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Some Geometrical Consideration on Complexes of Tripod-Like Ligands

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Calculations of ligand and complex geometry for trigonal bipyramidal and octahedral species containing tripod-like ligands $(o\text{–}R_2L\,.\,C_6H_4)_3L'$ ($L = N$, P, and As; $L' = P$, As and Sb) and $(o\text{–}RL\,.\,C_6H_4)_3P$ ($L = S$ and Se) are reported. It is shown that, in many cases, bond-distances and angles have to be severely distorted to form the complexes. The extent of the distortions are related to a number of physical and chemical properties of the complexes.

Introduction

The coordinating properties of potentially quadridentate ligands of the types $L'(YLR_2)_3$, I, and $L'(YLR)_3$, II, have been extensively studied.[1] Those discussed in the present paper, generically referred to as $L'L_3$, are:

	L′	L	Y	R	Notation	Ref.
I(a)	P	P	o–C_6H_4	Ph	QP	2
(b)	As	P	o–C_6H_4	Ph	ASTP	3
(c)	Sb	P	o–C_6H_4	Ph	SBTP	3
(d)	P	As	o–C_6H_4	Ph	PTAS	3
(e)	P	As	$CH_2CH_2CH_2$	Me	ptas (TAP)	4
(f)	As	As	o–C_6H_4	Ph	QAS	1_c
(g)	As	As	o–C_6H_4	Me	Qas	5
(h)	Sb	As	o–C_6H_4	Ph	SBTAS	3
(i)	P	N	o–C_6H_4	Me	Ptn	6
(j)	N	P	CH_2CH_2	Ph	nTP (NP_3)	7
II(a)	P	S	o–C_6H_4	Me	Pts (TSP)	8
(b)	P	Se	o–C_6H_4	Me	Ptse (TSeP)	3

These ligands form complexes with a variety of coordination numbers and geometries although the majority of them are either trigonal bipyramidal, of the type $[M^{n+}X(L'L_3)]^{(n-1)+}$, (*e.g.*, for $Y = o\text{–}C_6H_4$, see Figure 1) or octahedral, of the type $[M^{n+}X_2(L'L_3)]^{(n-2)+}$, (*e.g.* for $Y = o\text{–}C_6H_4$, see Figure 2). Their study shows that some of the structural features and physical properties are not readily accounted for by consideration of the electronic properties of the donor atoms alone and, therefore, calculations were undertaken to establish to what extent these unexpected properties might be caused by geometric factors imposed by the ligand structure.

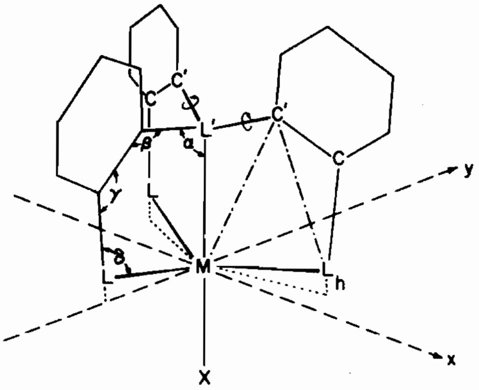

Figure 1. A schematic representation of the structure of trigonal bipyramidal complexes $[MX(L'L_3)]Z$.

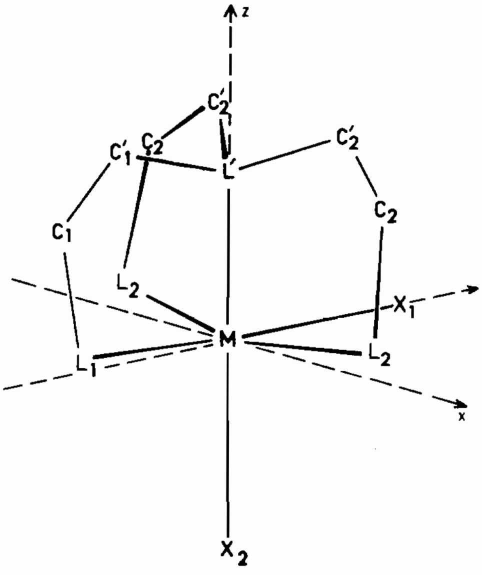

Figure 2. A schematic representation of the structure of pseudooctahedral complexes $[MX_2(L'L_3)]$.

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(2) J. G. Hartley, D. G. E. Kerfoot, and L. M. Venanzi, *Inorg. Chim. Acta*, *1*, 145 (1967) and references quoted therein.

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(6) (a) H. P. Fritz, I. R. Gordon, K. E. Schwarzhans, and L. M. Venanzi, *J. Chem. Soc.*, 5210 (1965). (b) R. E. Christopher, I. R. Gordon, and L. M. Venanzi, *J. Chem. Soc.*, (A), 205 (1967).

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(8) G. Dyer and D. W. Meek, *Inorg. Chem.*, *6*, 149 (1967) and references quoted therein.

1. Trigonal Bipyramidal Complexes

The main observations which are not easily reconciled with the electronic properties of the ligands are:

(1) Molecular structure determinations show that the metal ions in $[CoCl(QP)][BPh_4]$,[9] $[NiCl(Pts)](ClO_4)$,[10] $[PtI(QAS)][BPh_4]$,[11] and also $[NiI(nTP)]I$,[7] reside a significant distance below the plane of the three equatorial atoms. On the other hand, the metal atom in $[Ni(CN)(ptas)](ClO_4)$,[12] lies above the plane of the equatorial arsenic atoms.

(2) The ligand $(o\text{–}Me_2N\,.\,C_6H_4)_3P$ (Ptn) forms tetrahedral complexes with cobalt(II) and nickel(II),[6b] and square planar compounds with palladium(II) and platinum(II),[6a] and in each case the phosphorus and only one nitrogen atom is coordinated to the metal atom.

(3) The ligand SBTP forms more than one type of complexes with palladium(II) and platinum(II).[13]

(4) The electronic spectra of the $[NiCl(L'L_3)]^+$ ($L'L_3$ = QP, ASTP, SBTP) cations show that the $^1A_1 \rightarrow a^1E$ transition decreases in energy in the order

$$QP \gtrsim SBTP > ASTP$$

as the apical atom is changed,[3] in contrast to the spectrochemical order $R_3P > R_3As > R_3Sb$ found for complexes of the monodentate ligands R_3L.[14]

In the light of the above observations, calculations concerning the relative positions of metal and quadridentate ligand donor atoms were carried out for known and hypothetical complexes of the ligands $(o\text{–}R_2L\,.\,C_6H_4)_3L'$ (L = N, P and As; L' = P, As and Sb) and $(o\text{–}MeL\,.\,C_6H_4)_3L'$ (L = S and Se). Such calculations have now become meaningful because of the wealth of acceptable X-ray data which indicate that there are reliable ranges for bond lengths and bond angles in complexes formed by the ligands of types I and II, as most of the parameters are within narrow ranges. Calculations were carried out on complexes where Y = $o\text{–}C_6H_4$ because (1) the rigidity of the bridging group makes them more reliable than for similar ligands where Y is an alkyl chain (*e.g.* I(e) and I(j)); and (2) there are three X-ray structure determinations of trigonal bipyramidal ions $[M^{2+}X(L'L_3)]^+$ which allow a check of the calculations.

Calculation and Results

The calculation was based upon a model in which it is assumed that all the complexes have C_{3v} microsymmetry with planar $M\text{–}L'\text{–}o\text{–}C_6H_4\text{–}L$ rings, as this is the case in all such compounds studied by X-ray diffraction. Thus only one chelate ring need be considered. Angles and atoms are labelled as shown in Figure 1. Metal-donor atom distances, L(or L')–C_{arom} distances and bond angles M–L–C_{arom} were obtained, where possible, from X-ray data on complexes of monodentate ligands. The parameters used are given

Table I. Bond length used in calculation (in Å)

L (or L')	L–C_{arom}	L–Ni	L–Pt
N	1.44 [a]	1.96-2.16 [b]	2.05 [c]
P	1.83 [d]	2.24 [e]	2.28 [f]
As	1.95 [g]	2.29 [h]	2.38 [i]
Sb	2.12 [j]	2.49 [j]	2.56 [j]
S	1.80 [k]	2.20 [l]	2.29 [m]
Se	1.93 [n]	2.27 [o]	2.36 [o]

[a] An average, taken from such compounds $[p\text{–}CH_3C_6H_4\,.\,NH_3]Cl$, (1.45(1) Å) (G. von Eller, *Bull. Soc. Fr. Mineral Cristallogr., 78*, 257 (1955)); Ph_3N, (1.42(4) Å) (Y. Sasaki, K. Kimura, and M. Kubo, *J. Chem. Phys., 31*, 447 (1959)), and $CH_3\,.\,CONPh_2$ (ave 1.44(1) Å). (W. R. Kringbaum, R. J. Roe, and J. D. Woods, *Acta Crystallogr., B-24*, 1304 (1968)); [b] May be as low as 1.96 Å, (see the difference in bond-length between *h* and *i*), and unlikely to be more than 2.15 Å, *e.g.*, $[Ni(en)_3][NO_3]_2$, (L. N. Swink and M. Atoji, *Acta Crystallogr., 13,* 639 (1960)); [c] An average, taken from such compounds as *cis*- and *trans*–$[PtCl_2(NH_3)_2]$, (ave values 2.01(4) Å and 2.05(4) Å respectively) (G. H. W. Milburn and M. R. Truter, *J. Chem. Soc.*, (A), 1609 (1966)); $K[PtCl_3(NH_3)]\,.\,H_2O$ (2.06(2) Å, (V. P. Jeannin and D. R. Russell, *Inorg. Chem.*, 9, 778 (1970)); [d] An average, taken from such compounds as $[Mn(CO)_2(NO)(PPh_3)_2]$, (ave. 1.84(1) Å), (J. H. Enemark and J. A. Ibers, *Inorg. Chem., 6,* 1575 (1967)); $[RhH(CO)(PPh_3)_3]$ (ave. 1.83(1) Å), (S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr., 18,* 511 (1965)); [e] From $[Ni(CN)_2\{P(Ph)(CH_3)_2\}_3]$, (ave. 2.24(3), (J. K. Stalik and J. A. Ibers, *Inorg. Chem., 8,* 1090 (1969) and from *trans*–$[NiBr_2Ph_2BzP)_2]$ (2.263(7)), (B. T. Kilbourn and H. M. Powell, *J. Chem. Soc.* (A), 1688 (1970)); [f] An average, taken from such compounds as *trans*–$[PtCl_2(PPhMe_2)_2]$ (2.30(2) Å) and *trans*–$[PtBr_2(PPhMe_2]$ (2.32(4) Å), (G. G. Messmer and E. L. Amma, *Inorg. Chem., 5,* 1775, (1966)); *cis*–$[PtCl_2\{P(CH_3)_3\}_2]$ (ave. 2.25(1) Å), (E. L. Amma and J.(A. Ibers, *Inorg. Chem., 6,* 725 (1966)). Even $[Pt_4(PPhMe_2)_4(CO)_5]$, (R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Amer. Chem. Soc., 91,* 1574 (1969)) has a similar Pt–P bond length; [g] An average, taken from $[RhCl_3\{o\text{–}CH_3O\,.\,C_6H_4\,.\,AsMe_2\}_2]$, (ave. 1.95(8) Å), (R. Graziani, G. Bombieri, L. Volponi, C. Panattoni, and R. J. H. Clare, *J. Chem. Soc.*, (A), 1236, (1969)); $[NiI_2(Das)_2]$ (ave. 1.95(4) Å), (N. C. Stephenson, *Acta Crystallogr., 17,* 592 (1964)); [h] From the structure of $[NiI_2(Das)_2]$ (ave. 2.293(2)), (N. C. Stephenson, *loc. cit.*,); [i] From the structures of $[PtCl_2(Das)_2]$ (ave. 2.375(4) Å), (N. C. Stephenson, *Acta Crystallogr., 17,* 1517, (1964)), and $[PtI_2(Das)]$ (2.38 Å), (*idem, J. Inorg. Nucl. Chem., 24,* 791 (1962)); [j] An estimate. No suitable data on antimony bond distances were found. Examination of the bond lengths of compounds XY_3 (X=P, As, Sb; Y=H, Cl, Br, CH_3, CF_3) (L. E. Sutton. Tables of *Interatomic Distances,* Chem. Soc. London, 1958 and Supplement 1965) showed that on average the bond lengths of antimony compounds are 0.28 Å longer than those in the corresponding phosphorus compound, and 0.17 Å longer than in the corresponding arsenic compound; [k] From the structure of diphenyl disulfide (ave. 1.80(1) Å), (J. D. Lee and M. W. R. Bryant, *Acta Crystallogr.*, B-25, 2094, (1969)); [l] For discussion, see L. P. Haugen and R. Eisenberg, *Inorg. Chem., 8,* 1077 (1969). Other data from $[Ni(C_{20}H_{19}PS_2)I_2]$ ($Ni\text{–}S_2$ = 2.19(1) Å), (D. W. Meek and J. A. Ibers, *Inorg. Chem., 8,* 1915 (1969), and $[NiS(CH_2CH_2S)_2]_2$ ($Ni_1\text{–}S_2$, $Ni_2\text{–}S_3$; (ave. bond length = 2.15 Å), (D. C. Goodall and D. S. Moss, *Chem. Comm.*, 325 (1969)); [m] No suitable direct measurements. The Pt(II) radius was estimated to be *ca.* 0.09 Å larger than that of Ni(II) (c.f., *h* and *i*); [n] From the structure of diphenyl diselenide (1.93(5) Å), (R. Marsh, *Acta Crystallogr., 5,* 458 (1952)); [o] Estimated as 0.02 Å less than the corresponding distances for arsenic, (c.f., *d* and *n*).

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(12) D. L. Stevenson and L. F. Dahl, *J. Amer. Chem. Soc., 89,* 3424 (1967).

(13) (a) C. A. McAuliffe, R. J. Mynott, and L. M. Venanzi, unpublished observations; (b) C. A. McAuliffe, D. Phil. Thesis, Oxford 1967; (c) R. J. Mynott, B Sc. Thesis, Oxfird 1968.

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in Table I. Using this data, one can obtaine an idea of the « match » or « mismatch » between the relative positions of metal and donor atoms, compared with their predicted positions in corresponding complexes of monodentate ligands.

The model is constructed by placing the metal, M, at the origin and taking the appropriate M–L′ distance (where L′ is that donor atom in a monodentate ligand), to obtain the position of L′ in the hypothetical $[MX(L'L_3)]^+$ cation. The chelate ring is then defined by taking the appropriate L′–C_{arom} distance at an angle α (also obtained from X-ray data of structures of complexes with monodentate ligands), and adding the C–C′ distance, taking β and γ as 120°. Once the C–L distance is fixed, one obtains the relative positions of the metal ion and of the equatorial donor atoms. This procedure was carried out for a variety of metal ions and ligands, and the results are given in Table II.

Table II. Mismatch Parameters for Some Trigonal Bipyramidal Complexes of Tripod-Like Ligands

Ligand	Parameters [b]	Nickel(II) ℓ(Å)	Nickel(II) h(Å)	Platinum(II) [a] ℓ(Å)	Platinum(II) [a] h(Å)
QP	c	0.43	0.39	0.40	0.43
	d	0.32	0.25	0.28	0.29
	e	0.20	0.12	0.16	0.16
	f	0.29	0.34	0.25	0.38
	g	0.14	0.30	0.11	0.34
	h	0.24	0.41	0.21	0.45
ASTP	c	0.56	0.49	0.54	0.58
SBTP	c	0.76	0.76	0.74	0.83
PTAS	c	0.36	0.27	0.24	0.31
QAS	c	0.48	0.37	0.33	0.46
SBTAS	c	0.68	0.64	0.61	0.71
Ptn	c, i	0.66	0.78	0.78	0.82
Ptn	c, j	0.85	0.78		
Pts	c	0.48	0.41	0.39	0.45
Ptse	c	0.38	0.29	0.30	0.33

[a] As the radii of palladium(II) and platinum(II) appear to be practically identical these parameters apply also to palladium(II) complexes. [b] The values of bond-lengths given in Table I have been used. [c] $\alpha=115°$, $\beta=120°$ and $\gamma=120°$. [d] $\alpha=112°$, $\beta=120°$ and $\gamma=120°$. [e] $\alpha=109°$, $\beta=120°$ and $\gamma=120°$. [f] $\alpha=115°$, $\beta=117°$ and $\gamma=120°$. [g] $\alpha=115°$, $\beta=114°$ and $\gamma=120°$. [h] $\alpha=115°$, $\beta=120°$ and $\gamma=114°$. [i] For Ni–N=1.96Å. [j] For Ni–N=2.15 Å.

It is found using this model that the ligands $(o\text{–}R_2L\,.\,C_6H_4)_3L'$ and $(o\text{–}MeL\,.\,C_6H_4)_3P$ do not form idealized trigonal bipyramids in which metal and equatorial donor atoms are co-planar. In fact (1) the bond M–L would have to be longer than that found in complexes containing monodentate ligands and (2) the metal atom would be below the plane of the three equatorial atoms. Distortions from regular structure can then be analyzed in terms of (1) a length mismatch, ℓ, i.e., the difference between the calculated M–L distance and that expected for an M–L bond involving the monodentate ligand and (2) a height mismatch, h, i.e. the distance between the metal atom and the plane defined by the equatorial ligands. It must be emphasized here that the relative importance of these parameters, which are not orthogonal, is unknown. Furthermore, it should be noted that if ℓ were zero, the M–L bond would probably be « bent », and if h were zero a considerable distortion of C_6H_4–L–R and R–L–R angles would be required to direct the lone pair of an equatorial atom along the M–L line.

The mismatch parameters ℓ and h will change as the bond lengths and angles alter as shown in Table II. The main trends are:

(1) an increase in the radius of metal M (*i.e.*, Ni < Pd ∼ Pt) for a given L′ and L, results in a decrease in ℓ and an increase in h;

(2) an increase in the radius of L′ (*i.e.*, P < As < Sb) for a given M and L, causes an increase in both ℓ and h;

(3) an increase in the radius of L (*i.e.*, N < S < P < As), for a given M and L′, decreases both ℓ and h;

(4) a decrease in an angle α reduces both ℓ and h effectively;

(5) a reduction of β decreases ℓ but only diminishes h by a small amount;

(6) a reduction of γ decreases ℓ somewhat but increases h.

Thus, for a given complex it is expected that the mismatch parameters will be reduced by changes in angles α and β rather than γ. In terms of bond lengths, a reduction in M–L′ will have a favourable effect on the overlap in all three M–L bonds, whereas changes in L′–C′, C′–C, and C–L lengths will have a small effect on the ℓ and h parameters for only one equatorial atom L.

Discussion

The validity of this model can be discussed in terms of the experimental data for the complexes $[CoCl(QP)][BPh_4]$,[9] $[NiCl(Pts)](ClO_4)$,[10] and $[PtI(QAS)][BPh_4]$.[11] Their relevant structural data are given in Table III.

It is found that in these complexes the parameters ℓ and h are reduced by (1) shortening the M–L′ bonds and (2) reducing angles α and β, and also γ in the cobalt complex. The angle δ (M–L–C) have the unusually small values of 105-106° whereas similar angles in a complex of a monodentate ligand would be near 115°. The optimum overlap in the M–L bond must therefore be accomplished by appropriate changes in the angles M–L–R. For the cations $[CoCl(QP)]^+$ and $[PtI(QAS)]^+$ the average values for these angles are 118.2(7)° and 120.2(9)° respectively. It is apparent, therefore, that the mismatch for a tripod-like ligand with a given metal atom can be reduced by a number of distortions involving angles and the M–L′ bond rather than by a large change in just one structural parameter. Thus calculations on complexes of ligands $(o\text{–}R_2L\,.\,C_6H_4)_3L'$ and $(o\text{–}MeL\,.\,C_6H_4)_3P$ indicate that the metal atom *should* reside below the plane of the equatorial donor atoms and this is found experimentally. On the other hand, Stevenson and Dahl[12] found the nickel atom in $[Ni(CN)(ptas)](ClO_4)$ to be 0.19 Å above the plane of the three equivalent

Table III. Selected Bond lengths and Angles for Some $[MX(L'L_3)]Z$ Complexes

	$[CoCl(QP)][BPh_4]$ [9]	$[NiCl(TSP)](ClO_4)$ [10]	$[PtI(QAS)][BPh_4]$ [11]
ML′ (Å)	2.057(4)	2.113(7)	2.306(3)
Mean L′C′ (Å)	1.79(2)	1.80(2)	1.93(3)
Mean CL (Å)	1.79(2)	1.78(2)	1.98(3)
Mean ML (Å)	2.286(4)	2.267(7)	2.455(3)
Mean α	112.2(5)°	110.1(6)°	112.4(9)°
Mean β	114.5(1.3)°	116.2(1.3)°	116.0(2.1)°
Mean γ	115.2(1.4)°	118.9(1.3)°	119.7(2.1)°
Mean δ	105.9(7)°	105.5(6)°	105.3(9)°

Table IV. Relative Lengths of Axial and Equatorial Bonds in Some Trigonal Bipyramidal Complexes

Compound	d^n	Mean Axial Bond Length (Å)	Mean Equatorial Bond Length (Å)	Ref.
$[Ni(CN)_5]^{3-}$	d^8	1.839(13)	1.936(13)	15
$[Ni\{P(OCH)_3(CH_2)_3\}_5]_2^{+}$	d^8	2.14(1)	2.19(1)	16
$[Co(CNMe)_5]^+$	d^8	1.84(2)	1.88(2)	17
$[CuCl_5]^{3-}$	d^9	2.2964(12)	2.3912(13)	18

atoms, and attributed the difference from $[PtI(QAS)][BPh_4]$ to minimization of non-bonding atomic repulsions without undue weakening of the metal-ligand bonds. Haugen and Eisenberg,[10] however, suggested that chelate ring size is the determining factor. While the explanation of Stevenson and Dahl may be correct for $[Ni(CN)(ptas)][ClO_4]$, it is probable that the position of the nickel atom above the equatorial plane in this complex is related to the use of three bridging carbons in the ligand $(Me_2AsCH_2CH_2CH_2)_3P$ because in $[NiI(nTP)]I$ the nickel atom is 0.12 Å below the equatorial plane.[7]

The Ni–P′ bond length in $[NiCl(Pts)](ClO_4)$ is 2.113(7) Å but is 2.206(8) Å in $[Ni(CN)(ptas)](ClO_4)$. Haugen and Eisenberg[10] considered that strong metal-cyanide $d\pi$–$d\pi$ bonding would reduce the π-overlap in the Ni–P bond of the ptas complex resulting in a bond length difference of *ca.* 0.1 Å from the Ni–P bond in the Pts complex, where the central phosphorus atom is *trans* to a weak π-donor chlorine atom. Our approach suggests that π-bonding arguments need not be invoked, and that the short nickel-phosphorus bond in $[NiCl(Pts)](ClO_4)$ is related to (1) the different electronic nature of axial and equatorial bonds in trigonal bipyramidal complexes and (2) the steric requirements of the quadridentate ligands. It is found that in low-spin-d^8-, and d^9-transition metal complexes with D_{3h} symmetry the axial bonds are somewhat shorter (0.05-0.10 Å) than the equatorial bonds (see Table IV). However, M–L′ axial bonds in $[MX(L'L_3)]^+$ complexes are shorter (0.03-0.12 Å) than M–L′ *axial bonds in complexes of monodentate ligands* (see Tables III and IV). It is also interesting to note that M–L equatorial bonds in complexes $[MX(L'L_3)]^+$ are larger than M–L equatorial bonds in complexes of monodentate ligands (see Tables III and IV).

The mismatch parameters ℓ and h are large for nickel(II), palladium(II), and platinum(II) complexes of Ptn, and are also quite large for complexes of SBTP. The ligand Ptn only forms square planar complexes with palladium(II) and platinum(II),[6a] and gives tetrahedral compounds with cobalt(II) and nickel(II),[6b] with the phosphorus atom and one nitrogen atom bonded in each case. Fritz *et al.*[6a] considered that this was due to the deactivation of the weak dimethylamino nitrogen atoms by electron withdrawal of the two coordinated donor atoms, transmitted through the phenylene ring. The mismatch, however, is so large that the bidentate nature of Ptn in the above complexes is likely to be of steric origin.

The mismatch between second and third transition row elements and SBTP is somewhat less than for Ptn, but the compounds $[MX(SBTP)]X$ (M = Pd, Pt; X = halogen) show considerable variation in stereochemistry, and the ligand does not readily form trigonal bipyramidal cations.[13]

The spectrochemical series for monodentate phosphines, arsines and stibines is $P > As > Sb$.[14] When these atoms are the central atoms of a tripod-like ligand forming a trigonal bipyramidal complex, the M–L′ distances and the M–L′–C′ angles will differ from those complexes containing Ph_3P, Ph_3As, and Ph_3Sb. The energy of the a_1 level will be sensitive to the specific overlap of the central donor atom lone pair and the metal s and d_{z^2} orbitals, whereas the e_a and e_b sets will be less affected.[19] As the M–L′ bond lengths and M–L′–C′ angles in $[MX(L'L_3)]^+$ cations may not vary regularly in the sequence P, As, Sb, then the relative order of the ${}^1A_1 \rightarrow a{}^1E$ ($e_a \rightarrow a_1$) transition need not be $PL_3 > AsL_3 > SbL_3$. In fact the energies of this transition for $[NiCl(L'L_3)][BPh_4]$ ($L'L_3$ = QP, ASTP, SBTP) are,[3]

QP >	SBTP >	ASTP
17.2	16.8	16.3 kK

and for $[NiCl(L'L_3)][BPh_4]$ ($L'L_3$ = PTAS, QAS, SBTAS) the order is[3]

PTAS >	SBTAS >	QAS
16.4	16.3	16.0 kK

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2. Pseudo-Octahedral Complexes

Complexes of the type $[M^{n+}X_2(L'L_3)]^{(n-2)+}$ exhibit fewer unusual features.[1c] Thus, the energies of the ligand field bands in complexes $[RuCl_2(L'L_3)]$ ($L'L_3$ = QAS, PTAS and SBTAS) follow the sequence

PTAS > QAS > SBTAS.[20]

The only apparent anomaly is the failure to obtain the complex $[RuCl_2(SBTP)]$.[20] As calculations on the trigonal bipyramidal complexes showed that SBTP is a ligand which gives rise to very large mismatch parameters, calculations were attempted also on octahedral complexes of the above type.

Calculation and Results

These were based on the structural data obtained for $[RuBr_2(QAS)]$ which has a geometry of the type shown in Figure 2. The main features relevant to the following discussion are:[21]

(1) The M–L′ bond is unusually short (2.308(5)Å), as would be expected from the preceding calculation;

(2) The unique ruthenium-terminal arsenic bond $M–L_2$ is bent towards L′ so that the $L_1–M–L'$ bond-angle is 87°, and

(3) the M, L′, C_1', C_1, L_1, X_1 and X_2 atoms are coplanar.

It was found that the angles around the central arsenic atom are not appreciably different from those found in trigonal bipyramidal complexes, but that the ruthenium atom is not coplanar with the two *trans* bridging phenylene rings. The average M–L′–C′ angle is 111.9(1.1)°, which is comparable to the corresponding mean angles in $[CoCl(QP)]^+$, $[NiCl(Pts)]^+$ and $[PtI(QAS)]^+$ cations. Similarly, the mean L′–C′–C angle is 113.0(2.6)°, whereas the C′–C–L angles remain close to 120°.

The two $M–L_2$ bonds are bent about 7° towards L′ and 7° towards X_1 (see Figures 1 and 2). Thus, on formation of the pseudo-octahedral complex $[RuBr_2(QAS)]$, the trigonal symmetry of the ligand QAS, which is present in its trigonal bipyramidal complexes, is removed by rotation of the C′–C–L plane relative to the M–L′–C′ plane, by an angle Θ about the L′–C′ bond (see Figure 1), *i.e.*, the two L atoms swing toward the x-axis.

Assuming values of $\alpha = 115°$, $\beta = \gamma = 120°$, Ru–P′ = 2.30 Å, Ru–As′ = 2.40 Å and Ru–Sb′ = 2.55 Å, the variation in the Ru–L bond length and the height mismatch parameter h were calculated as a function of Θ for QP, ASTP, SBTP, PTAS, QAS, and SBTAS, and are shown in Table V (the detailed calculation procedure is given elsewhere).[22] Further calculations could be performed using different metals and various angles α, β, and γ, but this is not necessary as the general trends are obvious from Table 5: both ℓ and h increase as Θ increases. For $[RuBr_2(QAS)]$, Θ is found experimentally to be about 23° for the two $M–L_2$ bonds.

One cannot predict how in any one complex a distortion of the ligand from C_{3v} to C_{2v} (or C_s) symmetry will occur, but it seems reasonable to suppose that the main distortion will involve a rotation about the $L'–C_2'$ bonds which will occur until a low energy position is obtained where the non-bonding interactions are minimized, whilst good metal-ligand overlap is retained.

Table V. Mismatch Parameters of Some Octahedral Complexes of the Type $[RuX_2(L'L_3)]$

Ligand	Θ	ℓ [a] (Å)	h [a] (Å)
QP	0°	0.35	0.58
	20°	0.48	0.72
	23°	0.52	0.77
	25°	0.56	0.81
	30°	0.65	0.93
QAS	0°	0.35	0.61
	20°	0.49	0.76
	23°	0.53	0.81
	25°	0.57	0.85
	30°	0.66	0.97
ASTP	0°	0.39	0.73
	20°	0.53	0.89
	23°	0.57	0.95
	25°	0.61	0.99
	30°	0.70	1.10
SBTP	0°	0.44	0.97
	20°	0.60	1.14
	23°	0.65	1.20
	25°	0.69	1.24
	30°	0.79	1.33

[a] Calculated assuming values of $\alpha = 115°$, $\beta = \gamma = 120°$, Ru–P′ = 2.30 Å, Ru–As′ = 2.40 Å and Ru–Sb = 2.55 Å.

Discussion

The data given in Table V show clearly that in complexes of the ligand SBTP the values of ℓ and h are considerably larger than for any other of the ligands examined and this could account for the failure to obtain complexes $[RuX_2(SBTP)]$.[20]

The electronic spectra of some pseudo-octahedral complexes $[RuX_2(L'L_3)]$ ($L'L_3$ = PTAS, QAS, SBTAS) have the first well-defined electronic transition in the 25-30 kK range follow the order:[20]

PTAS > QAS > SBTAS
27.8 26.5 25.6 kK

in contrast to the variation in energy of the $^1A_1 \rightarrow a^1E$ transitions of complexes, $[NiCl(L'L_3)][BPh_4]$.[3] While, in the latter case, changes in the apical donor atom L′ affected primarily the a_1^* level, in pseudooctahedral complexes, which can be considered as having C_{2v} micro-symmetry, the low-energy transitions are not very sensitive to changes in L′ as the low-energy bands will have two components, $^1A_1 \rightarrow {}^1B_1$ and $^1A_1 \rightarrow ({}^1A_2, {}^1B_2)$ and, because of the low symmetry, there is extensive mixing of one-electron wave-functions in the excited terms and, therefore, the average environment rule is valid.[20]

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