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$NiBr_2$ Complexes with Triphenylarsine Oxide (Ph_3AsO). Two New Interesting Structures

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The synthesis and crystal structure of two complexes resulting from interaction between $NiBr_2$ *and triphenylarsine oxide* (Ph_3AsO) *is described. Green and orange complexes can be obtained from the blue, probably tetrahedral complex* $[NiBr_2(Ph_3AsO)_2]$*, depending on the solvents used for recrystallization.*

$NiBr_2 \cdot 4[(C_6H_5)_3AsO] \cdot 8H_2O$ *(green):* $M = 1650.2$, $P2_1/c$, $a = 13.731(2)$, $b = 16.267(3)$, $c = 17.647(2)$ Å, $\beta = 112.04(1)^\circ$, $V = 3651.4$ Å^3, $Z = 2$, $D_x = 1.501$ g cm^{-3}, CuKα, $\lambda = 1.54184$ Å, $\mu = 38.67$ cm^{-1}, $R = 0.039$, *3741 unique reflections, 3203 with* $I > 3\sigma(I)$.

$NiBr_2 \cdot 4[(C_6H_5)_3AsO] \cdot 3/2(C_6H_5CH_3) \cdot H_2O$ *(orange):* $M = 1663.7$, $P\bar{1}$, $a = 12.647(8)$, $b = 13.953(5)$, $c = 22.853(6)$ Å, $\alpha = 90.91(3)$, $\beta = 96.70(4)$, $\gamma = 111.16(4)^\circ$, $V = 3727.4$ Å^3, $Z = 2$, $D_x = 1.482$ g cm^{-3}, MoKα, $\lambda = 0.71073$ Å, $\mu = 30.48$ cm^{-1}, $R = 0.087$, *8600 unique reflections, 4293 with* $I > 3\sigma(I)$.

In the green complex the Ni(II) ion is sited on a center of symmetry and is octahedrally coordinated to six water molecules, hydrogen bonded to the Ph_3AsO *molecules and to the bromide anions forming a second coordination sphere in a nearly octahedral arrangement. In the orange complex the cation is pentacoordinated with the four oxygen atoms of the* Ph_3AsO *ligands forming the basis of a tetragonal pyramid and with one* Br^- *anion in the apical position. The absorption spectrum of the orange complex is compared with the spectra of other Ni(II) square pyramidal complexes described in the literature.*

Introduction

Nickel(II) complexes are of interest spectroscopically because of the large number of stereochemical forms in which the ion occurs. Many complexes are known in each stereochemical class [1], six-coordinate octahedral, four-coordinate tetrahedral and square planar being the most common structures. Stable Ni(II) complexes with phosphine and arsine oxides were thoroughly studied mainly by Cotton *et al.* [2–5] some years ago.

In the present paper the formation of compounds resulting from interaction between $NiBr_2$ and triphenylarsine oxide (Ph_3AsO) is described. The blue tetrahedral complex $[NiBr_2(Ph_3AsO)_2]$ was previously characterized by Cotton *et al.* [4]. These authors observed the formation of a mixture of blue, green and orange solids when a green ethanolic solution of $NiBr_2$ and Ph_3AsO in proportion of 1:2.25 was kept *in vacuo* over sulfuric acid for several days. The blue complex was isolated by dissolving the mixture of solids in hot chlorobenzene. After filtration the solution yielded blue crystals. In an attempt to prepare this blue complex for spectroscopic comparison purposes we observed that other complexes could be obtained by varying the experimental conditions. Depending on the solvents used, metal to ligand ratio, time of heating or cooling, recrystallization and drying, *etc.*, one, two or even a mixture of all three complexes could be prepared. The blue complex was easily obtained by evaporation of the ethanolic solution of an exactly 1:2 mixture ($NiBr_2$ to Ph_3AsO) on a hot plate and slow addition of chlorobenzene. On cooling to room temperature blue crystals of $[NiBr_2(Ph_3AsO)_2]$ precipitated.

Dissolution of this blue complex in hot chlorobenzene and addition of hot toluene yielded good crystals of an orange complex suitable for X-ray structure determination. An orange solid was also obtained directly by mixing hot ethanolic solutions of $NiBr_2$ and Ph_3AsO in a 1:4 metal to ligand ratio, after changing the solvent to chlorobenzene. This orange solid analysed as $NiBr_2 \cdot 4(Ph_3AsO)$ but did not give good crystals.

Dissolution of the blue complex in hot benzene gave a blue solid on cooling. After filtration, the clear

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TABLE I. Summary of Data Collection and Processing Parameters.

Molecular formula	$NiBr_2 \cdot 4(Ph_3AsO) \cdot 8H_2O$	$NiBr_2 \cdot 4(Ph_3AsO) \cdot 3/2(C_6H_5CH_3) \cdot H_2O$
Molecular weight	1650.2	1663.7
Space group	$P2_1/c$	$P\bar{1}$
Cell constants	a = 13.731(2)	12.647(8)
	b = 16.267(3)	13.953(5)
	c = 17.647(2)	22.853(6) A
	α = 90	90.91(3)
	β = 112.04(1)	96.70(4)
	γ = 90	111.16(4)°
	V = 3651.4	3727.4 A^3
Complexes per cell	2	2
Density (calcd)	1.501	1.482 g cm^{-3}
Radiation used	CuKα (λ = 1.54184 A)	MoKα (λ = 0.71073 Å)
Absorption coefficient	38.67	30.48 cm^{-1}
Collection range	$0 < \theta < 55°$	$0 < \theta < 23°$
Total data collected	3741	8600
Data with $I > 3\sigma(I)$	3203	4293
$R = \Sigma \| |F_o| - |F_c| \| / \Sigma |F_o|$	0.039	0.087

filtrate yielded good green crystals. The green complex contained water and $NiBr_2$ and Ph_3AsO in a 1:4 ratio. In solvents such as chloroform, dioxane and 1,2-dichloroethane the blue complex decomposes.

The crystal and molecular structures of the green and orange compounds were determined by X-ray diffractometric analysis and are reported in the present paper. We did not succeed in obtaining single crystals of the blue compound suitable for structure determination. The orange compound used was the one obtained with addition of hot toluene.

Experimental

Diffraction measurements were carried out on a CAD-4 Enraf-Nonius diffractometer, using crystals of irregular shapes and similar sizes with maximum and minimum linear dimensions of about 0.35 and 0.25 mm respectively. The orange complex crystal is hygroscopic and was sealed in a Lyndemann capillary for data collection. Cell dimensions and the orientation matrices were calculated by least squares from 25 centered reflections. In both crystals diffraction intensities were measured by the $\omega - 2\theta$ scan technique using a variable scan speed between 2.8–6.7° min^{-1}. The intensities of two standard reflections were essentially constant over the duration of both experiments. Data were corrected for Lorentz and polarization effects but not for absorption or extinction. A summary of data collection and processing parameters is given in Table I. The electronic spectrum was obtained for the orange compound, as nujol mull, in the region 2,000–300 nm using a Beckmann UV 5270 recording spectrophotometer.

Structure Solution and Refinement

Green compound

Density considerations indicated two molecules per unit cell. The nickel atom was accordingly placed on a center of symmetry and the rest of the structure was determined by the usual alternate difference Fourier and isotropic least squares refinement. The structure was refined anisotropically with the phenyl treated as rigid and the corresponding hydrogen atoms located on geometrical grounds. Only five of the eight water hydrogens could be located from difference synthesis. All hydrogen atoms were given a common fixed U value of 0.06 $Å^2$. Unit weights were found appropriate for the refinement procedure. The final R factor was 0.039.

Orange compound

The heavy atoms were located by direct methods from the 500 highest E values in the range $1.41 \leqslant E \leqslant 2.58$. All other non-hydrogen atoms were determined from alternate cycles of difference Fourier synthesis and isotropic least squares. In the unit cell three solvent molecules (one of which is disordered) and two water molecules were found. Due to the rather large size of the structure and the relative low number of observations per parameter (less than 5 for an anisotropic model), only the heavy atoms and the arsine oxygens were refined anisotropically.

TABLE II. Final Atomic Coordinates and Equivalent Isotropic Temperature Factors Calculated as Described by Hamilton [10] for All non-H Atoms (with estimated standard deviations in parentheses) for the Green Complex.

Atom	x/a	y/b	z/c	B_{iso}
Br	0.1271(1)	−0.0196(1)	0.2601(1)	5.98(3)
Ni	0	0	0	2.56(4)
O(W1)	−0.1362(3)	0.0216(3)	0.0193(2)	3.1(1)
O(W2)	0.0332(3)	−0.1004(2)	0.0787(2)	3.2(1)
O(W3)	0.0780(3)	0.0834(2)	0.0931(2)	2.9(1)
O(W4)	0.3462(5)	0.0176(5)	0.2276(4)	10.5(3)
As(1)	0.3468(1)	0.1648(0)	0.0573(0)	2.92(2)
O(1)	0.2666(3)	0.0974(3)	0.0752(3)	3.5(1)
C(111)	0.4760(3)	0.1161(3)	0.0662(3)	3.0(2)
C(112)	0.5372(3)	0.0807(3)	0.1409(3)	3.8(2)
C(113)	0.6347(3)	0.0466(3)	0.1518(3)	4.3(3)
C(114)	0.6712(3)	0.0479(3)	0.0879(3)	4.4(2)
C(115)	0.6100(3)	0.0833(3)	0.0131(3)	4.5(3)
C(116)	0.5125(3)	0.1174(3)	0.0022(3)	3.9(2)
C(121)	0.3871(4)	0.2492(3)	0.1372(3)	3.9(2)
C(122)	0.4812(4)	0.2913(3)	0.1530(3)	5.3(3)
C(123)	0.5123(4)	0.3528(3)	0.2124(3)	6.6(3)
C(124)	0.4492(4)	0.3723(3)	0.2561(3)	6.8(3)
C(125)	0.3551(4)	0.3302(3)	0.2403(3)	7.1(4)
C(126)	0.3240(4)	0.2687(3)	0.1809(3)	5.2(3)
C(131)	0.2797(3)	0.2127(3)	−0.0474(2)	3.5(2)
C(132)	0.1835(3)	0.1807(3)	−0.0993(2)	4.4(3)
C(133)	0.1288(3)	0.2182(3)	−0.1744(2)	5.8(3)
C(134)	0.1703(3)	0.2878(3)	−0.1976(2)	6.4(3)
C(135)	0.2665(3)	0.3198(3)	−0.1457(2)	6.3(3)
C(136)	0.3212(3)	0.2823(3)	−0.0706(2)	4.8(3)
As(2)	−0.1605(1)	0.2596(0)	0.0331(0)	2.90(2)
O(2)	−0.1677(3)	0.1789(3)	−0.0257(3)	3.7(1)
C(211)	−0.0364(3)	0.3207(3)	0.0494(3)	3.3(2)
C(212)	0.0143(3)	0.3123(3)	−0.0055(3)	4.7(3)
C(213)	0.0999(3)	0.3624(3)	0.0019(3)	6.0(3)
C(214)	0.1347(3)	0.4209(3)	0.0641(3)	6.8(3)
C(215)	0.0840(3)	0.4293(3)	0.1190(3)	7.0(3)
C(216)	−0.0015(3)	0.3792(3)	0.1116(3)	4.9(3)
C(221)	−0.2777(3)	0.3296(3)	−0.0195(3)	3.4(2)
C(222)	−0.2844(3)	0.4085(3)	0.0093(3)	5.0(3)
C(223)	−0.3716(3)	0.4577(3)	−0.0317(3)	6.7(3)
C(224)	−0.4520(3)	0.4281(3)	−0.1015(3)	6.4(3)
C(225)	−0.4452(3)	0.3492(3)	−0.1303(3)	5.9(3)
C(226)	−0.3580(3)	0.3000(3)	−0.0893(3)	4.3(2)
C(231)	−0.1612(3)	0.2284(3)	0.1372(2)	3.1(2)
C(232)	−0.2251(3)	0.2668(3)	0.1722(2)	4.5(3)
C(233)	−0.2242(3)	0.2399(3)	0.2475(2)	5.6(3)
C(234)	−0.1594(3)	0.1747(3)	0.2878(2)	5.5(3)
C(235)	−0.0955(3)	0.1364(3)	0.2528(2)	5.0(3)
C(236)	−0.0964(3)	0.1632(3)	0.1775(2)	4.0(2)

No hydrogen atoms were included in the model. Unit weights were also found appropriate in this case. The final R factor was 0.087.

In both crystals the refinement was made by minimization of the function $\Sigma(|F_o| - |F_c|)^2$ through iterative-blocked full-matrix least-squares and conducted until all parameter shifts were less than 10% of the corresponding standard deviation.

Bonded H-atom scattering factors [6] and complex neutral scattering factors [7–8] for the remaining atoms were employed. Most of the calculations were performed on a VAX computer with the SHELX76 system of programs [9]. The final positional parameters and equivalent isotropic temperature factors, calculated as described by Hamilton [10] for all non-hydrogen atoms, are given in Tables

TABLE III. Final Atomic Coordinates and Isotropic Temperature Factors (* = equivalent isotropic as described by Hamilton [10]) with Estimated Standard Deviations in Parentheses for All non-H Atoms in the Orange Complex.

Atom	x/a	y/b	z/c	B_{iso}
Br(1)	−0.2038(3)	0.1864(3)	0.6248(1)	3.7(1)*
Br(2)	0.4525(5)	0.3234(3)	0.0619(2)	7.7(2)*
Ni	−0.0531(3)	0.2447(3)	0.7129(2)	2.2(1)*
As(1)	0.1969(3)	0.2998(2)	0.6529(1)	2.75(9)*
O(1)	0.081(1)	0.225(1)	0.6822(8)	2.6(3)*
C(111)	0.292(1)	0.418(1)	0.7032(7)	3.0(5)
C(112)	0.353(1)	0.512(1)	0.6807(7)	3.6(5)
C(113)	0.425(1)	0.594(1)	0.7188(7)	5.5(6)
C(114)	0.437(1)	0.583(1)	0.7795(7)	5.3(6)
C(115)	0.377(1)	0.490(1)	0.8021(7)	4.7(6)
C(116)	0.305(1)	0.407(1)	0.7639(7)	4.3(5)
C(121)	0.158(1)	0.344(1)	0.5768(7)	3.0(5)
C(122)	0.239(1)	0.374(1)	0.5376(7)	5.2(6)
C(123)	0.212(1)	0.408(1)	0.4828(7)	6.7(6)
C(124)	0.103(1)	0.412(1)	0.4671(7)	5.5(6)
C(125)	0.022(1)	0.382(1)	0.5063(7)	6.1(6)
C(126)	0.049(1)	0.348(1)	0.5611(7)	3.2(5)
C(131)	0.290(2)	0.221(1)	0.6400(8)	3.5(5)
C(132)	0.244(2)	0.134(1)	0.6010(8)	5.2(6)
C(133)	0.310(2)	0.075(1)	0.5915(8)	8.4(7)
C(134)	0.420(2)	0.103(1)	0.6209(8)	7.7(7)
C(135)	0.466(2)	0.190(1)	0.6598(8)	6.4(6)
C(136)	0.401(2)	0.249(1)	0.6693(8)	4.3(5)
As(2)	−0.2075(3)	0.2127(2)	0.8248(1)	2.72(9)*
O(2)	−0.148(1)	0.276(1)	0.7666(8)	2.8(4)*
C(211)	−0.325(1)	0.080(1)	0.8054(7)	3.8(5)
C(212)	−0.354(1)	0.039(1)	0.7470(7)	3.5(5)
C(213)	−0.437(1)	−0.059(1)	0.7333(7)	4.2(5)
C(214)	−0.492(1)	−0.116(1)	0.7779(7)	5.4(6)
C(215)	−0.462(1)	−0.075(1)	0.8363(7)	5.4(6)
C(216)	−0.379(1)	0.022(1)	0.8500(7)	5.3(6)
C(221)	−0.093(1)	0.202(1)	0.8867(7)	3.1(5)
C(222)	−0.093(1)	0.108(1)	0.9057(7)	5.0(6)
C(223)	−0.005(1)	0.104(1)	0.9473(7)	7.0(6)
C(224)	0.084(1)	0.195(1)	0.9698(7)	6.3(6)
C(225)	0.084(1)	0.290(1)	0.9507(7)	5.4(6)
C(226)	−0.005(1)	0.293(1)	0.9092(7)	4.2(5)
C(231)	−0.283(1)	0.294(1)	0.8563(8)	3.9(5)
C(232)	−0.296(1)	0.299(1)	0.9160(8)	3.8(5)
C(233)	−0.348(1)	0.363(1)	0.9366(8)	5.7(6)
C(234)	−0.388(1)	0.422(1)	0.8976(8)	6.5(6)
C(235)	−0.376(1)	0.417(1)	0.8379(8)	5.9(6)
C(236)	−0.323(1)	0.353(1)	0.8172(8)	3.3(5)
As(3)	0.0072(3)	0.5028(2)	0.7314(1)	2.72(9)*
O(3)	0.018(2)	0.397(1)	0.7026(8)	3.0(3)*
C(311)	0.119(1)	0.619(1)	0.6993(7)	2.8(5)
C(312)	0.145(1)	0.603(1)	0.6431(7)	3.7(5)
C(313)	0.222(1)	0.684(1)	0.6169(7)	6.1(6)
C(314)	0.273(1)	0.781(1)	0.6470(7)	6.1(6)
C(315)	0.247(1)	0.796(1)	0.7032(7)	4.7(6)
C(316)	0.170(1)	0.715(1)	0.7293(7)	4.8(6)
C(321)	−0.140(1)	0.511(1)	0.7044(7)	3.1(5)
C(322)	−0.162(1)	0.598(1)	0.7213(7)	4.3(5)
C(323)	−0.267(1)	0.606(1)	0.7010(7)	6.0(6)
C(324)	−0.349(1)	0.527(1)	0.6638(7)	4.8(6)
C(325)	−0.327(1)	0.441(1)	0.6469(7)	4.8(6)

(continued on facing page)

TABLE III. *(continued)*

Atom	x/a	y/b	z/c	B_{iso}
C(326)	−0.222(1)	0.433(1)	0.6672(7)	3.7(5)
C(331)	0.040(2)	0.532(1)	0.8163(7)	3.5(5)
C(332)	−0.044(2)	0.533(1)	0.8500(7)	3.7(5)
C(333)	−0.017(2)	0.557(1)	0.9107(7)	4.8(6)
C(334)	0.095(2)	0.580(1)	0.9377(7)	6.2(6)
C(335)	0.179(2)	0.578(1)	0.9041(7)	7.0(6)
C(336)	0.152(2)	0.554(1)	0.8434(7)	5.9(6)
As(4)	−0.0004(3)	0.0349(2)	0.7494(1)	2.49(9)*
O(4)	−0.077(2)	0.111(1)	0.7514(7)	2.3(3)*
C(411)	−0.018(1)	−0.035(1)	0.6735(7)	2.4(5)
C(412)	0.008(1)	−0.124(1)	0.6687(7)	4.8(6)
C(413)	−0.005(1)	−0.173(1)	0.6134(7)	6.4(6)
C(414)	−0.042(1)	−0.134(1)	0.5629(7)	5.7(6)
C(415)	−0.068(1)	−0.045(1)	0.5676(7)	5.7(6)
C(416)	−0.056(1)	0.004(1)	0.6229(7)	3.6(5)
C(421)	−0.065(1)	−0.078(1)	0.7990(7)	3.0(5)
C(422)	0.006(1)	−0.117(1)	0.8342(7)	4.4(5)
C(423)	−0.041(1)	−0.198(1)	0.8697(7)	5.4(6)
C(424)	−0.159(1)	−0.240(1)	0.8700(7)	5.0(6)
C(425)	−0.230(1)	−0.201(1)	0.8348(7)	4.9(6)
C(426)	−0.183(1)	−0.120(1)	0.7993(7)	4.0(5)
C(431)	0.156(1)	0.097(1)	0.7831(7)	2.7(5)
C(432)	0.183(1)	0.163(1)	0.8337(7)	3.7(5)
C(433)	0.293(1)	0.199(1)	0.8643(7)	4.8(6)
C(434)	0.377(1)	0.169(1)	0.8444(7)	5.4(6)
C(435)	0.351(1)	0.103(1)	0.7939(7)	5.5(6)
C(436)	0.241(1)	0.067(1)	0.7632(7)	3.7(5)
C(T11)	0.511(2)	0.407(2)	0.481(1)	3.1(5)
C(T12)	0.494(3)	0.292(2)	0.464(1)	10.1(7)
C(T13)	0.396(3)	0.232(2)	0.427(1)	15.7(8)
C(T14)	0.374(3)	0.127(2)	0.416(1)	12.1(7)
C(T15)	0.449(3)	0.083(2)	0.443(1)	12.2(7)
C(T16)	0.546(3)	0.144(2)	0.481(1)	13.2(8)
C(T17)	0.568(3)	0.248(2)	0.491(1)	11.4(7)
C(T21)	0.712(5)	0.098(4)	0.044(3)	4.4(7)
C(T22)	0.627(3)	0.119(3)	0.032(2)	7.5(8)
C(T23)	0.513(3)	0.102(3)	0.010(2)	7.6(8)
C(T24)	0.440(3)	0.004(3)	−0.012(2)	11.0(8)
C(T25)	0.480(3)	−0.077(3)	−0.012(2)	11.6(8)
C(T26)	0.593(3)	−0.060(3)	0.009(2)	6.6(8)
C(T27)	0.667(3)	0.038(3)	0.031(2)	6.5(8)
O(W)	0.357(2)	0.444(2)	0.956(1)	7.2(5)

TABLE IV. Interatomic Distances (A) with Estimated Standard Deviations in Parentheses for the Green Complex.

Ni–O(W1)	2.053(4)	As(2)–C(221)	1.904(4)
Ni–O(W2)	2.080(4)	As(2)–C(231)	1.909(4)
Ni–O(W3)	2.089(4)	O(W1)–H(W1)	0.94(4)
Ni···Br	4.267(1)	O(W3)–H(W3)	0.94(6)
Ni···O(1)	3.745(5)	O(W3)–H′(W3)	0.94(4)
Ni···O(2)	3.631(5)	O(W4)–H(W4)	0.98(4)
As(1)–O(1)	1.666(5)	O(W4)–H′(W4)	0.97(6)
As(1)–C(111)	1.895(4)	Br···H′(W3)	2.29(4)
As(1)–C(121)	1.895(4)	Br···H′(W4)	2.41(5)
As(1)–C(131)	1.895(4)	O(1)···H(W1)	1.83(5)
As(2)–O(2)	1.652(4)	O(1)···H(W3)	1.89(5)
As(2)–C(211)	1.899(4)	O(1)···H(W4)	1.84(4)

TABLE V. Bond Angles (°) with Estimated Standard Deviations in Parentheses for the Green Complex.

O(W1)–Ni–O(W2)	90.5(2)	O(2)–As(2)–C(231)	111.9(2)
O(W1)–Ni–O(W3)	89.3(2)	C(211)–As(2)–C(221)	107.9(2)
O(W2)–Ni–O(W3)	93.7(1)	C(211)–As(2)–C(231)	108.8(2)
Br···Ni···O(1)	72.51(7)	C(221)–As(2)–C(231)	108.6(2)
Br···Ni···O(2)	79.72(7)	As(2)–C(211)–C(212)	119.8(3)
O(1)···Ni···O(2)	78.7(1)	As(2)–C(211)–C(216)	120.0(4)
O(1)–As(1)–C(111)	112.0(2)	As(2)–C(221)–C(222)	122.1(3)
O(1)–As(1)–C(121)	111.4(2)	As(2)–C(221)–C(226)	117.9(3)
O(1)–As(1)–C(131)	109.9(2)	As(2)–C(231)–C(232)	122.5(3)
C(111)–As(1)–C(121)	103.8(2)	As(2)–C(231)–C(236)	117.4(4)
C(111)–As(1)–C(131)	110.5(2)	Ni–O(W1)–H(W1)	106(3)
C(121)–As(1)–C(131)	109.1(2)	Ni–O(W3)–H(W3)	107(3)
As(1)–C(111)–C(112)	117.7(3)	Ni–O(W3)–H'(W3)	107(3)
As(1)–C(111)–C(116)	122.4(3)	H(W3)–O(W3)–H'(W3)	122(5)
As(1)–C(121)–C(122)	119.6(4)	H(W4)–O(W4)–H'(W4)	116(5)
As(1)–C(121)–C(126)	120.5(3)	O(W1)–H(W1)···O(1)	162(4)
As(1)–C(131)–C(132)	118.7(3)	O(W3)–H(W3)···O(1)	148(5)
As(1)–C(131)–C(136)	121.1(3)	O(W3)–H'(W3)···Br	175(4)
O(2)–As(2)–C(211)	110.4(2)	O(W4)–H(W4)···O(1)	174(4)
O(2)–As(2)–C(221)	109.1(2)	O(W4)–H'(W4)···Br	157(4)

TABLE VI. Bond Distances (A) with Estimated Standard Deviations in Parentheses for the Orange Complex.

Ni–Br(1)	2.506(5)	As(2)–C(231)	1.91(2)
Ni–O(1)	2.01(2)	As(3)–O(3)	1.66(2)
Ni–O(2)	1.96(2)	As(3)–C(311)	1.95(2)
Ni–O(3)	2.02(2)	As(3)–C(321)	1.94(1)
Ni–O(4)	2.01(2)	As(3)–C(331)	1.94(2)
As(1)–O(1)	1.68(2)	As(4)–O(4)	1.68(2)
As(1)–C(111)	1.92(1)	As(4)–C(411)	1.93(2)
As(1)–C(121)	1.92(2)	As(4)–C(421)	1.94(1)
As(1)–C(131)	1.92(2)	As(4)–C(431)	1.91(1)
As(2)–O(2)	1.70(2)	C(T11)–C(T12)	1.58(4)
As(2)–C(211)	1.92(2)	C(T21)–C(T22)	1.22(8)
As(2)–C(221)	1.95(2)	O(W)···Br(2)	3.33(6)
		O(W)···Br(2)	3.34(6)

II (green) and Table III (orange). Interatomic bond distances and angles are given in Tables IV and V for the green complex and Tables VI and VII for the orange one.

Results and Discussion

Following the experimental procedures mentioned in the introduction, it is possible to obtain three complexes with different structures from the reaction between $NiBr_2$ and Ph_3AsO. We believe these complexes to correspond to the three described as a mixture by Cotton *et al.* [4].

In the green complex $NiBr_2 \cdot 4(Ph_3AsO) \cdot 8H_2O$ the metal ion, sited on a center of symmetry, is bound to six water oxygen atoms (only three of

TABLE VII. Bond Angles (°) with Estimated Standard Deviations in Parentheses for the Orange Complex.

O(1)–Ni–Br(1)	102.2(6)	C(232)–C(231)–As(2)	123.0(5)
O(2)–Ni–Br(1)	96.7(6)	C(236)–C(231)–As(2)	117.1(5)
O(3)–Ni–Br(1)	101.6(5)	C(311)–As(3)–O(3)	106.6(8)
O(3)–Ni–O(1)	89.5(7)	C(321)–As(3)–O(3)	111.1(8)
O(3)–Ni–O(2)	88.0(7)	C(321)–As(3)–C(311)	105.4(7)
O(4)–Ni–Br(1)	101.1(5)	C(331)–As(3)–O(3)	119.1(8)
O(4)–Ni–O(1)	86.1(7)	C(331)–As(3)–C(311)	104.7(7)

(continued on facing page)

TABLE VII. *(continued)*

O(4)–Ni–O(2)	89.1(7)	C(331)–As(3)–C(321)	108.9(7)
C(111)–As(1)–O(1)	113.5(8)	As(3)–O(3)–Ni	135.6(9)
C(121)–As(1)–O(1)	112.5(8)	C(312)–C(311)–As(3)	117.1(5)
C(121)–As(1)–C(111)	109.1(7)	C(316)–C(311)–As(3)	122.7(5)
C(131)–As(1)–O(1)	108.9(8)	C(322)–C(321)–As(3)	119.2(5)
C(131)–As(1)–C(111)	106.6(7)	C(326)–C(321)–As(3)	120.7(5)
C(131)–As(1)–C(121)	105.8(8)	C(332)–C(331)–As(3)	121.6(5)
As(1)–O(1)–Ni	136.0(8)	C(336)–C(331)–As(3)	118.5(5)
C(112)–C(111)–As(1)	122.2(5)	C(411)–As(4)–O(4)	114.1(8)
C(116)–C(111)–As(1)	118.1(5)	C(421)–As(4)–O(4)	107.0(8)
C(122)–C(121)–As(1)	119.9(5)	C(421)–As(4)–C(411)	102.7(7)
C(126)–C(121)–As(1)	120.2(5)	C(431)–As(4)–O(4)	115.0(8)
C(132)–C(131)–As(1)	118.6(6)	C(431)–As(4)–C(411)	112.4(7)
C(136)–C(131)–As(1)	121.2(6)	C(431)–As(4)–C(421)	104.2(7)
C(211)–As(2)–O(2)	115.6(8)	As(4)–O(4)–Ni	128.3(9)
C(221)–As(2)–O(2)	112.4(8)	C(412)–C(411)–As(4)	120.6(5)
C(221)–As(2)–C(211)	109.6(7)	C(416)–C(411)–As(4)	119.6(5)
C(231)–As(2)–O(2)	105.6(8)	C(422)–C421)–As(4)	120.4(5)
C(231)–As(2)–C(211)	104.7(7)	C(426)–C(421)–As(4)	119.6(5)
C(231)–As(2)–C(221)	108.3(7)	C(432)–C(431)–As(4)	118.6(5)
As(2)–O(2)–Ni	130.9(9)	C(436)–C(431)–As(4)	121.4(5)
C(212)–C(211)–As(2)	120.3(5)	C(T13)–C(T12)–C(T11)	118(2)
C(216)–C(211)–As(2)	120.0(5)	C(T17)–C(T12)–C(T11)	120(2)
C(222)–C(221)–As(2)	122.4(5)	C(T23)–C(T22)–C(T21)	157(3)
C(226)–C(221)–As(2)	117.3(5)	C(T27)–C(T22)–C(T21)	37(3)

which are crystallographically-independent) in a distorted octahedral configuration. The oxygen atoms of four Ph_3AsO molecules and two bromide anions are bonded to the ligating water molecules forming a second coordination sphere through a net of strong hydrogen bonds. A fourth crystallographically-independent water molecule forms a bifurcated hydrogen bond to a bromine atom and the oxygen atom of an As–O group. Distances and angles between atoms involved in hydrogen bonds are given in Table VIII. The general pattern can be seen in the stereoscopic projection [11] of Fig. 1.

TABLE VIII. Distances (A) and Angles (°) Involved in Hydrogen Bonds.

	Distance		Distance		Angle
A	A–B	B	B–C	C	A–B–C
O(1)	2.711(8)	O(W1)	2.665(8)	O(2)	120.5(3)
Br	3.241(5)	O(W2)	2.665(8)	O(2)	118.1(3)
Br	3.227(6)	O(W3)	2.702(9)	O(1)	105.9(2)
Br	3.297(9)	O(W4)	2.784(10)	O(1)	102.2(2)

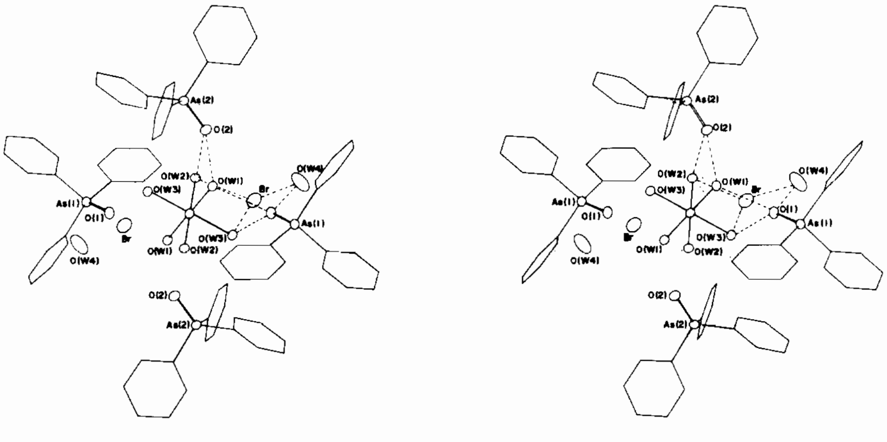

Fig. 1. A stereoview of the Ni(II) green complex showing the hydrogen bonds (dashed lines).

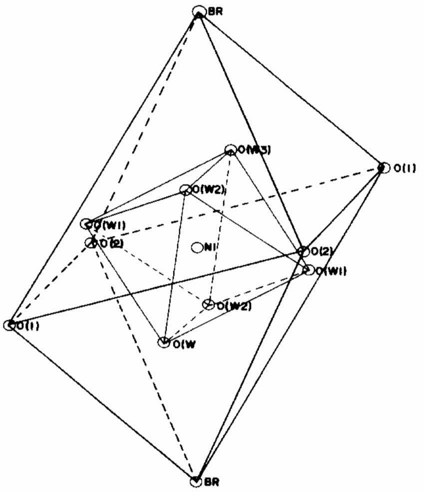

Fig. 2. A view of the two coordination spheres of the Ni atom in the green complex.

This green complex is better formulated as $Ni(H_2O)_6Br_2 \cdot 4(Ph_3AsO) \cdot 2H_2O$. The water molecules can originate from solvents (particularly ethanol) from the hydrated $NiBr_2$, or even from the hydrated Ph_3AsO. This is an important complex in that it has a well defined second coordination sphere formed predominantly by four Ph_3AsO molecules in a nearly square planar arrangement, with the Ni(II) ion at the center, in the same plane. The two Br^- anions complete the second octahedral structure (Fig. 2). Relevant interatomic distances of this second coordination sphere are given in Table IV.

In the orange compound $NiBr_2 \cdot 4(Ph_3AsO) \cdot 3/2(C_6H_5CH_3) \cdot H_2O$ the nickel(II) ion is coordinated by the oxygen atoms of four crystallographically-independent Ph_3AsO molecules and by a bromide ion in a distorted truncated tetragonal pyramid configuration. The oxygen atoms form the square base which is planar (within experimental accuracy). The nickel(II) ion is off this plane by 0.361(4) Å in the direction of the bromine atom. The mean Ni–O distance is 2.00(3) Å and the Ni–Br is 2.506(2) Å. The other independent bromine atom is not coordinated to the nickel(II) ion but is hydrogen-bonded to two crystallographically-related water molecules. A stereoscopic projection of the complex is shown in Fig. 3.

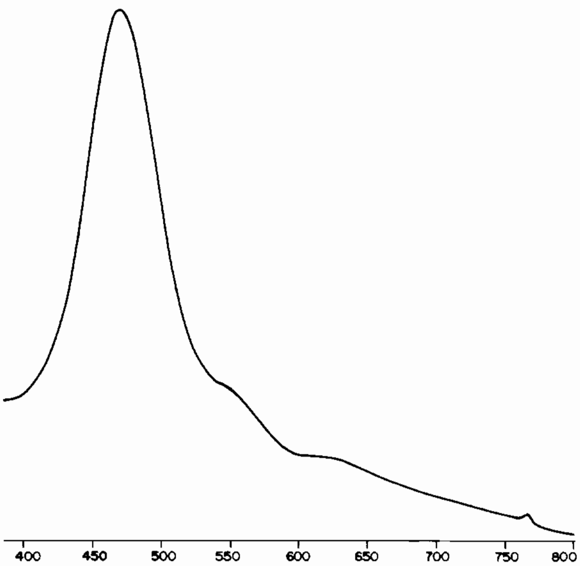

Fig. 4. Electronic spectrum of the orange Ni(II) complex (solid sample, nujol mull).

The orange complex is better formulated as $[NiBr(Ph_3AsO)_4]Br \cdot 3/2(C_6H_5CH_3) \cdot H_2O$. The crystal contains toluene and water molecules but they do not take part in the coordination sphere. One of the solvent molecules is approximately sited on a center of symmetry. Since this molecule lacks inversion symmetry, it is necessarily disordered. Its presence gives rise to the 3/2 ratio between solvent and complex.

A few examples of five-coordinate square pyramidal nickel(II) complexes are known (see ref. 1 and refs. cited therein). Gerloch *et al.* [12] have

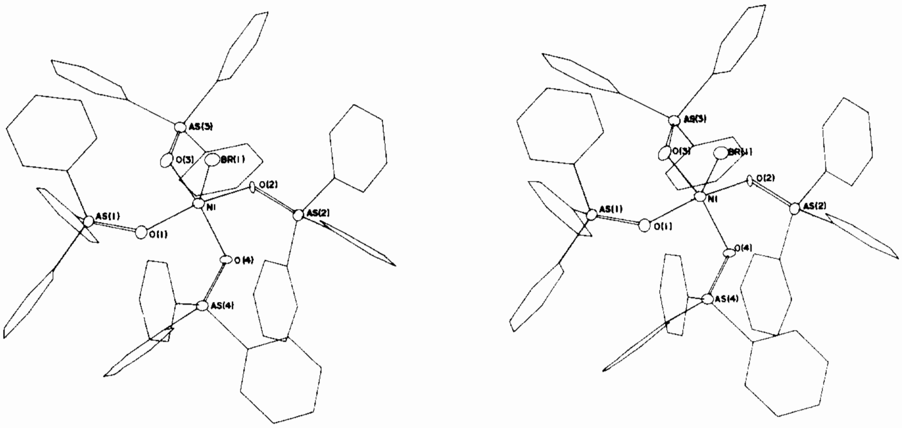

Fig. 3. A stereoview of the orange Ni(II) complex.

reported a very thorough analysis of the polarised spectra of the high spin square pyramidal $[Ni(Ph_2MeAsO)_4(NO_3)]^+$ ion. Low spin nickel(II) complexes of the type $[Ni(diarsine)_2X]^{n+}$ (X = Cl, Br, I, NCS, thiourea and As) were also described [13].

The electronic spectrum of the solid orange complex (Fig. 4) seems to be consistent with a square pyramidal structure. There are three well-defined peaks at 470, 550 and 625 nm. These peaks are displaced to high energy regions in relation to the ones found for the $[Ni(Ph_2MeAsO)_4(NO_3)]^+$ ion [12]. This comparison should be interpreted with care, since the Ph_2MeAsO complex is high spin and the Ph_3AsO complex is low spin. Furthermore, the NO_3 group was substituted by a Br atom.

It is interesting that square pyramidal structures were previously described in the literature for some metal–arsine oxide complexes, but the ligands contained one ethyl or one methyl and two phenyls bonded to the As atom [14, 15]. The orange complex described in the present paper contains Ph_3AsO and it is certainly the only well-defined square pyramidal metal–(Ph_3AsO) complex. It is also important to mention that Ph_3AsO and Ph_3PO are among the most extensively used oxygen ligands during the last twenty five years.

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References

1 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam (1968), 2nd Edition, 1984.
2 F. A. Cotton and E. Bannister, *J. Am. Chem. Soc., 82,* 1873 (1960).
3 F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc., 82,* 5771 (1960).
4 D. M. L. Goodgame and F. A. Cotton, *J. Am. Chem. Soc., 82,* 5774 (1960).
5 D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc., 82,* 4161 (1961).
6 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42,* 3175 (1965).
7 D. T. Cromer and D. Liberman, *J. Chem. Phys., 53,* 1891 (1970).
8 D. T. Cromer and J. B. Mann, *Acta Cryst., A24,* 321 (1968).
9 G. M. Sheldrick, SHELX76 program for Crystal Sructure Determination, University of Cambridge (1976).
10 W. C. Hamilton, *Acta Cryst., 12,* 609 (1959).
11 C. K. Johnson, ORTEP, Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1965).
12 M. Gerloch, J. Kohl, J. Lewis and W. Urland, *J. Chem. Soc. (A),* 3269 (1970).
13 H. B. Gray and J. R. Preer, *J. Am. Chem. Soc., 92,* 7306 (1970).
14 J. Lewis, R. S. Nyholm and G. A. Rodley, *Nature, 207,* 72 (1965).
15 P. Pauling, G. B. Robertson and G. A. Rodley, *Nature, 207,* 73 (1965).

Note added in proof: the following material is deposited with the editor: atomic coordinates of the H-atoms for the green complex; anisotropic thermal parameters for the green and orange complexes; structure factors tables for the green and orange complexes.