ligand-field analysis [N. D. Fenton & M. Gerloch (1987). *Inorg. Chem.* Submitted].

Introduction. Lewis, Nyholm & Rodley (1965) described the preparation of complexes $[M(Ph_2MeAsO)_4X]^+.X^-$; $M = Ni^{II}, Co^{II}$; $X = ClO_4^-, NO_3^-$, and a preliminary crystallographic report (Pauling, Robertson & Rodley, 1965) on the perchlorate species characterized square-based pyramidal pentacoordination of the metal atoms. Isomorphism between all four systems was reported and, since the metal atoms lie on crystal tetrads in the space group $P4/n$, the coordinated perchlorate or nitrate ligands are required to be rotationally disordered in these lattices. Single-crystal paramagnetic susceptibilities have been measured in the temperature range 80–300 K for both nitrate complexes, together with crystal polarized absorption spectra at liquid hydrogen, liquid nitrogen and room temperatures (Gerloch, Kohl, Lewis & Urland, 1970). More recently, the principal electron spin resonance **g** values and their orientations have been determined for $[Co(Ph_2MeAsO)_4NO_3]^+.NO_3^-$ by Bencini, Benelli, Gatteschi & Zanchini (1979). While the susceptibility data refer to the crystal properties, the ESR experiment dramatically revealed the lack of fourfold molecular symmetry in these species within a rhombic **g** tensor that is characterized by in-plane principal values of 1·3 and 8·6. Bencini *et al.* attempted a ligand-field analysis of their data within the angular overlap model but were obliged to guess many details of the molecular geometry as atomic coordinates were not given in the original note (Pauling *et al.*, 1965) and a full report has not since been published. The crystal structure of $[Ni(Ph_2MeAsO)_4NO_3]^+.NO_3^-$ has now been determined and is reported here in full. A recent ligand-field analysis (Fenton & Gerloch, 1987) within the cellular ligand-field approach, employing the detailed molecular geometry described here, has yielded accurate and simultaneous reproduction of all susceptibility, ESR and optical spectral data on both nickel(II) and cobalt(II) nitrates for the first time.

Experimental. Red crystals of tabular habit were grown from the ethanolic reaction mixture described by Lewis *et al.* (1965). Crystal structure determination carried out on a crystal of size 0·42 × 0·35 × 0·16 mm; Syntex $P2_1$ diffractometer; unit-cell parameters from angular values of 15 centred reflections in range $45 < 2\theta < 55°$; 2148 reflections with $2\theta < 120°$ and h −11→11, k 0→16, l 0→12 (quadrant of data, some repeated); no significant intensity variation for two standard reflections; empirical absorption correction based on 340 azimuthal scan data from 9 unique reflections, transmission factors 0·635–0·763; 1012 unique reflections, 1000 with $F > 5\sigma(F)$, $R_{int} = 0{\cdot}009$; As- and Ni-atom positions from Patterson synthesis, and remaining non-H atoms from Fourier difference syntheses; blocked full-matrix refinement on F; anisotropic thermal parameters for As, Ni and O(1); the coordinated nitrate group shows fourfold disorder about the tetrad axis and the site occupancies for the O atoms in this group were fixed at 0·25 and these atoms were assigned a common isotropic temperature factor; the non coordinated nitrate group exhibits positional disorder about a twofold axis, N(2) and O(5) lie on the axis and O(6) occupies two disordered positions which were assigned occupancies of 0·3 and 0·2, all O atoms in this group were assigned a common isotropic temperature factor; within the disordered groups the N—O distances were constrained at 1·230 (1) Å and the O···O separations at 2·130 (1) Å; phenyl H atoms fixed with C—H 1·08 Å and C—C—H 120°, and allowed to ride on the relevant C-atom position; these H atoms were assigned a common isotropic temperature factor; scattering factors from *International Tables for X-ray Crystal-*

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lography (1974); 99 parameters, $R = 0·056$, $wR = 0·061$, $w = [\sigma^2(F) + 0·0006F^2]^{-1}$; mean $\Delta/\sigma = 0·012$, max. 0·03; largest peak in final difference map = 0·69 e Å^{-3}, largest hole = 0·56 e Å^{-3}; programs *SHELX*76 (Sheldrick, 1976).

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$) *for* $[Ni(Ph_2MeAsO)_4NO_3]^+.NO_3^-$

$U_{eq} = \frac{1}{3}$(trace of the U_{ij} matrix).

	x	y	z	U_{eq}
Ni	2500	2500	1684 (3)	46 (16)
O(2)	2898 (20)	2264 (21)	−150 (19)	90 (7)^a
N(1)	2500	2500	−1059 (18)	81 (6)
O(3)	2634 (27)	2185 (20)	−2077 (18)	90 (7)^a
O(4)	2017 (17)	3095 (14)	−966 (24)	90 (7)^a
O(1)	1636 (4)	1617 (4)	2024 (7)	56 (4)
As	606 (1)	1729 (1)	2121 (1)	49 (1)
C(1)	154 (7)	2356 (7)	770 (10)	64 (3)
C(2)	137 (6)	628 (7)	2112 (10)	52 (3)
C(3)	458 (9)	71 (8)	3000 (13)	86 (4)
C(4)	155 (8)	−739 (9)	3053 (12)	84 (4)
C(5)	−456 (8)	−996 (8)	2267 (12)	73 (4)
C(6)	−771 (8)	−442 (8)	1436 (13)	77 (4)
C(7)	−492 (8)	379 (8)	1353 (12)	71 (4)
C(8)	266 (6)	2230 (6)	3656 (10)	49 (5)
C(9)	863 (8)	2409 (7)	4562 (10)	64 (3)
C(10)	617 (8)	2794 (8)	5661 (12)	72 (4)
C(11)	−236 (9)	2983 (8)	5827 (13)	84 (4)
C(12)	−814 (9)	2812 (8)	4959 (13)	82 (4)
C(13)	−557 (8)	2421 (8)	3832 (12)	70 (4)
N(2)	7500	2500	1945 (19)	96 (10)
O(5)	7075 (20)	3013 (16)	1377 (19)	132 (8)^b
O(6)	7695 (36)	3137 (11)	1377 (19)	132 (8)^c
O(7)	7500	2500	3082 (19)	132 (8)

Occupancy factors: $a = 0·25$, $b = 0·30$, $c = 0·20$.

Table 2. *Bond lengths* (Å) *and interbond angles* (°) *for* $[Ni(Ph_2MeAsO)_4NO_3]^+.NO_3^-$

Ni—O(1)	2·011 (7)	C(4)—C(5)	1·359 (15)
Ni—O(2)	2·118 (23)	C(5)—C(6)	1·359 (15)
N(1)—O(2)*	1·230	C(6)—C(7)	1·390 (17)
N(2)—O(5)*	1·230	C(7)—C(2)	1·359 (15)
O(1)—As	1·661 (6)	C(8)—C(9)	1·399 (14)
As—C(1)	1·915 (11)	C(9)—C(10)	1·396 (15)
As—C(2)	1·915 (11)	C(10)—C(11)	1·410 (17)
As—C(8)	1·923 (10)	C(11)—C(12)	1·345 (18)
C(2)—C(3)	1·407 (15)	C(12)—C(13)	1·427 (16)
C(3)—C(4)	1·385 (17)	C(13)—C(8)	1·395 (15)
O(1)—Ni—O(12)	88·8 (9)	As—C(2)—C(3)	115·9 (9)
O(1)—Ni—O(13)	158·9 (8)	As—C(2)—C(7)	124·3 (9)
O(2)—Ni—O(1)	104·6 (9)	C(2)—C(3)—C(4)	119·6 (13)
O(2)—Ni—O(12)	80·6 (9)	C(3)—C(4)—C(5)	120·5 (14)
O(2)—Ni—O(13)	95·1 (8)	C(4)—C(5)—C(6)	119·0 (14)
O(2)—Ni—O(14)	120·4 (8)	C(5)—C(6)—C(7)	122·6 (13)
Ni—O(2)—N(1)	122·5 (22)	C(6)—C(7)—C(2)	118·4 (12)
O(2)—N(1)—O(3)*	120·0	C(7)—C(2)—C(3)	119·8 (12)
O(5)—N(2)—O(6)*	120·0	As—C(8)—C(9)	119·7 (8)
Ni—O(1)—As	128·2 (4)	As—C(8)—C(13)	118·6 (9)
O(1)—As—C(1)	112·5 (4)	C(8)—C(9)—C(10)	119·5 (12)
O(1)—As—C(2)	106·9 (4)	C(9)—C(10)—C(11)	118·5 (13)
O(1)—As—C(8)	112·3 (4)	C(10)—C(11)—C(12)	122·2 (14)
C(1)—As—C(2)	109·3 (5)	C(11)—C(12)—C(13)	120·5 (14)
C(1)—As—C(8)	109·4 (5)	C(12)—C(13)—C(8)	117·7 (12)
C(2)—As—C(8)	106·1 (4)	C(13)—C(8)—C(9)	121·7 (11)

* Constrained.

Discussion. Atomic coordinates given in Table 1 and bond lengths and angles in Table 2 refer to the atomic numbering scheme shown in Fig. 1.*

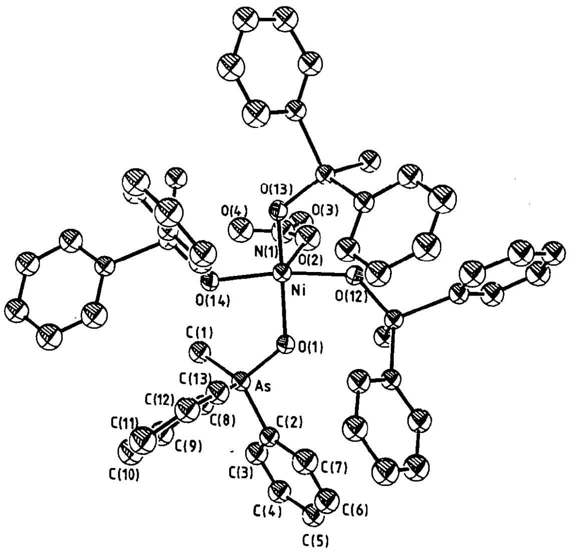

Fig. 1. The $[Ni(Ph_2MeAsO)_4NO_3]^+$ cation, showing atom labelling.

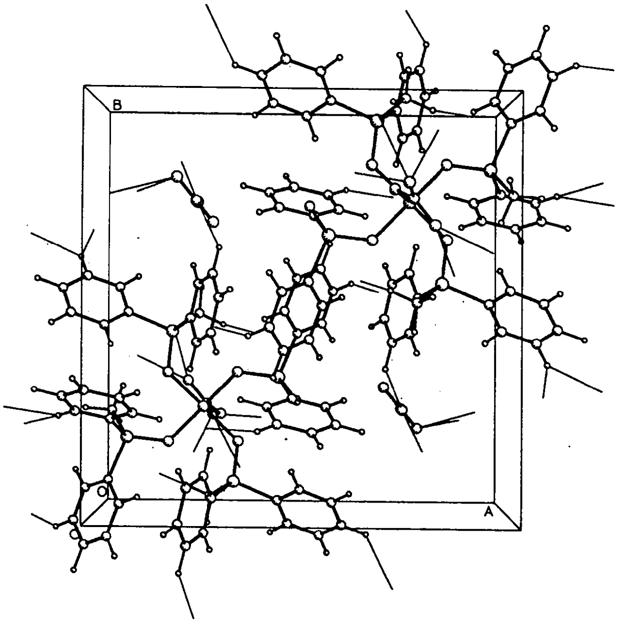

Fig. 2. Lattice packing in the crystal of $[Ni(Ph_2MeAsO)_4NO_3]^+.NO_3^-$. Hydrogen-bonding contacts are indicated by the thin lines.

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* Lists of structure factors, anisotropic thermal parameters for As, Ni and O(1) atoms, H-atom coordinates, and short O···H contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44183 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The crystal structure comprises complex cations $[Ni(Ph_2MeAsO)_4NO_3]^+$ together with nitrate anions. The metal atom is pentacoordinated by four arsine oxides, related by crystallographic fourfold rotation, and one nitrate forming a square-based pyramidal array of ligands. The plane NiO(1)As makes an angle of 11·2 (1)° to the basal plane of the four arsine oxide donor atoms. Not uncommonly, the angle Ni—O(1)—As of 128·2 (4)° is larger than the 'ideal' expected for sp^2 hybridization at the donor atom. Coordination of the As atoms closely approximates tetrahedral and the detailed geometry of the phenyl groups is normal. The Ni atom lies 0·37 (1) Å above the basal plane defined by the arsine oxide donors.

The coordinated nitrate ligand is disordered amongst four rotationally equivalent sites with the central N(1) atom lying on the crystallographic tetrad. The angle subtended at the donor O atom, *i.e.* N(1)—O(2)—Ni, is 123 (2)°, indicative of oxygen donation to the metal *via* sp^2-hybridized electron lone pairs, so maximizing π-electron delocalization throughout the nitrate group, as expected. However, the Ni atom lies some 0·38 (1) Å out of the nitrate plane so that the oxygen donor lone pair must be presumed not to be oriented exactly towards the metal atom. The misdirected nature of this oxygen–nickel valency provides the focus of a recent ligand-field analysis (Fenton & Gerloch, 1987) and contributes significantly to the very large anisotropy (1·3 and 8·6) of the ESR g tensor in the basal plane, as observed by Bencini *et al.* (1979). The tilting of the nitrate plane that causes this bent bonding presumably indicates a compromise between the primary coordination forces and those deriving from the lattice, most particularly from a network of C—H···O contacts, with H···O in the range 2·43–2·75 Å. Packing in the lattice is illustrated in Fig. 2.

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Structure du Borate d'Uranium UB_2O_6

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Abstract. $M_r = 355{\cdot}71$, monoclinic, $C2/c$, $a = 12{\cdot}504\,(3)$, $b = 4{\cdot}183\,(1)$, $c = 10{\cdot}453\,(3)$ Å, $\beta = 122{\cdot}18\,(3)°$, $V = 462{\cdot}7\,(8)$ Å^3, $Z = 4$, $D_x = 5{\cdot}10$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 33{\cdot}7$ mm^{-1}, $F(000) = 600$, $T = 290$ K; 1707 contributing reflexions, $R(F) = 0{\cdot}066$, $wR = 0{\cdot}082$. This compound has a true lamellar structure with neutral layers held together by van der Waals forces between oxygen atoms (O—O 2·91 Å). Inside the layers U^{6+} has a uranyl bond (U—O 1·75 Å) perpendicular to four other neighbours (U—O 2·38–2·49 Å) and these polyhedra are shared by opposite edges. B atoms are in BO_3 triangles (B—O 1·32–1·39 Å) which lie in chains between the UO_6 octahedra arrays.

Introduction. En 1967, Hoekstra synthétisa le borate d'uranium UB_2O_6 sous forme de poudre et en étudia les spectres Raman et infra-rouge. Quelques années plus tard, Holcombe & Johnson (1980) obtenaient des monocristaux de formule identique mais petits et toujours maclés et ils ne purent que confirmer leur symétrie monoclinique. L'obtention de grands cristaux non maclés, dont le cliché de poudre est identique à celui décrit par les auteurs précédents, nous a permis d'en établir la structure.

Partie expérimentale. Chauffage à l'air à 1423 K pendant 15 heures de U_3O_8, $SrCO_3$ et B_2O_3 avec 1U + 1Sr + 12B. Grands cristaux lamellaires transparents, en masse jaune pâle. La microsonde de Castaing ne décèle pas de strontium.

Symétrie monoclinique $C2$, Cc ou $C2/c$ mise en évidence sur films. Plaquette (001) allongée suivant $[\bar{2}01]$. Après coupure au rasoir, dimension maximale

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