*Contribution from the Inorganic Chemistry Laboratory,
University of Oxford, and the School of Chemistry,
University of Bristol, United Kingdom*

The Spectrochemical Position of Antimony(III) Ligands

P. L. Goggin, R. J. Knight, L. Sindellari[1] and L. M. Venanzi[2]

Received September 14, 1970

The electronic spectra of a number of complexes of the types $[n\text{–}Pr_4N][MX_3L]$ *and* cis– *and* trans–$[MX_2L'_2]$ *($M=Pd$ and Pt; $X=Cl$, Br, and I; $L=Me_3P$, Me_3As, and Me_3Sb; $L'=L$ and Et_3P, Et_3As, and Et_3Sb) are reported. It is shown that, for complexes of the above types, the spectrochemical series is as follows:* $Cl < R_2Te < R_2Se \sim R_3Sb < R_2S \sim H_2O < R_3As \sim NH_3 < R_3P < (RO)_3P$.

Introduction

Although there are now a fair number of coordination compounds containing antimony(III) reported in the literature[3] there does not appear to be any published record of their electronic spectra. As it is found that the spectrochemical order of the heavy Group VI ligands is:[4]

$$S > Se > Te$$

and that R_3P exerts a greater ligand field than R_3As,[4,5] it has generally been assumed that the spectrochemical position of antimony(III) would follow that of arsenic.

A study of the electronic spectra of complexes $[MX\{(o\text{–}Ph_2L\,.\,C_6H_4)_3L'\}]Y$ ($L=P$ and As; $L'=P$, As, and Sb; M = Ni, Pd, and Pt; X = anionic ligand; Y = other anion)[6], however, indicates that the apparent spectrochemical order of the heavy Group V donors is:

$$P > As < Sb$$

As it was suspected that this anomalous order might be due to an artefact caused by the structure of the quadridentate ligands, the electronic spectra of a number of complexes containing phosphorus, arsenic and antimony donor atoms in unidentate liganrs were examined. There are only a limited number of classes of compounds suitable for this study and those discussed here are: $[n\text{–}Pr_4N][MX_3L]$ ($M=Pd$ and Pt; $X=Cl$ and Br; $L=Me_3P$, Me_3As, and Me_3Sb), *cis*–$[MCl_2(Me_3A)_2]$ ($M=Pd$ and Pt; $A=P$, As, and Sb), *cis*–$[PtCl_2(Et_3A)_2]$ ($A=P$, As, and Sb) and *trans*–$[MI_2(Me_3A)_2]$ ($M=Pd$ and Pt; $A=P$, As, and Sb).

Experimental Section

Compounds $[n\text{–}Pr_4N][MX_3(Me_3A)]$ ($M=Pd$ and Pt, $X=Cl$ and Br, $A=P$ and As),[7] *cis*–$[MCl_2(Me_3P)_2]$ and *trans*–$[MI_2(Me_3P)_2]$ ($M=Pd$ and Pt),[8] *cis*–$[MCl_2(Me_3As)_2]$ and *trans*–$[MI_2(Me_3As)_2]$ ($M=Pd$ and Pt),[9] *cis*–$[PtCl_2(Et_3A)_2]$ ($A=P$, As, and Sb),[10] $[n\text{–}Pr_4N][MX_3(Me_3Sb)]$ ($M=Pd$ and Pt; $X=Cl$ and Br),[11] *cis*–$[MCl_2(Me_3Sb)_2]$ ($M=Pd$ and Pt),[11] and *trans*–$[MI_2(Me_3Sb)_2]$,[11] were prepared as described in the references above. Their electronic spectra were recorded as described elsewhere.[12]

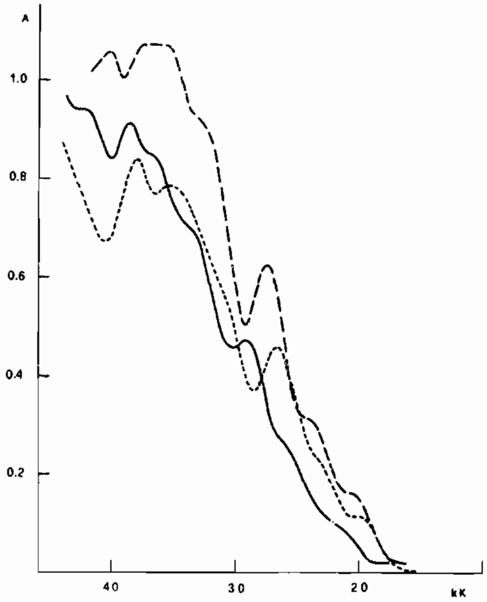

Figure 1. The Reflectance Spectra of Complexes $[n\text{–}Bu_4N][PtBr_3L]$ in arbitrary absorbance units: ——— $L=Me_3P$, — — — $L=Me_3As$, - - - - -. $L=Me_3Sb$.

---

[1] Present address: Istituto di Chimica Generale, Università di Padova, 35100 Padova, Italy.

[2] Author to whom correspondence should be addressed. Present address: Department of Chemistry, State University of New York at Albany, Albany, New York, 12203.

(3) G. Booth, *Adv. in Inorg. Chem. and Radiochem.*, 6, 1 (1964).

(4) J. Chatt, G A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, (A),

(5) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, (A), 1970 (1968).

(6) B. R. Higginson, C. A. McAuliffe, and L. M. Venanzi, *Inorg. Chim. Acta*, 5, 37 (1971), and unpublished observations.

(7) D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.*, (A), 545 (1970).

(8) J. G. Evans, P. L. Goggin, R. J. Goodfellow, and J. G. Smith, *J. Chem. Soc.*, (A), 464 (1968).

(9) R. J Goodfellow, J. G. Evans, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc.*, (A), 1604 (1968).

(10) K. A. Jensen, *Z. anorg. Chem.*, *229*, 255 (1936).

(11) P. L. Goggin *et al.*, to be published.

(12) R. E. Christopher, I. R. Gordon, and L M. Venanzi, *J. Chem. Soc.*, (A), 205 (1968).

Table I. The Visible and Ultraviolet Spectra[a] of Some Palladium(II) and Platinum(II) Complexes.

Complex	Medium	$^1A_{1g}\rightarrow{}^3E_g$	$^1A_{1g}\rightarrow{}^3A_{2g}$	$^1A_{1g}\rightarrow{}^1A_{2g}$	$^1A_{1g}\rightarrow{}^1E_g$	Other bands
$[n\text{—}Bu_4N]_2[PtCl_4]$[14]	[b]	17.86 (7.9)	20.14 (18.2)	24.75 (61.2)	29.72 (79.0)	37.04 (427) [c]
$K[PtCl_3(H_2O)]$[19,16]	H_2O	[d]	21.4 (18.5)	26.1 (17.5)	31.4 (19.5)	ca. 44.00 (ca. 25)
$K[PtCl_3(NH_3)]$[15]	H_2O	20.7 (2.8)	24.1 (19.8)	28.9 (118)	33.3 (74.0)	
$[n\text{—}Pr_4N][PtCl_3(Me_3P)]$	CH_2Cl_2	22.7 (2.3) [c]	27.8 (14.4) [c]	31.3 (544)	36.4 (67.5) [c]	
	HCl	23.5 (0.07) [c]	27.5 (0.20) [c]	31.2 (0.35)	36.7 (0.38)	40.2 (1.01), 43.0 (1.04)
$[n\text{—}Pr_4N][PtCl_3(Me_3As)]$	CH_2Cl_2	[d]	25.5 (12.8) [c]	29.3 (500)	34.2 (500)	
	HCl	22.0 (0.06) [c]	25.7 (0.14) [c]	29.5 (0.32)	34.5 ((0.29)	39.3 (0.86), 41.7 (0.98)
$[n\text{—}Bu_4N]_2[PtBr_4]$[14]	[b]	16.21 (10.2) [c]	18.69 (26.4)	23.15 (126)	26.5 (221) [c]	29.67 (640),[c] 33.11 (3,650),[c] 35.84 (8,100)
$[n\text{—}Pr_4N][PtBr_3(Me_3P)]$	CH_2Cl_2	[d]	[d]	29.2 (590)	33.5 (0.69) [c]	37.3 (2,380),[c] 38.5 (2,500) [c]
	HCl	21.5 (0.09) [c]	26.5 (0.27) [c]	29.3 (0.47)		36.8 (0.85),[c] 38.5 (0.91), 42.5 (0.94) [c]
$[n\text{—}Pr_4N][PtBr_3(Me_3As)]$	CH_2Cl_2	[d]	24.5 (130) [c]	27.6 (610)		
	HCl	20.5 (0.16) [c]	24.5 (0.32) [c]	27.5 (0.63)	33.3 (0.93) [c]	35.5 (1.07), 37.5 (1.07), 40.1 (1.06)
$[n\text{—}Pr_4][PtBr_3(Me_3Sb)]$		[d]	23.0 (180) [c]	27.2 (830)	31.0 (2,000) [c]	36.0 (6,750), 39.1 (10,220)
		20.2 (0.12)	23.2 (0.22) [c]	26.8 (0.46)	30.5 (0.53) [c]	35.1 (0.79), 38.0 (0.84)
$K_2[PdCl_4]$[20]	[e]	18.0 [f]	21.5		31.5 [f]	36.5
	[g]	17.0 (19) [h,i]	20.0 (67)	22.6 (128),[h] 23.0 [z]	29.5 (67)	36.0 (12,000),[21] 44.9 (30,000) [21]
$[n\text{—}Pr_4N][PdCl_3(Me_3P)]$	CH_2Cl_2	[d]		26.9 (1.190) [j]		35.5 (7,970)
	HCl	[d]		27.2 (0.55) [j]		34.9 (0.55)
$[n\text{—}Pr_4N][PdCl_3(Me_3As)]$	CH_2Cl_2	[d]	24.5 (790)	25.7 (790)		
	HCl	[d]	24.2 (0.61)	26.2 (0.62)		
$[n\text{—}Pr_4N][PdCl_3(Me_3Sb)]$	CH_2Cl_2	[d]	23.5 (800)	26.0 (800)		
	HCl	[d]	23.1 (0.60)	26.3 (0.57)	31.2 (1.07)	
$K_2[PdBr_4]$[21]	H_2O	[d]	[d]	[d]	30.1 (10,400)	40.5 (30,400)
	[e]	16.0	20.0	26.0		
$[n\text{—}Pr_4N][PdBr_3(Me_3P)]$	CH_2Cl_2	[d]	25.0 (1,458) [c]	27.5 (2,169) [c]	30.9 (4,700)	
	HCl	[d]	[d]	27.0 (0.73) [c]	30.5 (0.9)	36.3 (0.91),[c] 32.9 (1.00), 41.3 (0.92) [c]
$[n\text{—}Pr_4N][PdBr_3(Me_3As)]$	CH_2Cl_2	[d]	23.5 (1,802) [c]	26.0 (2,951) [c]	29.5 (7,820)	39.3 (25,000)
	HCl	18.0 (0.21) [c]	23.0 (0.78) [c]		29.0 (1.02)	37.5 (1.05)
$[n\text{—}Pr_4N][PdBr_3(Me_3Sb)]$	HCl	17.0 (0.18) [c]	22.5 (0.64)		28.8 (0.86)	36.9 (0.90)
cis—$[PtCl_2(Me_3P)_2]$	CH_2Cl_2	[d]	[d]	32.2 (410)	38.6 (2,020)	
	HCl	[d]	[d]	32.2 (0.52)	38.2 (0.52)	42.2 (0.57)
cis—$[PtCl_2(Et_3P)_2]$	CH_2Cl_2	[d]	[d]	31.0 (354)	38.0 (1,990)	
	HCl	[d]	[d]	31.5 (0.54)	38.0 (0.74)	
cis—$[PtCl_2(Me_3As)_2]$	CH_2Cl_2	[d]	[d]	28.5 (280)	34.8 (1,390) [c]	
cis—$[PtCl_2(Et_3As)_2]$	CH_2Cl_2	[d]	[d]	28.2 (230)	34.0 (1,084) [c]	
	HCl	[d]	[d]	28.2 (0.40)	33.7 (0.64)	
cis—$[PtCl_2(Me_3Sb)_2]$	CH_2Cl_2	[d]	[d]	27.5 (340) [c]	32.3 (2,480)	38.5 (6,000),[c] 41.2 (12,000)
	HCl	[d]	[d]	27.5 (0.49) [c]	34.0 (0.95) [c]	36.0 (1.0), 38.5 (0.97) [c]
cis—$[PtCl_2(Et_3Sb)_2]$	CH_2Cl_2	[d]	[d]	26.7 (400)		
	HCl	[d]	[d]	27.5 (0.24)	31.8 (0.40)	33.7 (0.64)
trans—$[PtI_2(Me_3P)_2]$	CH_2Cl_2	[d]	[d]	30.4 (2,110)	35.2 (6,860)	
	HCl	23.4 (0.13)	[d]	29.8 (0.61)	34.4 (0.64)	32.5 (0.61),[c] 36.5 (0.59) [c]
trans—$[PtI_2(Me_3As)_2]$	CH_2Cl_2	[d]	[d]	29.7 (3,720)	35.0 (7,210)	33.0 (3,530),[c] 40.0 (13,710)[c]
	HCl	21.7 (0.28)	26.0 (0.69) [c]	29.0 (1.04)	34.0 (1.00)	36.8 (0.94)
trans—$[PtI_2(Me_3Sb)_2]$	CH_2Cl_2	[d]	[d]	27.3 (6,580)	33.8 (4,650) [c]	
	HCl	[d]	23.5 (0.68) [c]	26.5 (0.95)		36.0 (0.98)
cis—$[PdCl_2(Me_3P)_2]$	HCl	[d]	[d]	30.5 (0.66)		39.5 (0.74)
cis—$[PdCl_2(Me_3As)_2]$	HCl	[d]	[d]	28.0 (0.79)		37.5 (0.88)
cis—$[PdCl_2(Me_3Sb)_2]$	HCl	[d]	[d]	26.7 (0.75)	33.2 (0.95) [c]	37.5 (0.83),[c] 42.0 (0.83) [c]
trans—$[PdI_2(Me_3P)_2]$	CH_2Cl_2	[d]	25.8 (5,400)	30.3 (10,200)	34.9 (20,200)	38.0 (22,750),[c] 40.3 (44,000)
	HCl	20.5 (0.35) [c]	25.0 (0.90)	29.7 (0.82)	33.7 (0.83)	
trans—$[PdI_2(Me_3As)_2]$	CH_2Cl_2	[d]	24.4 (4,900)	29.0 (6,600)	33.6 (14,500)	37.5 (15,950),[c] 39.5 (23,300)
	HCl	19.5 (0.56) [c]	24.0 (1.03)			
trans—$[PdI_2(Me_3Sb)_2]$	CH_2Cl_2	[d]	22.2 (4,200)	29.0 (2,230) [c]	32.5 (6,900)	36.5 (7,300),[c] 38.0 (11,500)
	HCl	18.0 (0.44) [c]	21.5 (0.71)	30.2 (0.66) [j]		

[a] Band maxima, ν, in kK and, in brackets, their intensities: (1) for solutions, ε, l. mole^{-1} cm^{-1}; (2) for solids, an arbitrary absorbance scale. [b] 2-Methyltetrahydrofuran/propionitrile (2:1). [c] Shoulder (ε is for value of ν given). [d] Not recorded or observed. [e] Solid reflection spectrum. [f] Shoulder. [g] Single crystal. [h] *xy*-Polarized. [i] Additional band at 18.0 (7). [z] Polarized. [j] Broad maximum, probably containing more than one band.

Results and Discussion

The spectral data are given in the Table I. The electronic spectra of $K_2[PdCl_4]$,[13] and of $[n\text{—}Bu_4N]_2[PtX_4]$ (X = Cl and Br),[13,14] have been extensively studied and satisfactory assignments have been made for the observed transitions. Some spectral assignments have also been made for complexes $[PtCl_3(NH_3)]^-$,[15] $[PtCl_3(H_2O)]^-$,[16] *cis*— and *trans*—$[PtCl_2(NH_3)_2]$,[15]

---

(13) H. Basch and H. B. Gray, *Inorg.Chem.*, 6, 365 (1967).

(14) W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 5721 (1968).

(15) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

(16) D. S. Martin, A C. S. Advances in Chemistry Series, in the press.

trans–$[PtCl_2\{(n–C_5H_{11})_2NH\}_2]$,[15] *trans*–[$PtCl_2$L(piperidine)] (L = piperidine, $(MeO)_3P$, *n*–Pr_3P, *n*–Pr_3As, Et_2S, Et_2Se, and Et_2Te),[17] and *trans*–$[PtX_2L_2]$ (L = di–*n*–octylamine, 4–*n*–pentylpyridine, *n*–Bu_3P and *n*-Bu_3As; X = Cl, Br, and I).[18] Assignments were made using literature data and pattern of absorption as shown in Figure 1. As can be seen from the Table and the Figure, in all the sets of compounds examined the spectrochemical sequence for the heavy Group V donor atoms is

$$P > As > Sb$$

supporting the idea that the anomalous spectrochemical series in complexes of the quadridentate ligands mentioned earlier is caused by distortions in the complexes.[6]

Furthermore, our results and the literature data quoted earlier show that, in compounds of platinum(II), the spectrochemical series is: $Cl < R_2Te < R_2Se \sim R_3Sb < R_2S \sim H_2O < R_3As \sim NH_3 < R_3P < (RO)_3P$.

It is interesting to note that in the platinum(II) complexes oxygen and sulphur ligands appear to have come closer in spectrochemical position than they are in other metal ions. Speculations as to the reasons for this effect must await further study.

(17) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 1047 (1959).
(18) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, 1970 (1968).
(19) L. I. Elding, Dissertation, Lund 1970, Carl Bloms Bokthycheri A. B. p. 22.
(20) P. Day, A. F. Orchard, A. J. Thompson, and R. J. P. Williams, *J. Chem. Phys.*, *42*, 1973 (1965).
(21) H. B Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, *85*, 260 (1963).
(22) A. B. P. Lever, « Inorganic Electronic Spectroscopy », Elsevier, Amsterdam 1968, p. 204.