

## Five-co-ordinate Palladium(II). An Examination of the Electronic Spectra of Some Trigonal-bipyramidal Complexes Containing a Compressed Palladium–Antimony Linkage

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The trisubstituted stibine, tris(*o*-dimethylarsinophenyl)stibine, sbtas, forms complexes of type  $[\text{Pd}(\text{sbtas})\text{X}]\text{Y}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$ ;  $\text{Y} = \text{Cl}, \text{CNS}, \text{BPh}_4$ ) which are five-co-ordinate and trigonal bipyramidal. The electronic spectra of these complexes show a shift of the ligand-field bands to higher energy in the order  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ , and this nephelauxetic behaviour is discussed in relation to the compression of the Pd–Sb linkage as a result of chelation.

QUADRIDENTATE ligands such as tris(*o*-diphenylphosphinophenyl)phosphine, qp, (I), and its arsenic analogue, qas, (II), form a large number of essentially trigonal-bipyramidal complexes of the type  $[\text{M}^{n+}\text{X}(\text{ql})]^{(n-1)+}$  ( $\text{M} =$  transition metal;  $\text{X} =$  anionic ligand;  $\text{ql} =$  qp or qas) (see Scheme).<sup>1</sup> The electronic spectra of these complexes have been studied, and the observed absorptions were assigned using a ligand-field model.<sup>2</sup> The low-energy bands of these complexes show molar extinction coefficients in the range 3000–8000  $\text{l mol}^{-1} \text{cm}^{-1}$  which, at first, seemed to be too high to be due to simple ligand-field transitions.<sup>3</sup> An investigation of the u.v./visible spectra of some  $d^8$  complexes of the analogous tetra-arsine gasme has shown, however, that the ligand-field bands in  $[\text{MX}(\text{qasme})]^+$  complexes 'borrow' intensity

from  $\pi^* \leftarrow \pi$  transitions of the phenyl groups.<sup>4</sup> More recently, a spectral investigation of some  $[\text{NiX}(\text{L}'\text{TL})]^+$  ( $\text{L}'\text{TL} = \text{astp}, \text{sbtP}, \text{ptas}, \text{sbtA}$ ) complexes showed that as the apical donor atom,  $\text{L}'$ , was changed in any series of complexes an anomalous spectrochemical series for  $\text{L}'$  was obtained, *viz*:  $\text{P} > \text{As} < \text{Sb}$ .<sup>5</sup> This effect was attributed to compression of the apical  $\text{L}'\text{-Ni}$  bond, caused by chelation. Calculations<sup>6,7</sup> have shown that by increasing the size of the apical donor,  $\text{L}'$ , the length of the  $\text{M-L}$  distance increases and the  $\text{L-M}$  bonds are lifted out of the trigonal plane; 'compression' of the  $\text{L}'\text{-M}$  bond distance also occurs.

In order to investigate this compression phenomenon further we have synthesised the quadridentate tris(*o*-

<sup>1</sup> M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *Co-ordination Chem. Rev.*, 1967, **2**, 99, and references quoted therein.

<sup>2</sup> M. J. Norgett and L. M. Venanzi, *Inorg. Chim. Acta*, 1968, **2**, 107, and references quoted therein.

<sup>3</sup> G. Dyer and L. M. Venanzi, *J. Chem. Soc.*, 1965, 2771, and references quoted therein.

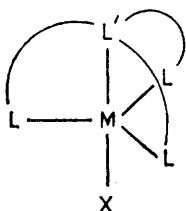
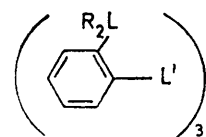
<sup>4</sup> O. St. C. Headley, R. S. Nyholm, C. A. McAuliffe, L. Sindellari, M. L. Tobe, and L. M. Venanzi, *Inorg. Chim. Acta*, 1970, **4**, 93.

<sup>5</sup> B. R. Higginson, C. A. McAuliffe, and L. M. Venanzi, *Inorg. Chim. Acta*, 1971, **5**, 37.

<sup>6</sup> C. A. McAuliffe, D.Phil. Thesis, Oxford University, 1967.

<sup>7</sup> J. W. Dawson, B. C. Lane, R. J. Mynot, and L. M. Venanzi, *Inorg. Chim. Acta*, 1971, **5**, 25.

dimethylarsinophenyl)stibine, sbtas (VIII). Our interest in this trisubstituted stibine also stems from our recent



Schematic structure of  $[MX(L'TL)]^+$  complexes \*

\* Other abbreviations have been used to describe some of the ligands referred to here. The abbreviations used in this paper follow I.U.P.A.C. recommendations.

- (I) L = P, R = Ph, L' = P; qp  
 (II) L = As, R = Ph, L' = As; qas  
 (III) L = P, R = Ph, L' = As; astp  
 (IV) L = P, R = Ph, L' = Sb; sbtp  
 (V) L = As, R = Ph, L' = P; ptas  
 (VI) L = As, R = Ph, L' = Sb; sbta  
 (VII) L = As, R = Me, L' = As; qasme  
 (VIII) L = As, R = Me, L' = Sb; sbtas

work on the stabilisation of metal-antimony bonds by chelation.<sup>5,8,9</sup>

#### EXPERIMENTAL

*o*-Bromophenyldimethylarsine was prepared from *o*-bromoaniline by standard methods.<sup>10</sup>

*Tris(o-dimethylarsinophenyl)stibine*.—*o*-Bromophenyldimethylarsine (21 g, 0.08 mol) was dissolved in dry, light petroleum (b.p. 40–60°; 300 ml) and a solution of *n*-butyllithium in light petroleum (96 ml, 0.91M; 0.087 mol) was

refluxed with sbtas (1 : 1 molar ratio) in ethanol for 1 h; the mixture was filtered to remove NaCl, and cooled. Addition of light petroleum precipitated the complex, which was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-EtOH.

*Method B.* An ethanolic solution of NaX (X = Br, I, CNS) was added to Pd(sbtas)Cl<sub>2</sub> in ethanol (4 : 1 molar ratio) and the mixture was refluxed for 1 h. The mixture was filtered and cooled and precipitation was effected by addition of light petroleum. The complexes were recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-EtOH.

*Method C.* To a hot ethanolic solution of Pd(sbtas)X<sub>2</sub> (X = Cl, Br, I, CNS) was added an ethanolic solution of NaBPh<sub>4</sub> (1 : 1 molar ratio); immediate precipitation of the [Pd(sbtas)X]BPh<sub>4</sub> complex occurred. This was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-EtOH.

*Physical Measurements.*—Conductivities were measured on a Cambridge Instruments Ltd. conductivity bridge. Infrared spectra were measured in Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 621 spectrophotometer, and electronic spectra on a Beckmann DK2 spectrophotometer (for reflectance spectra BaSO<sub>4</sub> was used as a dilutant).

#### RESULTS AND DISCUSSION

Reaction between Na<sub>2</sub>PdCl<sub>4</sub> and sbtas leads to immediate formation of the chloro-complex, from which other halogeno- and pseudohalogeno-complexes can be obtained by metathesis. Further reaction with NaBPh<sub>4</sub> leads to formation of the [PdX(sbtas)]BPh<sub>4</sub> derivatives. Table 1 contains analytical data and some physical properties of the complexes. Analyses indicate that the iodo-complex crystallises as a dichloromethane solvate. Pumping *in vacuo* did not remove this solvent, obviously

TABLE 1

Some physical properties and analytical data of the complexes

Complex	Colour	Decomp. pt. (°C)	Λ <sub>m</sub> <sup>a</sup>	Analyses: % Found (% Calc.)			Method of prepn.	% Yield
				C	H	Halide or N		
[PdLCI]Cl	Red-orange	204–207	77.5	33.5 (34.3)	3.8 (3.6)	8.5 (8.5)	A	35
[PdLCI]BPh <sub>4</sub>	Red-orange	203–205	73.5	53.0 (51.3)	4.7 (4.5)	3.1 (3.2)	C	54
[PdLBr]BPh <sub>4</sub>	Red	207–209	77.3	51.2 (50.3)	4.6 (4.3)	6.4 (6.8)	C	53
[PdLI]BPh <sub>4</sub> ·2CH <sub>2</sub> Cl <sub>2</sub>	Purple	232–234	75	43.2 (43.2)	4.0 (3.7)	10.4 (10.3)	C	57
[PdL(SCN)]CNS	Red	207–209	106	35.2 (35.2)	3.4 (3.4)	3.2 (3.2)	B	41
[PdL(SCN)]BPh <sub>4</sub>	Red	211	66.5	51.0 (51.3)	4.4 (4.4)	1.4 (1.2)	C	73

<sup>a</sup> In Ω<sup>-1</sup> cm<sup>2</sup> l mol<sup>-1</sup> for ca. 10<sup>-3</sup>M nitromethane solutions at 20°.

added under nitrogen; the mixture was stirred and refluxed for 2 h during which time a yellow precipitate of the lithio-derivative separated. Antimony trichloride (6.9 g, 0.03 mol) dissolved in light petroleum (40 ml) was added to the stirred mixture during 2 h and a white precipitate was deposited. Refluxing was continued for 4 h, after which hydrolysis was effected with deoxygenated water (100 ml). The organic layer was removed and dried overnight (Na<sub>2</sub>SO<sub>4</sub>). The ligand, after evaporation of solvent and distillation of unchanged *o*-bromophenyldimethylarsine, was obtained as a white solid, m.p. 135°. The <sup>1</sup>H n.m.r. spectrum in CDCl<sub>3</sub> shows a single methyl resonance at τ 8.80 (Found: C, 43.4; H, 4.8%. Calc. for C<sub>24</sub>H<sub>30</sub>AsSb: C, 43.5; H, 4.5%).

*Preparation of the Complexes.*—*Method A.* Na<sub>2</sub>PdCl<sub>4</sub> was

<sup>8</sup> B. R. Cook, C. A. McAuliffe, and D. W. Meek, *Inorg. Chem.*, 1971, **10**, 2676.

<sup>9</sup> C. A. McAuliffe and D. W. Meek, *Inorg. Chim. Acta*, 1971, **5**, 270.

trapped in the crystal lattice. All other complexes were obtained unsolvated.

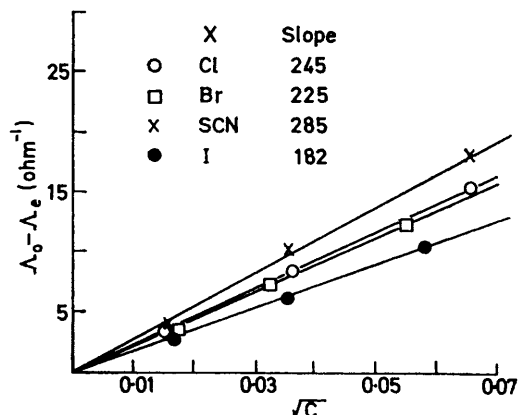
Table 1 also contains the conductivity values of the complexes in nitromethane solution at approx. 1 × 10<sup>-3</sup>M-concentration. These values vary from 66 to 78 for [PdLX]BPh<sub>4</sub> salts to 106 for [PdL(SCN)]CNS (conductivity values in Ω<sup>-1</sup> cm<sup>2</sup> l mol<sup>-1</sup>). These values are quite typical of values which have been assigned to 1 : 1 type electrolytes at 10<sup>-3</sup>M-concentration in nitromethane.<sup>11</sup> However, Feltham and Hayter have pointed out<sup>12</sup> that with ionised complexes of formula

<sup>10</sup> E. R. H. Jones and F. Cr. Mann, *J. Chem. Soc.*, 1955, 4472; R. D. Cannon, B. Chiswell, and L. M. Venanzi, *J. Chem. Soc. (A)*, 1967, 1277.

<sup>11</sup> M. D. Workman, G. Dyer, and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1543.

<sup>12</sup> R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.

$[ML_n]_z[X]_{y/z}$ , neither the molar conductivity  $\Lambda_m$  nor the equivalent conductivity  $\Lambda_o$  independently determines  $z$ . On the other hand, the *change* in  $\Lambda_o$  with concentration is a direct function of the charge on the ions involved and therefore of  $z$ . We have thus applied the method of Feltham and Hayter to determining the electrolyte-type for our complexes. The results are plotted in the Figure from which it can be seen that the slopes of the



Behaviour of  $\Lambda_0 - \Lambda_e$  vs.  $\sqrt{c}$  of the  $[PdLX]BPh_4$  complexes of nitromethane

plots of  $\Lambda_0 - \Lambda_e$  vs.  $\sqrt{c}$  have values between 182 and 245, which are in the range for 1:1 electrolytes.<sup>12</sup> It is remarkable that the method of Feltham and Hayter, which unequivocally determines electrolyte-type, is not used more.

TABLE 2

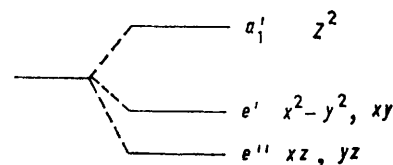
Visible and ultraviolet spectra of the complexes

Complex	$E_{max}^a$ ( $cm^{-1}$ )	$\epsilon_{max}^a$ ( $cm^{-1} l mol^{-1}$ )	$E_{max}^b$
[PdCl]Cl	20,750	540	20,650
	27,900	6800	25,000
	33,245	sh	
[PdCl]BPh <sub>4</sub>	20,800	990	21,250
			25,100
[PdLBr]BPh <sub>4</sub>	32,210	9800	
	21,215	1800	20,450
	24,110	2390	25,300
[PdLi]BPh <sub>4</sub> , 2CH <sub>2</sub> Cl <sub>2</sub>	32,885	8300	
	21,275	4500	19,400
	29,000	7600	21,300
[PdL(SCN)]CNS	35,140	27,000	27,300
	21,138	3800	20,200
	24,275	4600	23,800
[PdL(SCN)]BPh <sub>4</sub>	21,000	3400	20,450
	24,210	4200	24,400

<sup>a</sup> In dichloroethane. <sup>b</sup> Reflectance spectra.

The visible spectra of the complexes listed in Table 2, are characterised by two intense bands in the 20–29 kK range. Such spectra are typical of five-co-ordinate, essentially trigonal-bipyramidal palladium(II) complexes. These bands are assigned to the one-electron transitions between the orbitals  $e' \rightarrow a'$ , and  $e' \rightarrow a'$ , in the energy-level splitting diagram for  $C_{3v}$  symmetry

shown here. Comparison of the absorption maxima of the complexes in solution and in the solid state indicates that while there is a broad similarity, there is some



stereochemical alteration to the five-co-ordinate geometry on going from one physical state to the other. The band at *ca.* 33 kK is assigned to metal-arsenic or -antimony charge transfer; it is noticeable that its frequency and intensity varies as the co-ordinated anion varies.

Table 3 contains a comparison of the visible spectra on changing the apical donor, L', in the complexes

TABLE 3

Comparison of the ligand-field absorptions on changing the apical donor atom

$[PdX(o-Me_2AsC_6H_4)_3L']^+$	L' = As	L' = Sb
X = Cl	$\nu_1$ 21,400	20,750
	$\nu_2$ 27,400	27,900
Br	$\nu_1$ 20,400	21,215
	$\nu_2$ 24,600	24,110
I	$\nu_1$ 20,800	21,275
	$\nu_2$ 28,600	29,000
SCN	$\nu_1$ 20,700	21,138
	$\nu_2$ 24,400	24,276

Spectrochemical order:  $Cl^- > I^- > Br^- \sim SCN^-$ ;  $I^- > Br^- \sim SCN^- > Cl^-$ .

$[PdX(o-Me_2AsC_6H_4)_3L']^+$  (L = As<sup>4</sup> or Sb). It may be seen that within each group of compounds,  $[PdX(L'TL)]^+$ , the iodide ion exerts an apparently greater ligand-field strength than the bromide ion as shown by the slight shift of the ligand-field bands of both complexes to higher energies in the order  $I^- > Br^-$ . The nephelauxetic effect<sup>13</sup> results from the expanded radial function of the bonding molecular-orbital because the effective nuclear charge ( $Z'$ ) of the metal ion is decreased by delocalisation of the ligand electrons onto the central ion. Along the  $z$ -axis of these molecules lie the L'-Pd-Hal atoms, and both the L' (As or Sb) donors are conventionally thought to be polarisable.<sup>14</sup> Thus, it might have been expected that any competition by the L' or Hal<sup>-</sup> donors would result in an even polarisation of both halides and a normal spectrochemical order,  $Br^- > I^-$ , would obtain. However, because of the observed  $I^- > Br^-$  order (a nephelauxetic order) it is apparent that the palladium ion is exerting an increased polarising effect on the halides, presumably because the 'compressed' L' donor atoms are offering little competition to the metal ion, *i.e.* the normally polarisable As and Sb atoms are now no longer as polarisable because of the compression of the L'-Pd bond. It is pertinent to recall that in the studies by Meek and his co-workers of the systems  $[NiX(Me_2AsCH_2CH_2CH_2)_3L']^+$  (L' = P, As, Sb; X = Hal) where, because of increased chelate

<sup>13</sup> C. K. Jorgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon Press, Oxford, 1962, pp. 134–135.

<sup>14</sup> G. S. Benner and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1399.

chain length no compression of the L'-Ni bond results, a normal  $\text{Cl}^- > \text{Br}^- > \text{I}^-$  spectrochemical order results in each case.<sup>9,14,15</sup> Further evidence for a changeover from spectrochemical to nephelauxetic behaviour for the halide donors is obtained by observing the full series, Table 3 (when  $L' = \text{As}$ :  $\text{Cl}^- > \text{I}^- > \text{Br}^-$ ; when  $L' = \text{Sb}$ :  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ ), from which it is apparent that as the size of  $L'$  becomes bigger and thus compression of L'-Pd increases, the polarisability of  $L'$  falls.

There has been a good deal of interest recently in the mode of bonding of the thiocyanate ion in metal complexes,<sup>16</sup> and it has also been shown that the mode of  $\text{CNS}^-$  bonding can be affected by the nature of non-coordinating anions.<sup>17</sup> We have thus synthesised  $[\text{Pd}(\text{sbtas})(\text{SCN})]\text{BPh}_4$  and  $[\text{Pd}(\text{sbtas})(\text{SCN})]\text{CNS}$ . In the former complex we have assigned infrared bands at 2105, 715, and 420  $\text{cm}^{-1}$  to the  $\nu(\text{CN})$ ,  $\nu(\text{CS})$ , and  $\delta(\text{NCS})$  modes of S-bonded thiocyanate ion.<sup>18</sup> Similarly, in the latter complex the same modes are identified at 2105, 725, and 454  $\text{cm}^{-1}$  respectively. In  $[\text{Pd}(\text{sbtas})(\text{SCN})]\text{CNS}$  vibrations due to uncoordinated  $\text{CNS}^-$  can be identified at 2052  $\nu(\text{CN})$  and 735  $\text{cm}^{-1}$   $\nu(\text{CS})$ . In the case of both complexes the assignments of vibrational modes due to

<sup>15</sup> G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, 1964, **3**, 1544.

<sup>16</sup> D. W. Meek, P. E. Nicpon, and V. I. Meek, *J. Amer. Chem. Soc.*, 1970, **92**, 5351, and references therein.

thiocyanate ion were made by comparing the infrared spectra of the thiocyanate complexes to the chloro-analogues. It should also be pointed out that in a previous paper<sup>4</sup> an erroneous assignment of N-bonded isothiocyanate was made in the  $[\text{Pd}(\text{qasme})(\text{SCN})]\text{CNS}$  complex. Whilst the previous discussion of the electronic spectra of these  $[\text{Pd}(\text{sbtas})\text{X}]^+$  complexes has shown that the normal spectrochemical behaviour of co-ordinated anions is not obtained, it is probable, nevertheless, that the infrared-based assignment of S-bonding in the  $[\text{Pd}(\text{sbtas})(\text{SCN})]^+$  complexes is reinforced by electronic spectral data. Schaffer<sup>19</sup> and Jorgensen<sup>20</sup> have examined the position of -NCS and -SCN in the spectrochemical series and obtained an order  $-\text{NCS}^- > \text{Cl}^- > -\text{SCN}^-$ . The low energy of the electronic spectral bands in the  $[\text{Pd}(\text{sbtas})(\text{SCN})]^+$  complexes seems to confirm the S-bonded assignment.

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<sup>17</sup> J. L. Burmeister and J. C. Lim, *Chem. Comm.*, 1968, 1346.  
<sup>18</sup> J. L. Burmeister, *Co-ordination Chem. Rev.*, 1966, **1**, 205, and references therein.

<sup>19</sup> C. Schaffer, *Chem. Soc. Special Publ.* No. 13, 1959, no. 13.

<sup>20</sup> C. K. Jorgensen, *Acta Chem. Scand.*, 1954, 1505.