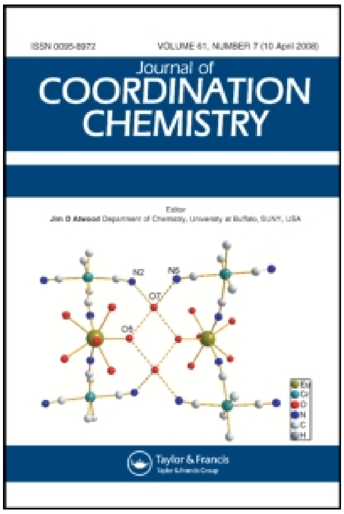

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The Structure of Dinitratobis(Triphenylarsineoxide)-Nickel(II)

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NOTE

THE STRUCTURE OF DINITRATOBIS(TRIPHENYLARSINEOXIDE)-NICKEL(II)

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$[Ni(NO_3)_2\{AsO(C_6H_5)_3\}_2]$ is monoclinic, space group $P2_1/n$, with $a = 10.128(5)$, $b = 19.026(7)$, $c = 18.054(8)$ Å, $\beta = 100.17(5)°$, $V = 3424(5)$ Å^3, $Z = 4$, $D_o = 1.61(1)$, $D_c = 1.604(5)$ g cm^{-3}. The single-crystal X-ray structure was solved and refined to $R = 0.053$ for 2413 observed reflections. The Ni ion has a distorted octahedral NiO_6 environment with the 0 atoms belonging to two bidentate nitrate groups and two triphenylarsine oxide ligands.

Keywords: Triphenylarsine oxide, nickel(II), nitrate, X-ray structure

INTRODUCTION

Studies in the literature show the great contribution of oxoligands to the development of coordination chemistry. The ligand triphenylarsine oxide is interesting because it is a large ligand that possesses the characteristics needed to promote the formation of tetrahedral nickel(II) complexes, of which few examples are known.[1,2,3] The ligand was synthesized[4] and characterized by its molar conductance and vibrational and electronic spectroscopy. The complex dinitratobis(triphenylarsine oxide)nickel(II), $[Ni(NO_3)_2\{AsO(C_6H_5)_3\}_2]$, was prepared according to the method of Goodgame and Cotton.[1] This complex shows good stability at room temperature even in contact with water. Analysis of the IR spectrum of the complex is difficult because of bands that are characteristic of monodentate nitrate and one band that could be from a bidentate nitrate.[4] The electronic spectrum is similar[5] to that of $[Ni\{PO(C_6H_5)_3\}_4]^{2+}$, and suggests a tetrahedral configuration for the metal.[4] With the aim of better interpretation of those data and also of defining the coordination environment of the Ni^{2+} ion, especially as involving nitrate, we have determined the crystal and molecular structure of the complex.

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EXPERIMENTAL

The choice of good quality single crystal (pale yellow: 0.4 × 0.3 × 0.2 mm) and the determination of space group was made by precession photography. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated MoKα radiation. The unit cell dimensions were determined from the angular settings of 25 selected reflections ($9 < \theta < 18°$). The data were corrected for Lorentz and polarization effects but not for absorption effects. The structure was solved

TABLE I
Data collection and processing parameters.

Formula	$[Ni(NO_3)_2\{AsO(C_6H_5)_3\}_2]$
MW	827.20
Space group	$P2_1/n$
a	10.128(5)
b	19.026(7)
c	18.054(8) Å
β	100.17(5)°
V	3424(5) Å^3
Z	4
D_c	1.604(5)
D_o	1.61(1) g cm^{-3}
$F(000)$	1672
μ	24.45 cm^{-1}
Radiation	0.71073 Å
θ range	1.0–23.0°
Unique reflections	4369
Reflections with $I > 3\sigma(I)$	2413
Refined parameters	442
R	0.053
R_w	0.055

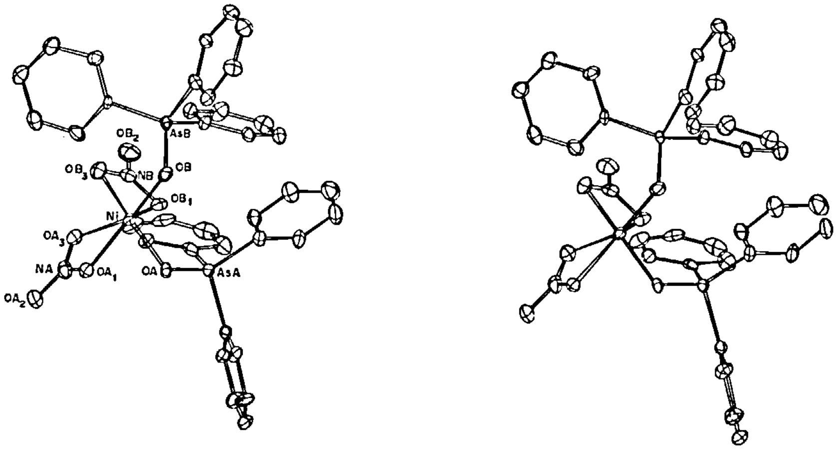

FIGURE 1 Numbering scheme and stereoview of the molecule.[14]

TABLE II

Atomic coordinates and equivalent isotropic thermal parameters[13] with e.s.d.'s in parentheses.

	x/a	y/b	z/c	B_{eq} (Å^2)
Ni	−0.0366(1)	0.2776(1)	0.2373(1)	3.01(4)
As(A)	−0.1137(1)	0.1132(1)	0.1852(1)	3.27(4)
As(B)	0.1323(1)	0.2010(1)	0.4012(1)	2.87(3)
O(A)	−0.1142(7)	0.2002(3)	0.1702(4)	3.6(2)
O(A1)	−0.0740(8)	0.3397(3)	0.1396(4)	3.8(2)
O(A2)	0.075(1)	0.3414(5)	0.0646(5)	6.1(3)
O(A3)	0.1192(7)	0.2927(4)	0.1755(4)	4.1(2)
O(B)	0.0278(7)	0.2112(3)	0.3204(3)	3.8(2)
O(B1)	−0.2022(7)	0.3168(4)	0.2817(4)	4.4(3)
O(B2)	−0.174(1)	0.4072(5)	0.3570(4)	6.3(3)
O(B3)	−0.0083(9)	0.3677(4)	0.3053(4)	4.7(3)
N(A)	0.040(1)	0.3257(5)	0.1247(6)	4.8(4)
N(B)	−0.129(1)	0.3664(5)	0.3158(5)	4.3(4)
C(A1)	−0.208(1)	0.0735(5)	0.0947(6)	3.7(4)
C(A2)	−0.147(1)	0.0256(6)	0.0503(6)	4.3(4)
C(A3)	−0.225(2)	0.0037(7)	−0.0150(7)	5.4(5)
C(A4)	−0.349(2)	0.0289(7)	−0.0404(7)	5.9(5)
C(A5)	−0.409(1)	0.0789(7)	0.0004(6)	5.4(5)
C(A6)	−0.338(1)	0.1001(5)	0.0680(6)	3.8(4)
C(A7)	−0.213(1)	0.0898(6)	0.2625(6)	3.6(4)
C(A8)	−0.232(1)	0.0185(7)	0.2767(8)	6.0(5)
C(A9)	−0.304(2)	0.0055(9)	0.3371(9)	6.9(6)
C(A10)	−0.351(2)	0.058(1)	0.3763(8)	6.9(7)
C(A11)	−0.332(2)	0.1285(8)	0.3592(8)	6.7(6)
C(A12)	−0.265(1)	0.1447(7)	0.2989(7)	5.1(5)
C(A13)	0.066(1)	0.0747(6)	0.2017(6)	3.9(4)
C(A14)	0.084(2)	0.0027(7)	0.2181(7)	5.7(5)
C(A15)	0.217(2)	−0.0220(7)	0.2277(8)	7.1(6)
C(A16)	0.322(2)	0.0213(8)	0.2241(7)	6.1(5)
C(A17)	0.301(1)	0.0909(7)	0.2063(8)	6.1(5)
C(A18)	0.167(1)	0.1184(6)	0.1939(6)	4.1(4)
C(B1)	0.046(1)	0.2220(5)	0.4859(6)	3.3(4)
C(B2)	−0.081(1)	0.2489(6)	0.4724(6)	3.9(4)
C(B3)	−0.143(1)	0.2576(7)	0.5361(7)	5.0(5)
C(B4)	−0.081(1)	0.2389(7)	0.6048(7)	5.3(5)
C(B5)	0.045(1)	0.2124(7)	0.6184(6)	5.2(5)
C(B6)	0.114(1)	0.2027(6)	0.5562(6)	4.0(4)
C(B7)	0.296(1)	0.2535(5)	0.4055(6)	2.9(3)
C(B8)	0.359(1)	0.2834(5)	0.4709(6)	4.0(4)
C(B9)	0.480(1)	0.3203(7)	0.4692(8)	5.2(5)
C(B10)	0.531(1)	0.3299(6)	0.4049(8)	5.1(5)
C(B11)	0.459(1)	0.2985(7)	0.3379(8)	5.7(5)
C(B12)	0.343(1)	0.2629(7)	0.3380(6)	5.0(5)
C(B13)	0.170(1)	0.1026(5)	0.4125(6)	2.9(3)
C(B14)	0.297(1)	0.0761(6)	0.4192(6)	4.2(4)
C(B15)	0.320(1)	0.0041(7)	0.4272(8)	6.2(5)
C(B16)	0.209(2)	−0.0392(6)	0.4287(7)	5.1(5)
C(B17)	0.079(1)	−0.0136(6)	0.4214(6)	4.3(4)
C(B18)	0.060(1)	0.0600(5)	0.4151(6)	4.4(4)

partially using MULTAN78[6] and subsequent difference Fourier maps showed all other atoms. The refinement[7] was carried out by least square methods minimizing $\Sigma\omega(|F_o| - |F_c|)^2$ with $\omega = 1/\sigma^2$ (F) and using anisotropic thermal parameters. No attempt was made to locate the H atoms. Scattering factors were from *International Tables for X-ray Crystallography*.[8] The data collection and processing parameters are given in Table I. Positional and equivalent isotropic thermal parameters are listed in Table II and selected bond distances and angles are given in Tables III and IV. The atom numbering scheme and a stereoview of the molecule are shown in Figure 1. Anisotropic thermal parameters and observed and calculated structure factor amplitudes are available as supplementary material from the authors.

TABLE III
Selected bond distances (Å) with e.s.d.'s in parentheses.

Ni-O(A)	1.979(6)	N(A)-O(A2)	1.23(2)
Ni-O(A1)	2.102(7)	N(A)-O(A3)	1.27(1)
Ni-O(A3)	2.106(8)	N(B)-O(B1)	1.29(1)
Ni-O(B)	1.981(6)	N(B)-O(B2)	1.22(1)
Ni-O(B1)	2.119(8)	N(B)-O(B3)	1.27(2)
Ni-O(B3)	2.099(7)	As(A)-O(A)	1.677(6)
N(A)-O(A1)	1.26(2)	As(B)-O(B)	1.655(6)

TABLE IV
Selected bond angles (°) with e.s.d.'s in parentheses.

O(A)-Ni-O(B3)	164.6(3)	O(B)-Ni-O(B3)	94.9(3)
O(A1)-Ni-O(B)	168.7(3)	O(B1)-Ni-O(B3)	61.7(3)
O(A3)-Ni-O(B1)	150.4(3)	O(A1)-N(A)-O(A2)	123(1)
O(A)-Ni-O(A1)	84.9(3)	O(A1)-N(A)-O(A3)	116(1)
O(A)-Ni-O(A3)	91.8(3)	O(A2)-N(A)-O(A3)	121(1)
O(A)-Ni-O(B)	91.8(3)	O(B1)-N(B)-O(B2)	121(1)
O(A)-Ni-O(B1)	103.8(3)	O(B1)-N(B)-O(B3)	115.7(9)
O(A1)-Ni-O(A3)	61.3(3)	O(B2)-N(B)-O(B3)	124(1)
O(A1)-Ni-O(B1)	94.7(3)	Ni-O(A1)-N(A)	91.4(6)
O(A1)-Ni-O(B3)	91.0(3)	Ni-O(A3)-N(A)	90.8(7)
O(A3)-Ni-O(B)	108.1(3)	Ni-O(B1)-N(B)	90.5(6)
O(A3)-Ni-O(B3)	99.2(3)	Ni-O(B3)-N(B)	92.1(6)
O(B)-Ni-O(B1)	96.6(3)		

RESULTS AND DISCUSSION

The Ni^{2+} ion is octahedrally coordinated by the oxygen atoms of the two bidentate nitrates and the two $[AsO(C_6H_5)_3]$ ligands. Distortion of the octahedron is due to the bidentate nitrates bite angles of 61.3(3) and 61.7(3)° (for nitrate A and B, respectively, Table IV). According to several authors[3,9,10,11] such a bidentate anion could be considered as occupying one coordination site of the metal, distorting toward a tetrahedral arrangement. Both nitrates can be classified as symmetrically bidentate, according to the criteria adopted by Kleywegt *et al.*,[12] with $(l_2 - l_1) = 0.01$ Å and $(A_1 - A_2) = 0.6°$ for nitrate A and 0.02 and 1.6 for B. No unusual bond distances or angles were observed in the $[AsO(C_6H_5)_3]$ ligands and nitrate groups. The crystal structure consists of four discrete molecules contained in the unit cell with no unusual intermolecular contacts.

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