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Anomalous Ligand Field Effects in Complexes of Quadridentate Ligands Containing Group V Donors

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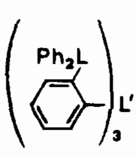
Trigonal bipyramidal complexes $[NiX(QL)][BPh_4]$ *(*$X=Cl$ *and* I*;* $QL=(o\text{–}Ph_2P\,.\,C_6H_4)_3P$*,* $(o\text{–}Ph_2P\,.\,C_6H_4)_3As$*,* $(o\text{–}Ph_2P\,.\,C_6H_4)_3Sb$*,* $(o\text{–}Ph_2As\text{-}C_6H_4)_3P$*,* $(o\text{–}Ph_2As\,.\,C_6H_4)_3As$*, and* $(o\text{–}Ph_2As\,.\,C_6H_4)_3Sb$*) were prepared and their electronic spectra examined. It is shown that a change of apical donor atom of the organic ligand gives the following anomalous spectrochemical order:* $P>As<Sb$*. This effect is attributed to compression of the apical bond caused by chelation.*

Introduction

Quadridentate ligands such as tris–(*o*–diphenylphosphinophenyl)phosphine, QP, (I), and its arsenic analogue, QAS, (II), form a large number of complexes



(I) L=P, L'=P, QP;
(II) L=As, L'=As, QAS;
(III) L=P, L'=As, ASTP;
(IV) L=P, L'=Sb, SBTP;
(V) L=As, L'=P, PTAS;
(VI) L=As, L'=Sb, SBTAS

of the type $[M^{n+}X(QL)]^{(n-1)+}$, (M=transition metal ion; X=anionic ligand; QL=QP or QAS) of the type shown in Figure 1.[3] Their spectra have been extensively studied and the absorption bands observed have been assigned using a ligand field model.[4]

We report here the preparation and properties of a number complexes of nickel(II) with quadridentate ligands containing phosphorus or arsenic and another Group V donor atom, *i.e.*, with ligands (III) to (VI).

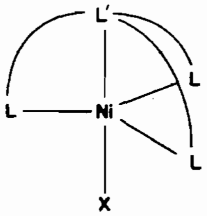


Figure 1. Schematic structure of complexes [NiX(QL)]Y.

Experimental Section

Preparation of Ligands. Tris–(o–diphenylphosphinophenyl)phosphine was prepared by the method of Hartley *et al.*,[5] using the modified procedure described by Chiswell *et al.*[6] *Tris–(o–diphenylphosphinophenyl) arsine* was prepared as above, substituting phosphorus trichloride with arsenic trichloride in the final stage. The pure product, obtained in 45% yield, after recrystallization from ethanol/tetrahydrofuran, had m. pt. 247-248°. (Found: C, 75.3; H, 5.0; As, 8.6; P, 10.8. $C_{54}H_{42}AsP_3$ requires C, 75.5; H, 4.9; As, 8.7; P, 10.6%). *Tris–(o–diphenylphosphinophenyl)stibine* was prepared and purified as above, using antimony trichloride for the last stage. The product, obtained in 57% yield, had m. pt. 250-252°. (Found: C, 71.9; H, 4.6; P, 10.0. $C_{54}H_{42}P_3Sb$ requires C, 71.6; H, 4.7; P, 10.3%). *Tris–(o–diphenylarsinophenyl)phosphine* and *tris–(o–diphenylarsinophenyl)arsine* were prepared by the method of Howell *et al.*,[7] using the modification described by Cannon *et al.*[8] *Tris–(o–diphenylarsinophenyl)stibine* was prepared as above, using antimony trichloride for the last stage. The pure product was obtained in 35% yield and had m. pt. 210-212° after purification by repeated washing with ethanol. (Found: C, 62.4; H, 3.9. $C_{54}H_{42}As_3Sb$ requires C, 62.5; H, 4.1%).

Preparation of complexes. Unless otherwise stated, all the complexes were recrystallized by dissolution in dichloromethane and reprecipitation by addition of ethanol and dried by pumping at 130° at 10^{-4} mm for 6-24 hr.

$[NiCl(ASTP)][BPh_4]$. Nickel chloride hexahydrate (0.09 g) and ASTP (0.3 g) in ethanol (20 ml) were refluxed for 2 hr. Sodium tetraphenylborate (0.13 g) in ethanol (5 ml) was added to the filtered solution and caused immediate precipitation of the product. $[NiCl(PTAS)][BPh_4]$ and $[NiCl(QP)][BPh_4]$,[9] were similarly prepared.

$[NiI(ASTP)][BPh_4]$. Nickel nitrate hexahydrate (0.5 g) and sodium iodide (0.5 g) were each dissolved in the minimum amount of ethanol, the solutions mix-

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Table I. General physical data, yields and analyses of complexes $[NiX(QL)][BPh_4]$ (X=Cl and I; QL=QP, ASTP, SBTP, PTAS, QAS and SBTAS)

Complex [a]	Colour	Decomp. pt.	Λ_M ([b])	Yield (%)	Nickel		Carbon		Hydrogen		P or As	
					([c])	([d])	([c])	([d])	([c])	([d])	([c])	([d])
$[NiCl(QP)][BPh_4]$ [e]	Dark blue	265-267°	15.1	85	4.8	4.7	76.3	76.2	5.1	5.0	10.1	10.0
$[NiI(QP)][BPh_4]$ [e]	Blue-black	233-235	14.9	67	4.5	4.4	71.0	71.2	4.7	4.9	9.4	9.3
$[NiCl(QAS)][BPh_4]$	Blue	214-216	13.5	55	4.2	4.2	66.7	66.4	4.5	4.6	21.4	21.2
$[NiCl(ASTP)][BPh_4]$	Dark blue	244-245	14.7	80	4.6	4.6	73.6	72.9	4.9	4.9	7.3	7.2
$[NiI(ASTP)][BPh_4]$	Blue-black	219-222	14.4	84	4.3	4.3	68.7	68.4	4.5	4.5		
$[NiCl(SBTP)][BPh_4]$	Blue	190-192	14.4	78			70.1	71.1	4.7	4.7	7.1	7.1
$[NiI(SBTP)][BPh_4]$	Blue-black	188-190	15.2	75			66.4	66.5	4.4	4.5	6.6	6.5
$[NiCl(PTAS)][BPh_4]$	Blue	242-244	14.9	78	4.3	4.2	68.9	68.6	4.6	4.6		
$[NiI(PTAS)][BPh_4]$	Blue-black	247-249	14.7	72	4.0	4.0	64.5	64.6	4.3	4.3		
$[NiCl(SBTAS)][BPh_4]$	Pale blue	175-177	14.6	60			64.6	64.5	4.3	4.3	15.5	15.3
$[NiI(SBTAS)][BPh_4]$	Blue-black	173-174	14.9	76			60.7	60.9	4.1	4.0	14.6	14.7

[a] All the complexes are diamagnetic with values of $\chi_{M(corr.)}$ at room temperature in the range $+10$ to $+80\times10^{-6}$ c.g.s. [b] In Ω^{-1} $cm^2 M^{-1}$ for approx. $10^{-3} M$ nitrobenzene solutions at 20°. [c] % Calcd. [d] % Found. [e] Previously reported by J. G. Hartley (D. Phil. Thesis, Oxford, 1962).

ed and the precipitate of sodium nitrate filtered off. This solution was made up to 50 ml and 10.5 ml of the stock solution thus prepared added to a refluxing suspension of ASTP (0.3 g) in ethanol (40 ml). Refluxing was continued for 2 hr., the solution filtered and the product precipitated by addition of sodium tetraphenylborate (0.13 g) in ethanol (5 ml). $[NiI(PTAS)][BPh_4]$ and $[NiI(QP)][BPh_4]$,[9] were similarly prepared.

$[NiCl(SBTP)][BPh_4]$. Nickel chloride hexahydrate (0.09 g) in ethanol (5 ml) and SBTP (0.3 g) in dichloromethane (25 ml) were refluxed for 3 hr. Sodium tetraphenylborate (0.13 g) in ethanol (5 ml) was added to the filtered solution. The product separated out on partial evaporation of the solvents and was recrystallized by dissolution in dichloromethane and reprecipitation by addition of *n*-butanol.

$[NiI(SBTP)][BPh_4]$ was similarly prepared using the stock solution of nickel iodide described above.

$[NiCl(SBTAS)][BPh_4]$. $[NiCl_2(PPh_3)_2]$,[10] (0.2 g) and SBTAS (0.3 g) were dissolved in dichloromethane (20 ml) and the solution stirred for 24 hr. in an atmosphere of dry nitrogen. Sodium tetraphenylborate (0.12 g) was added to the filtered solution and stirring was continued for 3 hr. The crude complex was precipitate from the filtered solution by addition of di—*iso*—propyl ether (20 ml). Purification was achieved by addition of di—*iso*—propyl ether to a dichloromethane solution of the complex. $[NiI(SBTAS)][PPh_4]$ was similarly prepared.

Analyses. Phosphorus and arsenic were determined spectrophotometrically.[11] It was found that antimony did not interfere with the above determinations. As arsenic interfered with the analysis for phosphorus, the determination of phosphorus in complexes of ASTP was carried out by a modification of the method of Kitson and Mellon:[12] the solid complex (ca. 15 mg) was boiled with 70% perchloric acid (5 ml) and concentrated nitric acid (2 ml) for ca. 1 hr. The solution was transferred by washing into a 250 ml standard flask and 70% perchloric acid (8 ml) added, followed by 0.04 *M* ammonium molybdate (25 ml) and 0.02 *M* ammonium vanadate (25 ml) and making up to volume with distilled water. A yellow colour developed in about 15 min. and absorption measurements were made at 460 $m\mu$ against a reagent blank using 4 cm glass cells. The calibration curve was plotted using « AnalaR » disodium hydrogen phosphate. It was found that a concentration of up to 30 ppm. of arsenic did not interfere with the phosphorus determination. Higher quantities of arsenic did interfere and thus this method could not be used for complexes of PTAS.

Nickel was analyzed using a Unicam Atomic Absorption Spectrophotometer Model S.P. 90. The complexes (ca. 10 mg) were dissolved in cyclohexanone (25 ml) and the transmittance measured at 232 $m\mu$. A calibration curve was plotted using bis-(salicylaldoximato)nickel(II) prepared as described elsewhere.[13]

Visible and ultraviolet spectra. These were recorded using a Unicam S.P. 700 recording spectrophotometer. Solution spectra were obtained using 10^{-4}–$10^{-6} M$ dichloromethane solutions in 1 cm fused silica cells. The spectra of solids were obtained using a Unicam S.P. 740 reflectance attachment. The spectrum of $[NiBr(QP)]Br$ was kindly provided by Mr. J. W. Dawson[14] and the data are given in Table II.

Magnetic susceptibility measurements were carried out as described elsewhere.[15]

Results and Discussion

The complexes prepared and some of their physical properties are listed in Table I. These complexes, like those of QP and QAS reported earlier,[11] have been assigned trigonal bipyramidal structure, both in solution and in the solid state, on the basis of their visible and ultraviolet spectra which are summarized in Table II. As done previously,[3] the low-energy bands occurring at *ca.* 17,000 cm^{-1} and at *ca.* 24,000 cm^{-1} have been assigned to the one-electron transitions

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$(e_2)^4(e_1)^4 \longrightarrow (e_2)^4(e_1)^3(a_1)^1$ and $(e_2)^4(e_1)^4 \rightarrow (e_2)^3(e_1)^4(a_1)^1$ respectively.

The most interesting feature of these spectra is the shift of the lowest energy band which occurs when the apical ligand L′ changes from phosphorus to arseinc and to antimony (see Figure 2). This gives an

Table II. Visible and ultraviolet spectra of complexes [NiX(QL)]Y (X=Cl and I; QL=ligands (I) to (VI); Y = BPh$_4$ and Br)

	Solution		Solid		Gaussian Analysis		
	ε_{max}	E_{max}	E_{max} (kK)	$F(R_\infty)$[a] (I)	E_{max} (kK)	ε_{max}	ΔE[b] (kK)
[NiCl(QP)][BPh$_4$]	36.9	sh	37.0	sh	36.8	19,900	7.4
	35.3	sh	33.8	sh	33.6	5,700	3.3
	32.3	sh			30.5	9,500	3.3
	26.5	sh			26.4	2,200	3.6
	17.2	4,500	17.2	1.2			
[NiBr(QP)]Br	38.0	sh			36.8	19,900	7.4
	35.0	sh			33.6	6,200	3.8
	32.3	sh			30.4	10,200	4.0
	27.3	sh			26.2	2,300	3.6
	16.5	4,400					
[NiI(QP)][BPh$_4$]	38.0	sh	37.5	sh	37.0	25,000	4.6
	35.6	sh			33.4	12,500	3.9
	31.9	sh			30.4	11,000	4.3
	28.2	sh	28.8	sh	26.8	3,600	3.1
	22.2	1,240	22.2	0.24			
	16.0	3,650	16.1	0.40			
[NiCl(QAS)][BPh$_4$]	37.7	sh			37.6	20,800	5.1
	36.3	sh			33.5	5,000	4.0
	30.5	13,700	30.8	2.23	30.1	13,000	4.3
	21.7	285	21.8	0.12			
	16.0	4,420	16.1	1.16			
[NiCl(ASTP)][BPh$_4$]	37.1	sh	36.8	sh	36.6	21,600	4.3
	34.1	sh	34.1	sh	33.8	7,900	3.0
	30.9	sh	31.0	sh	30.3	9,500	3.5
	22.8	sh	23.5	sh	26.8	1,500	2.8
	16.3	4,800	16.3	0.68			
[NiI(ASTP)][BPh$_4$]	36.6	25,600			36.4	20,200	4.8
					33.5	11,700	3.9
	30.8	sh			30.3	9,500	3.5
	27.6	sh	27.8	sh	26.8	4,200	4.4
	21.6	1,130	21.6	0.32			
	15.4	2,900	15.3	0.54			
[NiCl(SBTP)][BPh$_4$]	37.1	sh			36.5	24,000	5.6
	34.4	sh			33.3	5,500	3.2
	30.7	sh	31.0	sh	30.0	10,000	4.0
	27.5	sh	27.2	sh	26.5	2,600	3.1
	16.8	4,450	16.8	1.15			
[NiI(SBTP)][BPh$_4$]	35.7	27,800			36.8	19,600	6.4
					34.1	13,700	5.3
	30.0	sh	30.4	sh	29.3	8,100	4.1
					26.7	1,800	3.5
	22.0	755	22.1	0.32			
	16.0	3,200	16.2	0.95			
[NiCl(PTAS)][BPh$_4$]	37.5	sh			37.1	19,500	4.6
	32.0	16,200	32.6	3.60	34.1	4,500	2.8
					31,5	16,000	4.4
	29.5	sh	29.0	sh	28.2	4,400	2.9
	16.4	4,750	16.4	1.80			
[NiI(PTAS)][BPh$_4$]	37.6	25,100			37.1	22,000	4.8
					33.3	9,500	5.2
	31.3	16,400	32.1	1.70	30.5	10,100	3.8
					27.2	3,600	5.0
	21.3	1,050	21.3	0.25			
	15.2	3,150	15.3	0.60			
[NiCl(SBTAS)][BPh$_4$]	38.6	sh			37.5	24,100	5.9
					33.3	3,500	3.6
	30.0	13,300	31.5	2.20	30.0	12,600	4.3
	22.0	240	22.0	0.08			
	16.3	4,200	16.4	1.00			
[NiI(SBTAS)][BPh$_4$]	35.5	23,700			37.5	18,100	5.1
					34.3	15,600	4.2
	30.2	14,800	30.9	2.10	29,9	14,000	4.2
					26,2	2,400	2.8
	20.9	600	20.8	0.17			
	15.2	3,050	15.2	0.60			

[a] $F(R_\infty)$ = Kubelka-Munk function (see Wendlant and Hecht, 'Reflectance Sectroscopy', Interscience, New York, 1966, p. 63. formula III/47). [b] ΔE = Half-band width.

apparent order of ligand field strength:

$$P > As < Sb$$

which is different from that observed in complexes with these donor atoms contained in monodentate ligands,[16] *i.e.*,

$$PP > As > Sb$$

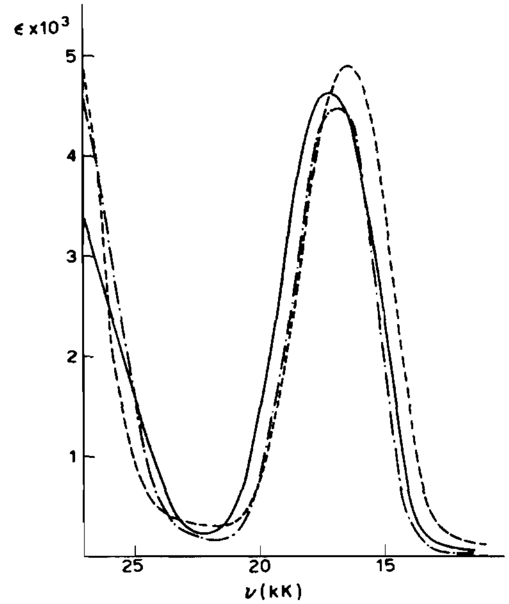

Figure 2. Electronic spectra of complexes [NiCl(QL)]-[BPh$_4$] in the region 10,000-27,000 cm^{-1}, for dichloromethane solutions. QL=QP, ————. QL=ASTP — — —. QL=SBTP —·—·—·—.

The anomalous ligand field order observed in complexes of the quadridentate ligands is attributed to a compression of the apical bond caused by chelation. Calculations[17] show that molecules (I) to (VI) cannot act as quadridentate ligands while preserving bond-distances and bond-angles like those found in complexes of related monodentate ligands: if the apical donor atom, in the trigonal bipyramidal complexes, were to preserve the atomic parameters typical of monodentate ligands the metal atom would be placed significantly below the plane defined by the equatorial atoms and at a distance from them which is longer than that of a normal Ni–L bond. Furthermore, such deviations from regularity increase in the order

$$P < As < Sb^{17}$$

As some of the compounds formed by ligands (I) to (VI) achieve chelation by forming a short apical M–L′ bond and by distorting some P–C–C angles,[18] the primary effect of these distortions on the metal *d*-orbitals is to raise the energy of the a_1-level relative to that of the e-levels.[3] Thus, one expects that ligands containing antimony in the apical position, *i.e.*, SBTP and SBTAS, will show the largest relative increase in energy of the a_1-levels and hence give rise to the anomalous spectrochemical position of antimony in these complexes.

It follows that when deducing the relative position of a donor atom in the spectrochemical series by observing the electronic spectra of a related series of complex of multidentate ligands care must be exercised to insure that there are no geometric constraints, due to the structure of the ligands, which result in the formation of abnormal bond-lengths and/or bond-angles which would affect the energies of the electronic levels.

Finally, it is interesting to note that changing the three equatorial donor atoms results in changes in position of the lowest energy band which are of the same order of magnitude as those caused by changes of one apical donor atom, as seen by comparing the spectra of corresponding complexes of QP, ASTP and PTAS (see Table II). This is in agreement with calculations of Jørgensen and Schmidtke[19] who give an estimate of the relative σ-antibonding character of a_1 and e_1 orbitals as 22/9.

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