137. Static and Dynamic Distortions in Five-Coordinate Complexes of Cobalt(II) and Rhodium(I)

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Summary. Five-coordinate complexes have been prepared, of the general formulae $[CoX(L'L_3)]^+$ and $[RhX(L'L_3)]$, where X = halogen and $L'L_3$ = a quadridentate tripod-like ligand containing various Group V donor atom sets. The electronic spectra and magnetism of the cobalt(II) series can be interpreted on the basis of a low-spin d^7-ion in a trigonal bipyramidal environment distorted by a static *Jahn-Teller* effect. Electronic spectral data for the trigonal bipyramidal rhodium(I) series show that the low-energy $^1A \rightarrow {}^1E$ ligand field transition is split at room temperature, but that the splitting collapses on reducing the temperature. This behaviour has been attributed to the operation of a dynamic *Jahn-Teller* effect.

Introduction. – Since the mathematical formulations were laid of what is now known as the *Jahn-Teller* effect [1], many examples of compounds showing *static* distortions from cubic symmetry have been reported and attributed to the operation of this effect [2]. The closely related *dynamic Jahn-Teller* effect [3] has also been invoked to explain "anomalies" in the vibrational [4] or in the electronic spectra [5] of transition-metal complexes with cubic symmetry.

More recently, the *Jahn-Teller* effect has been invoked to explain structural and physico-chemical properties in complexes with basic geometries other than cubic. Thus, distortions from trigonal bipyramidal structure in $[CoCl(QP)][BPh_4]$ (**2a**, QP = **1a**) [6], have been attributed to the operation of a static *Jahn-Teller* effect [7] and it has been postulated that the "anomalous" temperature-dependence of the electronic spectra of complexes $[MX(L'L_3)]Y$ (M = Ni, Pd and Pt; X = anionic ligand; $L'L_3$ = quadridentate tripod-like ligand, *e.g.*, QP (**1a**) [8] may be explained in terms of *either* a dynamic *Jahn-Teller* effect in the excited state *or* a temperature-dependent static distortion of the ground state or both.

We report here the preparation and characterization of two series of complexes with tripod-like ligands, one with cobalt(II) and the other with rhodium(I) which provide additional evidence for the operation of the effects mentioned above in trigonal bipyramidal complexes.

The ligands employed were QP, tris(*o*-diphenylphosphinophenyl)arsine (ASTP, **1b**), tris(*o*-diphenylphosphinophenyl)stibine (SBTP, **1c**), tris(*o*-diphenylarsinophenyl)arsine (QAS, **1e**), tris(*o*-diphenylarsinophenyl)phosphine (PTAS, **1d**), and the two series of complexes investigated have the general formulae $[CoX(L'L_3)]^+$ (X = anionic ligand; $L'L_3$ = ASTP (**2b**), SBTP (**2c**), PTAS (**2d**) and QAS (**2e**); and $[RhX(L'L_3)]$ (X = anionic ligand; $L'L_3$ = QP (**3a**), ASTP (**3b**), PTAS (**3c**), QAS (**3d**)).

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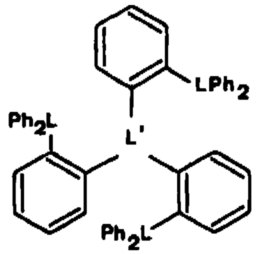
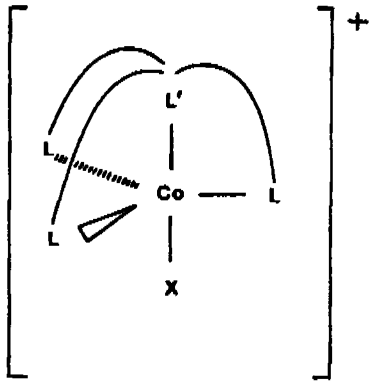


1

1a (= QP): L = L' = P
1b (= ASTP): L = P; L' = As
1c (= SBTP): L = P; L' = Sb
1d (= PTAS): L = As; L' = P
1e (= QAS): L = L' = As



2

2a L = L' = P; X = Cl
2b L = P; L' = As; X = Cl, Br, I, NCS
2c L = P; L' = Sb; X = Cl, Br, I, NCS
2d L = As; L' = P; X = Cl
2e L = L' = As; X = Cl

Experimental Part. – All solvents were dried and purified by standard methods [9]. The preparation of the ligands has been described elsewhere [10]. The complexes were prepared in analytically pure state as follows:

[CoCl(ASTP)][BPh$_4$]. 0.14 g (0.58 mmol) CoCl$_2$ · 6H$_2$O were dissolved in 5 ml ethanol and added to a refluxing suspension of 0.3 g (0.35 mmol) ASTP in 20 ml EtOH. The resulting dark blue mixture was refluxed for 2 h, cooled and filtered to remove any unreacted phosphine. The filtrate was treated with 0.13 g (0.39 mmol) sodium tetraphenylborate causing immediate precipitation of the dark blue complex which was recrystallized from a CH$_2$Cl$_2$/EtOH mixture (Yield = 80%). The bromo, iodo and thiocyanato derivatives were all prepared in an analogous manner.

[CoCl(SBTP)][BPh$_4$]. 0.38 g (0.56 mmol) [CoCl$_2$(Ph$_3$P)$_2$]in 5 ml dry CH$_2$Cl$_2$ was added to a refluxing solution of 0.3 g (0.33 mmol) SBTP in 15 ml CH$_2$Cl$_2$ under an atmosphere of dry nitrogen. After refluxing for 2 h, the solution was filtered and treated with 0.13 g (0.44 mmol) sodium tetraphenylborate in 10 ml dry *n*-BuOH. On reducing the volume of the solution, a dark blue solid separated out. This was filtered and redissolved in *ca.* 10 ml dry CH$_2$Cl$_2$. After the addition of an equal volume of dry *n*-BuOH, the CH$_2$Cl$_2$ was evaporated by passage of a fast stream of dry nitrogen through the solution, yielding dark blue crystals of the complex in 70% yield. The bromo, iodo and thiocyanato derivatives were prepared in the same manner.

[CoCl(QAS)]$_2$[CoCl$_4$]. 0.20 g (0.31 mmol) [CoCl$_2$(Ph$_3$P)$_2$] [11] and 0.30 g (0.30 mmol) QAS were dissolved in 20 ml chlorobenzene and the solution refluxed under nitrogen for 4 h. The resulting dark blue solution was evaporated almost to dryness, under nitrogen, giving a dark blue solid. This was filtered off and recrystallized from a CH$_2$Cl$_2$/ligroin mixture, giving dark blue needles of the complex in 69% yield.

[CoCl(QAS)][InCl$_4$]. 0.20 g (0.31 mmol) [CoCl$_2$(Ph$_3$P)$_2$] [11] in 15 ml chlorobenzene was added dropwise to a stirred suspension of 0.08 g (0.35 mmol) indium trichloride and 0.30 g (0.30 mmol) QAS in 20 ml chlorobenzene. After refluxing for 12 h, the volume of the solution was reduced by half by evaporation under nitrogen. The resulting dark blue solution was filtered and evaporated almost to dryness, giving a blue solid. This was purified by recrystallization from CH$_2$Cl$_2$/ligroin (Yield 65%). Yields and analytical data for the cobalt complexes are given in Table 1.

[RhX(L'L$_3$)]. [Rh$_2$X$_2$(cyclooctadiene)$_2$] [12] and the appropriate ligand were refluxed for 2 h in 25 ml abs. EtOH. The solid precipitates were filtered off at the pump and recrystallized from anisole giving dark red microcrystalline solids. Yields and analytical data for these complexes are given in Table 4.

Physical and Analytical Measurements. Variable temperature magnetic measurements were carried out on Faraday balances constructed in our laboratories [10] [13]. It is assessed that these instruments are capable of a precision of ± 0.3% and of errors as little as ± 0.4% (plus the error in the literature value of sodium chloride which was used as a calibrant) for a typical complex with molecular weight 600 and one unpaired electron. Conductivities were measured as described elsewhere [14]. Room-temperature VIS. and UV. spectra were recorded on a *Cary* 14 spectrophotometer in the usual way [10]. Low-temperature measurements were made using a *Cary* 14 spectrometer fitted with a *Research and Industrial Instruments* VLT-2 low-temperature attachment. Solution samples for the low-temperature measurements were in the form of 2-methyltetrahydrofuran glasses. Solid samples were in the form of thin films made by evaporation of dilute dichloromethane solutions on silica plates [15], or as thin polystyrene films [16]. Metal and arsenic analyses were carried out by atomic absorption spectrophotometry [10]. Carbon and hydrogen analyses were carried out by Dr. *A. Bernhardt*, Mikroanalytisches Laboratorium im *Max Planck Institut für Kohlenforschung*, Mülheim, West Germany and by *Galbraith Laboratories*, Knoxville, Tennessee.

Results and Discussion. – *Cobalt Complexes.* – On the basis of analytical results and conductivities (Tables 1 and 2), the complexes of cobalt(II) with the ligands

Table 1. *Yields and Analytical Data for Complexes* $[CoX(L'L_3)]Y$

Compd.	Yield %	% Co Calcd.	Found	% C Calcd.	Found	% H Calcd.	Found	% P (% As) Calcd.	Found
I	85	4.8	4.8	76.3	76.0	5.1	5.0	10.1	10.1
II	80	4.6	4.7	73.6	73.8	4.9	4.9	7.3	7.2
III	86	4.5	4.5	71.1	70.9	4.7	4.8	7.1	7.0
IV	80	4.3	4.2	68.7	68.6	4.5	4.5		
V	82	4.5	4.6	73.3	73.4	4.8	4.9	7.2	7.1
VI	70	4.4	4.5	71.1	71.0	4.7	4.7	7.1	7.0
VII	68	4.3	4.2	68.7	68.6	4.6	4.4	6.8	6.8
VIII	75	4.2	4.2	66.4	66.6	4.4	4.2	6.6	6.5
IX	62	4.4	4.4					6.9	6.7
X	78	4.3	4.3	68.9	68.8	4.6	4.6		
XI	69	7.5	7.4	54.7	54.7	3.6	3.4	(25.3)	(25.2)
XII	65	4.4	4.5	48.3	48.2	3.2	3.2	(22.3)	(21.9)

Table 2. *Physical Properties of Complexes* $[CoX(L'L_3)]Y$

Compound		Colour	Decomp. p.	Λ_M [a]	μ_{eff} [b]
I	$[CoCl(QP)][BPh_4]$	Dark red	262–274°	15.1	1.99
II	$[CoCl(ASTP)][BPh_4]$	Dark blue	237–239°	13.8	2.01
III	$[CoBr(ASTP)][BPh_4]$	Dark blue	236–238°	13.7	1.98
IV	$[CoI(ASTP)][BPh_4]$	Dark green	226–228°	13.5	1.96
V	$[Co(NCS)(ASTP)][BPh_4]$	Brown	241–243°	14.9	2.02
VI	$[CoCl(SBTP)][BPh_4]$	Dark blue	182–184°	*ca.* 14	1.98
VII	$[CoBr(SBTP)][BPh_4]$	Dark blue	177–180°	*ca.* 13.5	1.96
VIII	$[CoI(SBTP)][BPh_4]$	Dark green	174–176°	*ca.* 13.5	1.95
IX	$[Co(NCS)(SBTP)][BPh_4]$	Brown	180–183°	*ca.* 14	2.02
X	$[CoCl(PTAS)][BPh_4]$	Purple	222–225°	14.1	2.12
XI	$[CoCl(QAS)]_2[CoCl_4]$ [c]	Blue	266–268°	22.7	[d]
XII	$[CoCl(QAS)][InCl_4]$	Blue-black		32.1 [e]	2.23

[a] In Ω^{-1} cm^{2}M^{-1} for approx. 10^{-3}M nitrobenzene solutions at 20°. Reference range for 1:1 electrolytes 15–20 mhos. [b] At room temperature in B.M. [c] This compound is unstable in air, decomposition being complete within a few hours. [d] Values ranging between 2.2 and 2.5 B.M. were obtained on a number of runs with different samples, presumably due to partial decomposition. [e] For 10^{-3}M 1,2-dichloroethane solution. Reference range for 1:1 electrolytes 25–30 mhos.

ASTP, SBTP and PTAS, by analogy with the QP complexes [17], are assigned the general formula [CoX(L'L$_3$)] [BPh$_4$]. The magnetic susceptibility data obtained are given in Table 3. All the complexes are of low-spin type with magnetic moments in the range 1.9–2.2 B.M. On the basis of simple crystal field calculations one expects μ_{eff} values of 3.0 B.M. for d^7-ions in D$_{3h}$ symmetry. As the observed moments are closer to the spin-only value of 1.73 B.M., it appears that the contribution from the orbital angular momentum is largely quenched. This quenching is attributed to a static *Jahn-Teller* distortion which would lift the degeneracy of the ^{2}E ground-state of the d^7-metal ion in C$_{3v}$ symmetry. X-Ray diffraction studies have shown such a distortion to be present in [CoCl(QP)] [BPh$_4$] [6]. A detailed interpretation of the magnetic data was not attempted. The observed differences are not caused by experimental errors and do not appear to be due to the presence of impurities in the samples used. It is possible that these variations may be associated with the population of high-spin states.

Table 3. *Magnetic Susceptibility Data for Complexes* [*CoX*(*L'L$_3$*)] *Y*

Complex	Temp. (K)	$\chi_m' \times 10^6$	μ_{eff}(B.M.)
[CoI(QP)] [BPh$_4$] [17]	103	4254	1.88
	148	2954	1.88
	179	2477	1.89
	254	1811	1.93
	291.5	1605	1.94
	320.5	1446	1.93
	364	1292	1.95
[CoI(ASTP)] [BPh$_4$]	103	4120	1.85
	151	2904	1.88
	202	2230	1.90
	289.5	1654	1.96
	322	1502	1.98
	373	1326	2.00
[CoI(SBTP)] [BPh$_4$]	101	4060	1.82
	150	2724	1.82
	203	2189	1.89
	253	1890	1.96
	279	1687	1.95
	323	1804	1.98
[CoCl(PTAS)] [BPh$_4$]	130	3967	2.04
	160	3287	2.06
	230	2353	2.09
	270	1986	2.08
	290	1920	2.12
	330	1750	2.16
[CoCl(QAS)] [InCl$_4$]	150	3855	2.16
	190	3160	2.16
	230	2608	2.20
	280	2200	2.23
	320	1980	2.26

The complex [CoCl(QAS)] [BPh$_4$] could not be obtained by the methods used for complexes of the other ligands. The reaction of [CoCl$_2$(Ph$_3$P)$_2$] with the ligand QAS gave a product which has been formulated as [CoCl(QAS)]$_2$[CoCl$_4$] but attempts to replace the [CoCl$_4$]$^{2-}$ anion with [BPh$_4$]$^-$, ClO$_4^-$ or PhSO$_3^-$ resulted in decomposition. However, a complex has been obtained with the tetrachloroindate ion and has been formulated as [CoCl(QAS)] [InCl$_4$]. The presence of the [InCl$_4$]$^-$ anion was confirmed by the occurrence of bands at 329 cm^{-1} and 112 cm^{-1} in the infrared of a Nujol mull of the complex [18]. This complex had a magnetic moment of 2.23 B.M., showing it to be low-spin. This finding is in apparent contradiction to the predictions of *Sacconi* [19] which suggest that the donor set As$_4$ should lie beyond the crossover point from low- to high-spin species.

The electronic spectra of the complexes are summarized in Table 4. *Norgett & Venanzi* [20] have assigned the spectra for the QP-complexes assuming a distortion of the *Jahn-Teller* type which will split the d-orbitals as shown in Fig. 1, with the split-

Table 4. *Electronic Spectra of Complexes [CoX(L'L$_3$)]Y*

	Solution		Solid	
	E_{max} c)	ε_{max}	E_{max}	$F(R_\infty)$ b) d)
[CoCl(QP)] [BPh$_4$] a)	36.3	sh		
	25.4	sh		
	19.6	2,750	19.5	1.14 (0.75)
	16.5	sh	16.3	sh (0.40)
	9.5	280	9.5	0.17 (0.07)
[CoI(QP)] [BPh$_4$] a)	25.6	sh		
	18.3	2,140	18.2	0.84
	16.4	sh	16.0	sh
	9.2	400	9.1	0.23
[CoCl(ASTP)] [BPh$_4$]	36.6	sh		
	34.0	sh		
	31.8	sh		
	27.5	6,700	27.5	sh
	18.2	2,500	18.2	1.15 (0.82)
	16.5	sh	16.5	sh (0.50)
	8.8	210	8.8	0.12 (0.07)
[CoBr(ASTP)] [BPh$_4$]	36.5	sh		
	34.8	sh		
	32.5	sh		
	27.8	sh	27.8	sh
	23.7	sh	23.5	sh
	17.9	2,150	18.0	0.94
	16.0	sh	16.0	sh
	8.7	260	8.7	0.15
[CoI(ASTP)] [BPh$_4$]	37.8	sh		
	34.5	sh		
	27.5	8,200	27.5	sh
	16.9	1,980	16.9	0.47
	15.7	sh	15.7	sh
	8.4	360	8.4	0.12

Table 4. (contd.)

	Solution E_{max}[c])	ε_{max}	Solid E_{max}	$F(R_\infty)$
[Co(NCS)(ASTP)][BPh_4]	37.7	sh		
	36.6	sh		
	27.5	7.900	27.5	sh
	19.8	3,920	20.0	0.32
	16.8	sh	16.9	sh
	8.8	600	8.8	0.05
[CoCl(SBTP)][BPh_4]			26.0	0.78
			23.8	sh
			18.5	sh (0.63)
			16.8	1.15 (0.85)
			8.8	0.16 (0.09)
[CoBr(SBTP)][BPh_4]			26.5	0.78
			23.6	sh
			18.0	sh
			16.6	0.62
			8.6	0.09
[CoI(SBTP)][BPh_4]			27.2	sh
			23.2	sh
			16.3	0.58
			8.2	0.13
[Co(NCS)(SBTP)][BPh_4]			26.2	1.13
			22.0	0.94
			18.7	0.96
			8.8	0.23
[CoCl(PTAS)][BPh_4]	37.5	sh		
	36.5	sh		
	31.7	sh		
	24.4	2,900	24.3	1.05
	18.3	2,350	18.3	0.98
	16.2	sh	16.0	sh
	8.4	250	8.4	0.10
[CoCl(QAS)]$_2$[$CoCl_4$]	29.6	sh	29.3	sh
	24.4	sh	24.0	sh
	17.8	sh	17.8	sh
	16.7	3,150	16.7	0.84
	15.5	sh	15.6	sh
	14.7	sh	14.7	sh
	8.1	470	8.1	0.12
[CoCl(QAS)][$InCl_4$]	38.3	sh	37.9	sh
	33.8	sh	33.6	sh
	30.9	sh	31.0	sh
	28.9	sh	29.1	sh
	24.3	4,300	24.3	1.01
	16.8	3,000	16.8	0.64
	8.0	320	8.0	0.09

[a]) Previously reported in [17]. [b]) $F(R_\infty)$ = *Kubelka Munk* remission function. [c]) Room temperature data in kK for CH_2Cl_2 solutions. [d]) Figures in parentheses refer to spectra at 100 K in a polystyrene matrix.

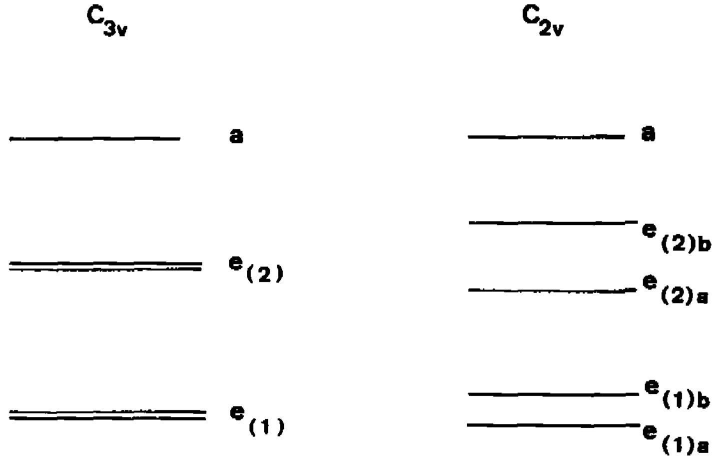


Fig. 1. *Schematic Representation of the* d-*Energy Level Splitting for Complexes* $[CoX(L'L_3)]^+$ *in* C_{3v} *and* C_{2v} *Symmetries*

ting between the components of the $e_{(1)}$ orbitals (xz, yz) being small, while that between the $e_{(2)}$ orbitals being large. The observed transitions were assigned as follows:

$^2E_{(2)b} \rightarrow {}^2E_{(2)a}$ (~ 9.5 kK), $^2E_{(2)b} \sim {}^2A$ (~ 16.5 kK) and $^2E_{(2)b} \rightarrow {}^2E_{(1)}$ (~ 19.6 kK).

The pattern of absorption bands in the ASTP and PTAS complexes is fully analogous to that found for compounds [CoX(QP)]Y and, thus, a similar spectral assignment can be made. The pattern of absorption for complexes [CoX(SBTP)]Y, however, differs from that of the complexes with QP, ASTP and PTAS (see Table 4 and Fig. 2) as the relative intensities of the two bands in the region 15–25 kK are reversed. This reversal is attributable to the steric effect of including, in the apical position, the relatively large antimony atom in the chelate framework which will have the effect of destabilizing the *a* (z^2) level. This effect has been observed in the analogous nickel(II) complexes [10]. It is noteworthy that the ligand QAS appears to present an intermediate case, since no shoulder is observed on this band. However, the intensity is very high, suggesting that the two transitions have comparable energy.

In conclusion, while static distortions appear to occur in all the cobalt(II) complexes with tripod-like ligands studied to date, care must be exercised in the assignment of their electronic spectra as steric effects may change the relative order of the d-levels.

Rhodium complexes. – In an earlier publication, *Mawby & Venanzi* [21] reported the preparation of complexes [RhX(QAS)], **3d**, which were assigned trigonal bipyramidal structure. Compounds **3a–d** were prepared and some of their physical properties are given in Table 5. Their electronic spectra (see Table 6 and Fig. 3) are characterized by two intense bands at ca. 30 kK and ca. 24 kK, the latter band showing a shoulder on the low-energy side.

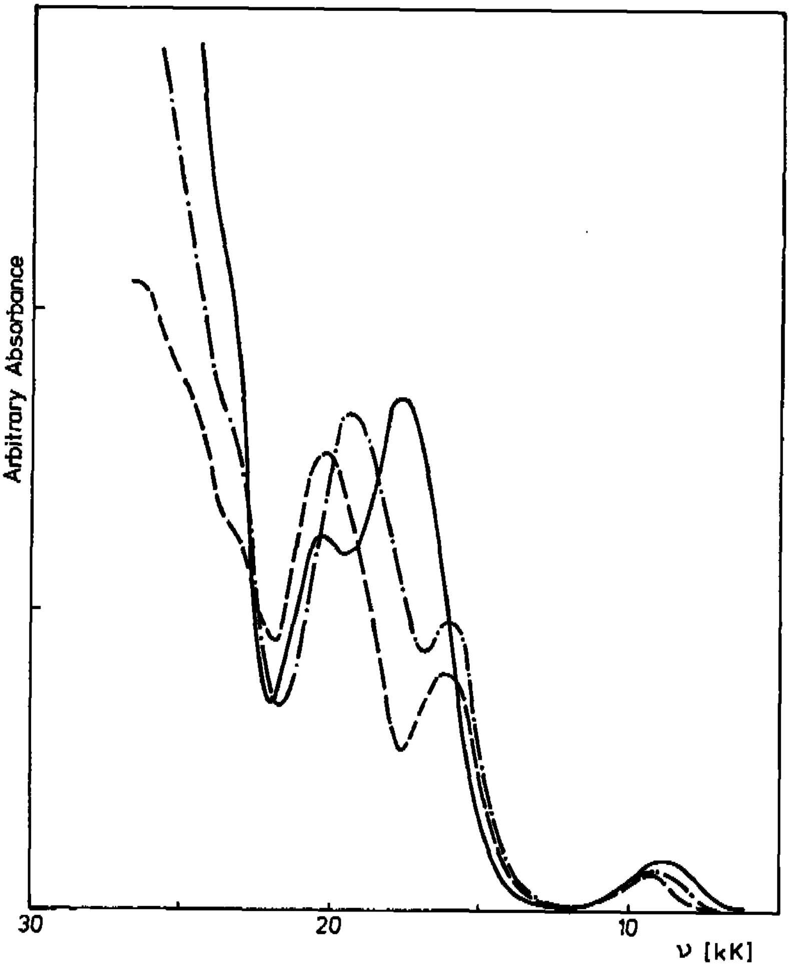
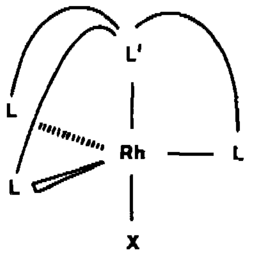


Fig. 2. *Electronic spectra of complexes $[CoCl(L'L_3)][BPh_4]$* in a 2-methyltetrahydrofuran/CH_2Cl_2 4:1 glass at *ca.* 100 K

– · – · – · – · – · – · – $[CoCl(QP)][BPh_4]$,
– – – – – – – – – – $[CoCl(ASTP)][BPh_4]$,
———————— $[CoCl(SBTP)][BPh_4]$.



3a: L = L' = P; X = Cl, I
3b: L = P; L' = As; X = Cl, I
3c: L = As; L' = P; X = Cl, I
3d: L = L' = As; X = Cl, Br, I

Table 5. *Yields, Analytical Data and Physical Properties for Complexes* $[RhX(L'L_3)]$

Compound[a])	Yield %	Decomp. p.	Λ_M[b])	% P(% As) Calcd.	% P(% As) Found	% Rh Calcd.	% Rh Found
[RhCl(QP)]	85	*ca.* 320°	1.0	13.0	12.9	10.8	10.6
[RhI(QP)]	87	325–330°	1.1	11.9	12.0	9.8	10.0
[RhCl(ASTP)]	65	*ca.* 320°	0.9	9.4	9.5	10.3	10.2
[RhI(ASTP)]	60	315–320°	0.7	8.6	8.5	9.4	9.3
[RhCl(PTAS)]	75	*ca.* 320°	0.5	20.7	20.2	9.5	9.5
[RhI(PTAS)]	69	305–310°	0.9	19.2	19.2	8.8	8.6

a) All complexes are red and diamagnetic with $\chi_{M(corr.)} = +20$ to $+100 \times 10^{-6}$ cgs.
b) In Ω^{-1} cm^{2}M^{-1} for approx. 10^{-3}M nitrobenzene solutions at 20°.

Table 6. *Electronic Spectra of Complexes* $[RhX(L'L_3)]$

	Solutions[a]) [b])		Glasses[a]) [c])		Solids[e]) 300 K		Solids[e]) 100 K	
	E_{max}[d])	ε_{max}	E_{max}[d])	ε_{max}	E_{max}[d])	'A'[f])	E_{max}[d])	'A'[f])
[RhCl(QP)]	20.4	sh	20.5	sh	20.4	sh	20.4	sh
	23.4	9,100	22.2	9,500	23.4	0.9	23.3	1.0
	29.7	14,500	29.7	16,200	29.6	1.6	29.7	1.8
[RhI(QP)]	20.1	sh	20.8	sh	20.2	sh	20.3	sh
	22.2	5,800	21.8	6,500	22.3	0.5	22.4	0.6
			26.1	sh			26.4	sh
	29.7	14,200	29.9	15,200	29.7	1.4	30.0	1.6
[RhCl(ASTP)]	20.1	sh	20.5	sh	20.0	sh	20.2	0.9
	22.7	9,200	22.2	10,300	22.5	0.9	22.5	1.1
	29.6	14,100	29.4	15,900	29.5	1.4	29.6	1.6
[RhI(ASTP)]	19.7	sh	20.0	4,950	19.6	sh	19.3	sh
	21.9	6,200	21.9	6,900	21.7	0.8	21.6	0.9
			25.2	sh	25.7	sh		
	29.6	14,100	29.7	15,100	29.5	1.3	29.4	1.5
[RhCl(PTAS)]	20.3	sh	21.2	sh	20.5	sh	20.8	0.5
	22.2	6,900	21.9	8,500	22.2	0.6	22.2	0.8
	29.9	12,400	30.0	14,100	29.9	1.0	30.0	1.2
[RhI(PTAS)]	19.8	sh	20.4	sh	19.7	sh	19.8	sh
	21.3	5,500	20.9	6,500	21.2	0.5	21.2	0.6
			24.5	sh			24.8	sh
	29.8	12,800	30.0	14,300	29.9	1.1	29.8	1.3

a) In 2-methyltetrahydrofuran/CH_2Cl_2(9:1). b) At 300 K. c) At 100 K. d) In kK. e) In a polystyrene matrix. f) A = Arbitrary absorbance scale.

Attempts were made to establish the trigonal bipyramidal geometry of these complexes using NMR techniques as done for complexes of other d^8-metal ions [22]. Compounds $[RhX(L'L_3)]$, however, proved to be too sparingly soluble for such measurements. The more soluble compound [Rh(CO)(QP)] [BPh_4] was examined. The

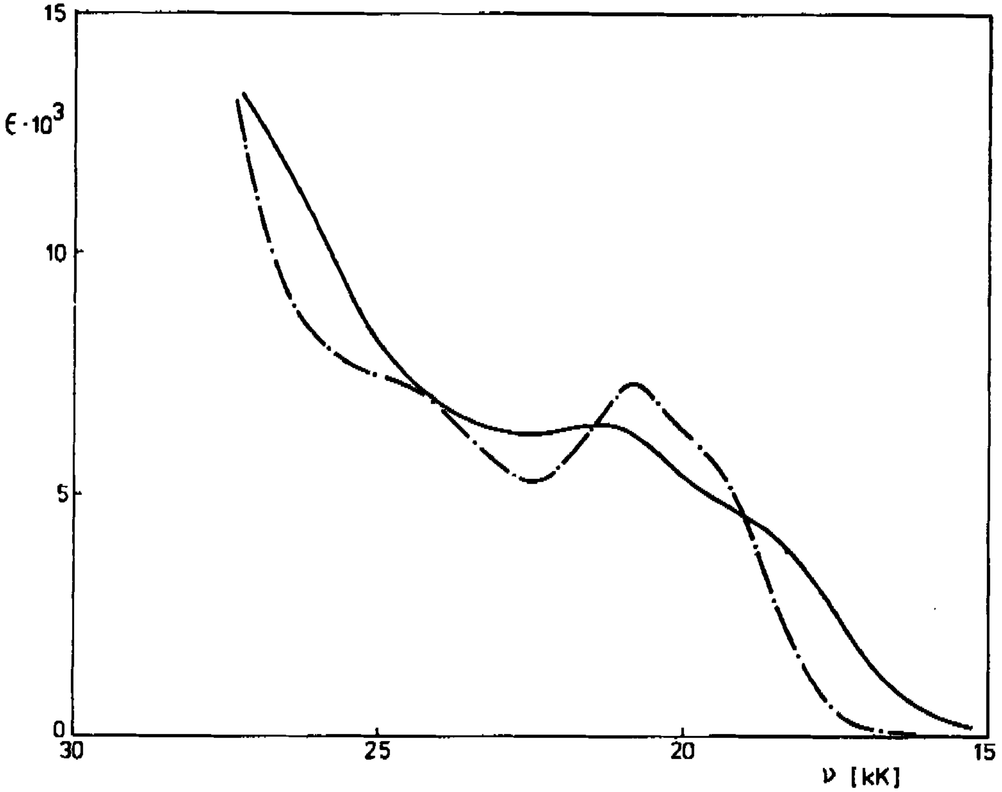


Fig. 3. *The temperature dependence of the electronic spectrum of* [*RhI*(*QP*)] in 2-methyltetrahydrofuran/CH_2Cl_2 4:1

——————— 300 K
–·–·–·–·–·– 100 K

spectrum consists of a doublet of quartets at low field and a doublet of doublets at high field. The following parameters were obtained [16]: $\delta_P = +56.92$ (2), $\delta_{P'} = -9.25$ (2), in ppm relative to external P_4O_6, $|^1J(\text{Rh-P})| = 131.0$ (2), $|^1J(\text{Rh-P}')| = 87.0$ (2) and $|^2J(\text{P}'\text{-M-P})| = 27.2$ (2) Hz. These data and the corresponding parameters for other trigonal bipyramidal complexes [16] [22] allow the assignment of this structure to $[Rh(CO)(QP)]^+$.

^{31}P-NMR. studies [16] have also established the trigonal bipyramidal structure for [Co(CO)(QP)] [BPh_4]. Furthermore, it has been observed that: (1) the ligand field bands in the isoelectronic species $[Co(CO)(QAS)]^+$ and $[Ni(CN)(QAS)]^+$ occur at very comparable energies [23]; (2) a similar spectral relationship exists between $[Rh(CO)(QAS)]^+$ [23] and $[Pd(CN)(QAS)]^+$ [24] and (3) the ligand-field spectra of compounds **3a–d** (see Table 6 and Fig. 3) are related to those of the corresponding compounds $[PdX(L'L_3)][BPh_4]$ [10] which are trigonal bipyramidal. Thus one can assign trigonal bipyramidal structure to complexes $[RhX(L'L_3)]$.

As the ligand field spectra of most trigonal bipyramidal complexes of nickel(II), palladium(II) and platinum(II) show "anomalous" temperature dependence [8] it was of interest to establish whether such behaviour was typical of trigonal bipyramidal complexes of d^8-ions or whether it was restricted to compounds formed by metal ions of the "nickel triad", the temperature dependence of complexes [RhX(L'L$_3$)] was investigated. It was found (see Fig. 3 and Table 6) that the splitting of their low-energy bands decreased with a decrease in temperature as found for complexes [MX(L'L$_3$)]Y (M = Ni, Pd and Pt; L'L$_3$ = tripod-like ligand). One can, therefore, conclude that the possible explanation for this phenomenon given earlier [8], *i.e.*, the operation of *either* a dynamic *Jahn-Teller* effect in the excited state *or* a temperature-dependent static distortion of the ground state or both, are likely to be operative also in the rhodium(I) complexes. As this temperature-dependence has also been found in compounds [IrX(L'L$_3$)] [25], it can be concluded that this phenomenon appears to be characteristic of all trigonal bipyramidal complexes of d^8 ions with tripod-like ligands.

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