

Synthesis, Stereochemistry and Electronic Spectroscopy of Nickel (II) Complexes with Triphenylarsine Oxide

L. F. C. de Oliveira* and A. C. Massabni

Departamento de Química Geral e Inorgânica, Instituto de Química, UNESP, Caixa Postal 174, 14800 Araraquara, SP, Brasil

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Dados espectroscópicos de dez complexos da interação entre Níquel (II) e óxido de trifenilarsina (O_3AsO) são descritos. Os resultados são discutidos visando a determinação da geometria dos complexos.

A preparação dos complexos $[\text{NiBr}_2(\text{Ph}_3\text{AsO})_2]$, $[\text{NiCl}_2(\text{Ph}_3\text{AsO})_2]$, $[\text{Ni}(\text{NO}_3)_2(\text{Ph}_3\text{AsO})_2]$, $\text{NiI}_2 \cdot 4(\text{Ph}_3\text{AsO})$ e $[\text{Ni}(\text{ClO}_4)(\text{Ph}_3\text{AsO})_4]\text{ClO}_4$ já foi descrita na literatura. Os complexos $[\text{NiBr}(\text{Ph}_3\text{AsO})_4]\text{Br}$ e $[\text{Ni}(\text{H}_2\text{O})_6]\text{Br}_2 \cdot 4(\text{Ph}_3\text{AsO}) \cdot 2\text{H}_2\text{O}$ também foram preparados em nossos laboratórios e a preparação dos complexos $[\text{NiI}_2(\text{Ph}_3\text{AsO})_2]$ e $[\text{Ni}(\text{NCS})_2(\text{Ph}_3\text{AsO})_2]$ é descrita.

Os complexos têm simetrias tetraédricas, piramidal ou octaédrica. Os parâmetros do campo cristalino (Δ_t) dos complexos tetraédricos são 4,100; 4,000; 3,920 e 3,950 cm^{-1} para os complexos $[\text{NiCl}_2(\text{Ph}_3\text{AsO})_2]$, $[\text{NiBr}_2(\text{Ph}_3\text{AsO})_2]$, $[\text{NiI}_2(\text{Ph}_3\text{AsO})_2]$ e $[\text{Ni}(\text{NCS})_2(\text{Ph}_3\text{AsO})_2]$, respectivamente. Os parâmetros intereletrônicos B são 825, 805 e 795 cm^{-1} para os complexos tetraédricos de Cl-, Br- e I-, respectivamente. Para o complexo tetraédrico $[\text{Ni}(\text{NO}_3)_2(\text{Ph}_3\text{AsO})_2]$ o (Δ_o) valor é 8,330 cm^{-1} e B é 823 cm^{-1} .

Magnetic and spectroscopic data of ten complexes resulting from the interaction between Nickel(II) and triphenylarsine oxide (Ph_3AsO) are described. The results are discussed in order to determine the geometry of the complexes.

The preparation of the complexes $[\text{NiBr}_2(\text{Ph}_3\text{AsO})_2]$, $[\text{NiCl}_2(\text{Ph}_3\text{AsO})_2]$, $[\text{Ni}(\text{NO}_3)_2(\text{Ph}_3\text{AsO})_2]$, $\text{NiI}_2 \cdot 4(\text{Ph}_3\text{AsO})$ and $[\text{Ni}(\text{ClO}_4)(\text{Ph}_3\text{AsO})_4]\text{ClO}_4$ was previously described in the literature. The complexes $[\text{NiBr}(\text{Ph}_3\text{AsO})_4]\text{Br}$ and $[\text{Ni}(\text{H}_2\text{O})_6]\text{Br}_2 \cdot 4(\text{Ph}_3\text{AsO}) \cdot 2(\text{H}_2\text{O})$ were also prepared in our laboratories and the preparation of the complexes $[\text{NiCl}(\text{Ph}_3\text{AsO})_4]\text{Cl}$, $[\text{NiI}_2(\text{Ph}_3\text{AsO})_2]$ and $[\text{Ni}(\text{NCS})_2(\text{Ph}_3\text{AsO})_2]$ is described in the present paper.

The complexes have tetrahedral, square pyramidal or octahedral geometrical forms. The crystal field parameters (Δ_t) of the tetrahedral complexes are 4,100; 4,000; 3,920 and 3,950 cm^{-1} for the complexes $[\text{NiCl}_2(\text{Ph}_3\text{AsO})_2]$, $[\text{NiBr}_2(\text{Ph}_3\text{AsO})_2]$, $[\text{NiI}_2(\text{Ph}_3\text{AsO})_2]$ and $[\text{Ni}(\text{NCS})_2(\text{Ph}_3\text{AsO})_2]$, respectively. The interelectronic parameters B are 825, 805 and 795 cm^{-1} for the tetrahedral complexes of Cl-, Br- and I-, respectively. For the octahedral complex $[\text{Ni}(\text{NO}_3)_2(\text{Ph}_3\text{AsO})_2]$ the Δ_o value is 8,330 cm^{-1} and B is 823 cm^{-1} .

Key Words: *Ni(II) complexes; triphenylarsine oxide.*

Introduction

Complexes of nickel(II) can be prepared in a various stereochemical forms, each having a extensive number of examples. This is probably the reason whereby Ni(II) is one of the most spectroscopically studied metal ions.

Tetrahedral Ni(II) compounds were obtained with monodentate O-ligands, such as phosphine oxides¹⁻⁵ and arsine oxides⁴⁻⁷. Especially in the case of triphenylarsine oxide (Ph_3AsO), some distinct geometries were observed depending mainly on the metal-ligand molar ratio and on the solvent employed in the synthesis. Cotton and co-work-

ers⁷ studied some complexes of Ni(II) containing Ph_3AsO , but only the tetrahedral compounds were characterized.

The main purpose of this work is the study of the coordination of Ni(II) ion and the stereochemistry of some of its complexes with Ph_3AsO . Spectroscopic and magnetic characteristics of the complexes are presented and discussed here.

The preparation of the following complexes were previously reported in the literature: $[\text{NiBr}_2(\text{Ph}_3\text{AsO})_2]$ ⁶,

$[\text{NiCl}_2(\text{Ph}_3\text{AsO})_2]^{6,8}$, $[\text{Ni}(\text{NO}_3)_2(\text{Ph}_3\text{AsO})_2]^9$, $[\text{Ni}(\text{ClO}_4)(\text{Ph}_3\text{AsO})_4]\text{ClO}_4^{8,10,11}$, and $\text{NiI}_2 \cdot 4(\text{Ph}_3\text{AsO})^{11}$. The complexes $[\text{Ni}(\text{H}_2\text{O})_6]\text{Br}_2 \cdot 4(\text{Ph}_3\text{AsO}) \cdot 2(\text{H}_2\text{O})$ and $[\text{NiBr}(\text{Ph}_3\text{AsO})_4]\text{Br}$ were prepared in our laboratories as previously described¹². The complexes $[\text{NiCl}(\text{Ph}_3\text{AsO})_4]\text{Cl}$, $[\text{NiI}_2(\text{Ph}_3\text{AsO})_2]$ and $[\text{Ni}(\text{NCS})_2(\text{Ph}_3\text{AsO})_2]$ have not yet described and are reported here by the first time.

Experimental

All compounds were prepared in our laboratories and some of them were already described in the literature, the composition being checked by elemental analysis. Three complexes (orange, blue and green) were obtained from NiBr_2 and Ph_3AsO and other three were synthesized from NiCl_2 (also orange, blue and green). NiI_2 formed two distinct compounds (brown and yellow), whereas $\text{Ni}(\text{ClO}_4)_2$, $\text{Ni}(\text{NO}_3)_2$ and $\text{Ni}(\text{NCS})_2$ originated only yellow compounds with Ph_3AsO . The green product obtained from NiCl_2 was not characterized. The seven known complexes were prepared by the following procedures described in the literature^{6,8-12}.

Preparation of the Complexes

$[\text{NiCl}(\text{Ph}_3\text{AsO})_4]\text{Cl}$ - Ethanolic solutions of NiCl_2 and Ph_3AsO in the 1:2 molar ratio were mixed and the resulting solution was dried in vacuo over sulfuric acid. Within a few days a blue tetrahedral complex $[\text{NiCl}_2(\text{Ph}_3\text{AsO})_2]$ was formed⁶ but sometimes a mixture of a blue, orange and green solids was obtained. Recrystallization of the mixture in chlorobenzene yielded orange $[\text{NiCl}(\text{Ph}_3\text{AsO})_4]\text{Cl}$ crystals. The same orange compound was also obtained from a 1:4 ethanolic NiCl_2 and Ph_3AsO mixture. Dissolution of the blue or orange complex in hot benzene followed by filtration and cooling produced a green solid which was not characterized. Calculated for $[\text{NiCl}(\text{Ph}_3\text{AsO})_4]\text{Cl}$: 60.96% C, 4.26% H. Found 61.96% C and 4.25% H.

$[\text{NiI}_2(\text{Ph}_3\text{AsO})_2]$ - Ethanolic solutions of NiI_2 and Ph_3AsO in a 1:2 molar ratio were mixed, resulting in a dark green solution; yellow crystals were separated at a room

temperature and washed with cold ethanol. Calculated for $[\text{NiI}_2(\text{Ph}_3\text{AsO})_2]$: 45.20% C, 3.16% H. Found: 43.55% C and 2.83% H.

$[\text{Ni}(\text{NCS})_2(\text{Ph}_3\text{AsO})_2]$ - Ethanolic solutions of $\text{Ni}(\text{NC})_2$ and Ph_3AsO in an 1:2 molar ratio were mixed and a slow solvent evaporation yielded a yellow solid, which was filtered and washed with cold ether. Calculated for $[\text{Ni}(\text{NCS})_2(\text{Ph}_3\text{AsO})_2]$: 55.71% C, 3.69% H. Found 53.73% C and 3.81% H.

Physical Measurements

Vibrational spectra of the complexes in the 4,000-400 cm^{-1} range were obtained in a Specord 75 IR spectrometer. Molar conductance measurements were carried out at 25°C in a Methrohm Herisau E-527 equipment. A Gouy balance was used for the magnetic measurements¹³. Preliminary results were previously reported¹⁴.

Absorption spectra of solutions and solid samples (Nujol or Fluorolube mulls) were obtained in a Beckman UV-5270 spectrophotometer with 10 mm (solution) and 2 mm (solids) optical path quartz cells. EPR spectra were measured in a Varian E-109 spectrometer and the X-ray diffractograms were obtained in an HZG/C diffractometer.

Results and Discussion

Table I contains the coordination formulae, molar conductance (Λ_M) and magnetic moment (μ_{eff}) values for the complexes.

The stereochemistry of the same anionic series probably changes on heating, since alterations of the color of the complexes were observed. In the case of the bromide complexes, after melting the orange compound gave a blue solid which melted again producing a green solid. A similar change was observed for the chloride complexes¹⁰.

The magnetic data¹⁴ indicate that the complexes of the type $[\text{NiX}_2(\text{Ph}_3\text{AsO})_2]$ ($\text{X} = \text{Cl}^-$, Br^- and NCS^-) have a tetrahedral geometry. The complex $[\text{NiI}_2(\text{Ph}_3\text{AsO})_2]$ is clearly paramagnetic; the μ_{eff} value found for this compound was very similar to the spin only value for nickel(II) ion, but the

Table 1 - Melting points, molar conductances and magnetic moments for nickel (II) complexes with triphenylarsine oxide (Ph_3AsO).

Complexes	M.P.(°C)	$\text{ohm}^{-1}\text{cm}^{-1}\text{mol}^{-1}$	μ_{eff} , B.M.
$[\text{NiBr}_2(\text{Ph}_3\text{AsO})_2]$	215.5-217.4	31.9 ^d	3.47
$[\text{NiCl}_2(\text{Ph}_3\text{AsO})_2]$	189.5-191.0	32.0 ^d	3.56
$[\text{NiI}_2(\text{Ph}_3\text{AsO})_2]$	237.0-238.3 ^a	36.5 ^d	h
$[\text{Ni}(\text{NCS})_2(\text{Ph}_3\text{AsO})_2]$	263.0-264.0 ^b	7.0 ^e	3.61
$[\text{NiBr}(\text{Ph}_3\text{AsO})_4]\text{Br}$	194.3-197.0 ^c	31.5 ^e	3.22
$[\text{NiCl}(\text{Ph}_3\text{AsO})_4]\text{Cl}$	161.9-163.5 ^c	31.5 ^e	3.14
$\text{NiI}_2 \cdot 4(\text{Ph}_3\text{AsO})$	201.5-203.5 ^c	f	3.04
$[\text{Ni}(\text{ClO}_4)(\text{Ph}_3\text{AsO})_4]\text{ClO}_4$	220.0-230.0	197.0 ^g	3.27
$[\text{Ni}(\text{NO}_3)_2(\text{Ph}_3\text{AsO})_2]$	220.0-223.0	45.2 ^d	3.34

^a turn to red on melting;

^b turn to blue on melting;

^c decomposed;

^d nitromethane solution;

^e ethanolic solution;

^f see text;

^g acetonitrile solution;

^h see text.

EPR spectrum revealed a great number of lines, denoting not only the interaction between Ni(II) and I⁻ ion but also the existence of a low symmetry, probably D_{2d}. The complexes of the type [NiX(Ph₃AsO)₄]X (X = Cl⁻, Br⁻ and ClO₄⁻) show μ eff values similar to other pentacoordinated Ni(II) complexes described in the literature^{10,15}. The magnetic moment value found for the nitrate compound (3.34 BM) also agrees with the octahedral structure, which has been determined by X-ray diffraction⁹.

Molar conductance data obtained for the complexes of a general formula [NiX₂(Ph₃AsO)₂] (X = Cl⁻, Br⁻, I⁻, NCS⁻ and NO₃⁻) indicate that the complexes are non-electrolytes¹⁶. The complexes of the type [NiX(Ph₃AsO)₄]X (X = Cl⁻ and Br⁻) show Λ_M values consistent with a 1:1 electrolyte behaviour¹⁶. The complex [[Ni(ClO₄)(Ph₃AsO)₄](ClO₄) shows a molar conductance value between those of 1:1 and 1:2 electrolytes, as described by Phillips and Thyree⁸. The infrared spectrum of the solid sample suggests that the perchlorate ions are present in both coordinated and ionic forms. The brown complex NiI₂.4(Ph₃AsO) dissolved in nitromethane, ethanol or acetonitrile gave yellow solutions; the Λ_M value in nitromethane is close to the value of the [NiI₂(Ph₃AsO)₂] yellow complex. The electronic spectra of these two compounds in ethanolic solution are also very similar. These facts suggest that in solution the brown complex dissociates with probable loss of the ligand to form the yellow compound.

The $\nu(\text{As-O})$ frequencies were observed from 845 cm⁻¹ for [NiCl₂(Ph₃AsO)₂] to 862 cm⁻¹ for [NiI₂(Ph₃AsO)₂]. The $\Delta\nu(\text{As-O})$ for the complexes is around 20 cm⁻¹; such shift is in general lower than those observed for some analogous complexes with Ph₃PO (around 50 cm⁻¹)¹⁷.

The X-ray diffractograms (powder) of [NiBr(Ph₃AsO)₄]Br (used as reference) and [NiCl(Ph₃AsO)₄]Cl revealed that the complexes are isomorphous. The [Ni(ClO₄)(Ph₃AsO)₄]ClO₄ compound showed some reflections in angles similar to the bromide ones. The diffractogram of NiI₂.4(Ph₃AsO) had no similarity with the complex used as reference.

Electronic Spectra

Hexacoordinated Complexes - The yellow complex [Ni(NO₃)₂(Ph₃AsO)₂] shows the Ni(II) ion octahedrally coordinated to six oxygen atoms; each nitrate group is symmetrically coordinated through two oxygen atoms and the two Ph₃AsO molecules are coordinated in a *cis*-position⁹.

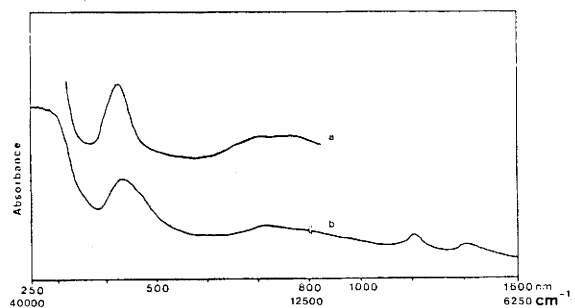


Figure 1. Electronic spectra of [Ni(NO₃)₂(Ph₃AsO)₂]: (a) ethanolic solution, and (b) Nujol mull.

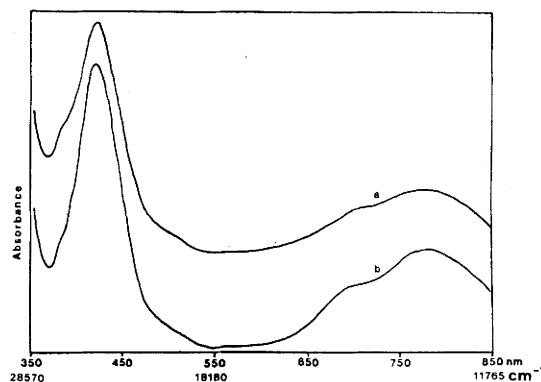


Figure 2. Electronic spectra of ethanolic solutions: (a) [Ni(H₂O)₆]Br₂.4(Ph₃AsO).2H₂O and (b) green complex of NiCl₂ with Ph₃AsO.

In the electronic spectra of this compound (Figure 1) the following bands were observed: 23,150 (ν_3) ($\epsilon \sim 11$); 14,185 (ν_2) ($\epsilon \sim 3.3$); 13,160 (ν_4) ($\epsilon \sim 3.5$); 8,330 (ν_1) and 7,250 cm⁻¹.

Assuming an O_h symmetry and using a procedure already described in the literature^{18,19} we obtained the parameter values $D_q = 833$ cm⁻¹, $B = 823$ cm⁻¹ and the ratios $D_q/B = 1.01$, $\nu_1/\nu_2 = 1.70$ and $\beta = 0.79$. The value 220 cm⁻¹ was found for the spin-orbit coupling constant (λ). Using the D_q value the corrected magnetic moment (3.25 BM) was calculated for [Ni(NO₃)₂(Ph₃AsO)₂]. These values calculated here are consistent with other values described in the literature for distorted O_h symmetry¹⁸. Many octahedral Ni(II) complexes show a double peak band²⁰ in the ν_2 region assigned by Jorgensen²¹ to a splitting of the ³T_{1g}(F) term by spin-orbit coupling. At room temperature the splitting is not very pronounced, since the spin-orbit coupling constant (ca. 200-300 cm⁻¹ for Ni²⁺) is smaller than the observed bandwidth (ca. 2,000 - 3,000 cm⁻¹). This splitting was observed for [Ni(NO₃)₂(Ph₃AsO)₂] and the two maximum peaks were assigned to ν_2 and ν_4 ; they can be considered as an "average" transition, due to the mixture of the ν_2 triplet-triplet and ν_4 triplet-singlet transitions.

The electronic spectra of the ethanolic solutions of the green complexes [Ni(H₂O)₆]Br₂.4(Ph₃AsO).2(H₂O) and of the analogous chloride can be observed in Figure 2. The structure of the bromide complex was determined by X-ray diffraction¹² showing a very interesting arrangement, composed of the two coordination spheres. In the first sphere, six water molecules are coordinated to the Ni(II) ion; in the second sphere, Ph₃AsO molecules are bonded through hydrogen bonds to the water molecules in the first coordination sphere. The spectrum of this compound shows two bands, one at ca. 23,800 cm⁻¹ and other at 12,770 cm⁻¹, the latter with a shoulder at ca. 14,500 cm⁻¹. The assignment of these bands follows those of the [Ni(H₂O)₆]²⁺ complex ion¹⁸. The green chloride complex in an ethanolic solution shows an electronic spectrum very similar to the bromide one; so, it probably has an octahedral structure.

Tetraordinated Complexes - In Table II are shown the maxima of the absorption bands, the values of the molar absorptivity (ϵ), Δ_t values (tetrahedral crystal field splitting), B and calculated for [NiX₂(Ph₃AsO)₂] (X = Cl⁻, Br⁻, I⁻ and NCS⁻) complexes. These parameters were calculated using transition energy diagrams¹⁸. Bands at ca. 8,000 cm⁻¹ were assigned to the 3T₁ → 3A₂ (ν_2) transition, bands at

Table 2. Electronic spectra of the tetrahedral Ni(II) complexes and crystal field parameters

Complexes	Sample	Wavenumber, cm ⁻¹ (*)	Δ_t , cm ⁻¹	B, cm ⁻¹	β
[NiBr ₂ (Ph ₃ AsO) ₂]	solid chlorobenzene sol.	16,000; 14,500; 7,900 21,300(sh); 16,630 (170); 14,550(150); 7,800(30)	4,000	805	0.78
[NiCl ₂ (Ph ₃ AsO) ₂]	solid acetone sol.	16,530; 14,925; 8,000 22,220(sh); 17,400(sh); 16,530(80); 15,000(75); 12,270(5)	4,100	825	0.80
[NiI ₂ (Ph ₃ AsO) ₂]	solid ethanolic sol.	31,750; 24,390; 14,950 12,050; 7,940; 7,040 28,090 (900); 18,020 (sh) 8,700; 6,850 (10)			
[Ni(NCS) ₂ (Ph ₃ AsO) ₂]	solid ethanolic sol.	2,780; 22,880; 17,860; 8,230; 7,110 24,815 (20); 15,150 (8); 13,515 (7)	3,950	990	0.96

(*) Molar absorptivity in parenthesis) in l.mol⁻¹.cm⁻¹

14,000-16,000 cm⁻¹ to the ³T₁ → ³T₁(P) (v₃) transition, bands at 20,000-25,000 cm⁻¹ to 1G level, spin forbidden, and the bands at ca. 12,500 cm⁻¹ to ¹D level, also forbidden. The iodide complex in ethanol also showed a band at ca. 28,000 cm⁻¹, of high intensity, probably due to a charge transfer transition.

Comparisons of Δ_t and B values of each series of compounds indicate that in the spectrochemical series the halide order is I⁻ < Br⁻ < Cl⁻, and in the nephelauxetic series the order is Cl⁻ < Br⁻ < I⁻; there is some discrepancy in the parameter values of the thiocyanate complex because the Δ_3 band at 17,860 cm⁻¹ (solid sample) was considered.

Comparisons of the Δ_t and B values of the Ph₃AsO halide complexes described here with those of the analogous com-

plexes [NiX₂(Ph₃PO)₂] (X = Cl⁻, Br⁻ and I⁻) reported in the literature⁷ show that the order of these two ligands in the spectrochemical series is Ph₃PO < Ph₃AsO. In the nephelauxetic series, the values for both ligands are comparable. There is also a good agreement between the calculated crystal field parameters for [NiX₂(Ph₃AsO)₂] (X = Cl⁻ and Br⁻) and the values previously reported⁶.

Electronic spectra and other experimental data suggest that the complexes with formula [NiX₂(Ph₃AsO)₂] (X = Cl⁻, Br⁻, I⁻ and NCS⁻) described here are all tetrahedral. Some distortions of the geometry may be present, mainly due the presence of distinct ligands around the nickel(II) ion. More pronounced distortions of T_d symmetry must be present in the thiocyanate complex.

Pentacoordinated Complexes - Figure 3 shows the electronic spectra of the [NiBr(Ph₃AsO)₄]Br complex. The structure of this compound was determined by X-ray diffraction¹². A square pyramidal structure with the Ph₃AsO₄ molecules in the plane and the bromide ions in the apical position with the coordination formula [NiBr(Ph₃AsO)₄]Br.1/2 toluene. Toluene was the solvent used for recrystallization.

Table III summarizes the electronic data for this compound and for [NiX(Ph₃AsO)₄]X (X = Cl⁻ and ClO₄⁻) and NiI₂.4(Ph₃AsO) complexes, the maxima of the absorption bands and also the corresponding molar absorptivities.

Spectra of the ethanolic solutions of the bromide, chloride and perchlorate complexes are similar to those of [Ni(NO₃)₂(Ph₃AsO)₂] (Figure 1).

This fact suggests that, in an ethanolic solution, the pentacoordinated complexes behave like the octahedral hexa-

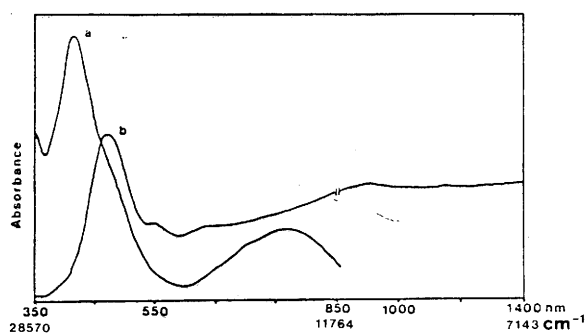


Figure 3. Electronic spectra of [NiBr(Ph₃AsO)₄]Br: (a) Nujol mull, and (b) ethanolic solution.

Table 3. Electronic spectra of the pentacoordinated nickel (II) complexes with Ph_3AsO .

Complexes	Wavenumber (cm^{-1})	
$[\text{NiBr}(\text{Ph}_3\text{AsO})_4]\text{Br}$	mull:	22,200; 18,200; 15,400 12,900; 11,100; 8,700; 7,900
	sol.:	22,200 (~100), 15,385 (8); 12,660 (4)
$[\text{NiCl}(\text{Ph}_3\text{AsO})_4]\text{Cl}$	mull:	23,800; 20,400; 17,400; 11,000; 8,600; 7,500; 6,900
	sol.:	23,530 (~85); 14,300 (~10) 13,100 (~15)
$[\text{Ni}(\text{ClO}_4)(\text{Ph}_3\text{AsO})_4]\text{ClO}_4$	mull:	23,690; 19,600; 17,200; 12,800; 8,850; 7,200; 6,370
	sol.:	25,000 (~70); 15,150 (~10); 13,400 (~12)
$\text{NiI}_2 \cdot 4(\text{Ph}_3\text{AsO})$	mull:	32,260; 25,650
	sol.:	27,850 (~900)

(*) molar absorptivity (in parenthesis) in $\text{l.mol}^{-1}.\text{cm}^{-1}$

coordinated ones, perhaps due to solvent coordination in the sixth position of the octahedral geometry. However, for the nitrate complex the molar absorptivity value in the ν_3 band is eight times smaller than those for other pentacoordinated complexes, this being the major difference between them.

By taking into consideration the calculation made by Gerloch and co-workers²², some assignments can be made regarding the observed bands in the electronic spectra of the pentacoordinated complexes in solid. The bands at 22,000 - 23,000 cm^{-1} can be assigned to ${}^3\text{B}_1 \rightarrow {}^3\text{E}$ (P), the band at 18,000 - 20,000 cm^{-1} to ${}^3\text{B}_1 \rightarrow {}^3\text{A}_2$ (P), the band at 11,000 - 13,000 cm^{-1} to ${}^3\text{B}_1 \rightarrow {}^3\text{E}$ (F). The bands observed bellow 10,000 cm^{-1} can be assigned to transitions to the levels ${}^3\text{A}_2$ (F) and ${}^3\text{E}$ (F). All these transitions are spin allowed. The other observed bands can be assigned to spin forbidden transitions to singlet levels originated by ${}^1\text{D}$ and ${}^1\text{G}$ splitting.

The electronic spectrum of the $[\text{NiBr}(\text{Ph}_3\text{AsO})_4]\text{Br}$ complex in solid seems to be coherent with a square pyramidal structure¹². There is also a good agreement between $[\text{Ni}(\text{ClO}_4)(\text{Ph}_3\text{AsO})_4]\text{ClO}_4$ spectrum and that described in the literature^{10, 11}. The spectra of both chloride and perchlorate complexes are very similar to that of the bromide complex. Evidence from these spectra combined with the results from other techniques provided the assignment of a square pyramidal stereochemistry around the Ni(II) ion in these complexes.

The electronic spectra of the brown complex $\text{NiI}_2 \cdot 4(\text{Ph}_3\text{AsO})$ are not consistent with those of complexes having a square pyramidal structure. This complex in solu-

tion shows a spectrum similar to the yellow $[\text{NiI}_2(\text{Ph}_3\text{AsO})_2]$ one. The spectrum of the solid sample shows two bands at 32,360 and 25,650 cm^{-1} which can be assigned to charge transfer bands from I⁻ to the Ni(II) ion. Goodgame *et al.*¹¹ described a complex with the same formula but with spectroscopic features distinct from those reported here; the inexistence of an agreement between their and our spectroscopic data suggest that the complex reported in the present work have not the same structure, despite of no statements about its geometry can be done.

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