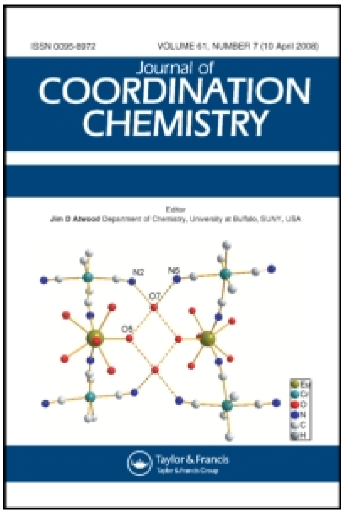

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Gushikem, Y. , Alves, O. L. , Hase, Y. and Kawano, Y.(1977) 'RAMAN SPECTRA OF ANTIMONY AND NIOBIUM PENTACHLORIDE COMPLEXES WITH PHOSPHORYL CHLORIDE', Journal of Coordination Chemistry, 6: 3, 179 — 183

To link to this Article: DOI: 10.1080/00958977708079907

URL: http://dx.doi.org/10.1080/00958977708079907

J. Coord. Chem.
1977, vol. 6, pp 179–183

RAMAN SPECTRA OF ANTIMONY AND NIOBIUM PENTACHLORIDE COMPLEXES WITH PHOSPHORYL CHLORIDE†

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(*Received June 3, in final form August 10, 1976*)

Raman spectra and normal coordinate treatments of $SbCl_5 \cdot POCl_3$ and $NbCl_5 \cdot POCl_3$ are presented. The calculations are performed based on C_s symmetry of the molecules and a modified Urey–Bradley force field. Calculated PO stretching force constant (7.499 mdyn/Å for the antimony complex and 7.942 mdyn/Å for the niobium complex) and PCl stretching force constants (about 2.90 mdyn/Å for both complexes) are consistent with coordination through the oxygen atom. Separation of the MCl stretching force constants into axial and equatorial components is analysed in terms of different trans influence along the $Cl_{eq}-M-Cl_{eq}$ and $Cl_{ax}-M-$ligand bonds. The low values of the MO stretching force constants (about 0.40 mdyn/Å) are reasonable taking into account the low charge density on the oxygen atom of phosphoryl chloride.

INTRODUCTION

The interest in the vibrational spectra of molecular complexes MX_5L, where M is metal of the Va and Vb groups, is considerably increasing with aid of normal coordinate treatments, in order to have a comprehensive assignment of MX_5 moiety.[1–5] Although complexes of many metals of IV and V groups with $POCl_3$ have been known for a long time,[6] very few data on the vibrational spectra have been available beside that reported by Smitskamp *et al.*[7] The major interest in the other studies[8–12] has been limited to a spectroscopic investigation of the nature of the metal-to-phosphoryl chloride interaction, through the PO stretching band shift.

X-ray data[13] has shown that coordination in $SbCl_5 \cdot POCl_3$ and $NbCl_5 \cdot POCl_3$ occurs exclusively through the oxygen atom. Since they are isostructural, the nature of the donor–acceptor bond strength given by the force constants, as well as the difference between them, can be correlated with the change in the central metal atom.

EXPERIMENTAL

The complexes were prepared according to described methods[7,14] with some modifications. The $SbCl_5$ was purified by distillation *in vacuo* directly into a calibrated break-seal ampoule. The $POCl_3$ was initially refluxed with phosphorus pentoxide and further distilled into a calibrated break-seal ampoule. In a dry atmosphere, the $SbCl_5$ was received in purified carbon tetrachloride breaking the seal through a magnetic bar, with the vessel cooled at 0°C. With stirring, the seal of the $POCl_3$ ampoule was broken after which a solid immediately precipitated. The solid was separated by filtration under dry nitrogen gas and the excess solvent was pumped off under vacuum for approximately two hours. The $NbCl_5$ was vacuum sublimed before using and suspended in purified hot carbon tetrachloride. The procedure for the preparation of the niobium complex was the same as that described

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† Note added in revision: after submitting this paper to publication, appeared in Inorg. Chem., 15, 1226 (1976) by M. Burgard, J. Brunette and M. J. F. Leroy a note on vibrational spectra of some oxo adducts of antimony pentachloride which reference we wish to mention now.

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TABLE I

Raman frequencies (cm^{-1}) of $MCl_5 \cdot POCl_3$ in solid and fused states

$SbCl_5 \cdot POCl_3$		$NbCl_5 \cdot POCl_3$		
solid	fused	solid	fused	Assignment
1158w	1187w,p	1188w	~1200w,p	νPO (A′)
622w	627w,dp	622w	625vw,?	$\nu_a PCl_3$ (A′,A″)
524w	518m,p	527m	525m,p	$\nu_s PCl_3$ (A′)
		409vw		$\nu NbCl_{eq}$ (A′,A″)
		398vs	394vs,p	$\nu NbCl_{ax}$ (A′)
383w		387vw		$\rho OPCl_3$ (A′)
363s		368vvw		$\rho OPCl_3$ (A′) $\nu SbCl_{eq}$ (A′,A″)
355w	354vw,sh			$\nu SbCl_{ax}$ (A′)
		356s	353vs,p	$\nu NbCl_{eq}$ (A′)
		345s		$\nu NbCl_{eq}$ (A′)
334vs	338vs,p			$\nu SbCl_{eq}$ (A′)
296s	297w,p	295m	295m,p	$\nu SbCl_{eq}$ (A′) $\delta_s PCl_3$ (A′)
209m	207vw,dp	212m	210w,dp	$\delta_a PCl_3$ (A′,A″)
180s	182w,dp	182m	181w,sh	δClMCl (A′)
168vw		168m	165vw,sh	δClMCl (A″)
150w		155w		δOMCl (A′,A″)
144s	145m,dp	145s	145s,p	δClMCl (A′,A″)
124w		130vvw		δClMCl (A′)
113vw		104vw		νMO (A′)
101w	98vw,p	98vvw	90w,br,p	δOMCl (A′,A″)
76vvw		84vw		
36vvw		31vvw		δMOP (A′)

above. It was necessary to purify the niobium complex by sublimation in order to obtain a good quality spectrum.

Raman spectra were obtained with the samples in an evacuated glass tube, using a Jarrell–Ash model 25-300 spectrometer equipped with an Ar$^+$ laser.

Vibrational Assignment

Table I gives the Raman frequencies of $SbCl_5 \cdot POCl_3$ and $NbCl_5 \cdot POCl_3$ in solid and fused states. For the molecule $MCl_5 \cdot POCl_3$, the C_s symmetry is considered and the twenty-seven normal vibrations are shared between 17A′(IR,R) + 10A″(IR,R) applying the selection rules.

The coordination through the oxygen atom causes the PO stretching band to shift to lower frequency region. The lowering of the bond order, responsible for the above observation, also results in a raising of the PCl stretching frequency.[15] According to this fact, the bands at 1158 and 1188 cm^{-1} are assigned to νPO (A′). The other two bands at about 620 and 520 cm^{-1} are respectively assigned to $\nu_a PCl_3$ (A′,A″) and $\nu_s PCl_3$ (A′).

For the five MCl stretching vibrations predicted theoretically as 4A′ + A″, only four bands are observed in the Raman spectra. The bands at 363, 355, 334 and 296 cm^{-1} of the antimony complex are assigned to the SbCl stretching modes. These bands of the niobium complex are expected at higher frequency region as a consequence of decrease in mass of the central atom and they are observed at 409, 398, 356 and 345 cm^{-1}. The highest frequencies for both complexes are assigned to the asymmetric stretching modes of the A′ and A″ species as an accidentally degenerated vibration. The bands at 398 and 356 cm^{-1} for niobium complex are polarized, while for antimony complex only the band at 334 cm^{-1} is clearly polarized and the band at 355 cm^{-1}, which is partially overlapped with that at 363 cm^{-1}, certainly can be assigned to a totally symmetric mode in comparison with that of $SbCl_5 \cdot NCX$.[5,16] The bands at 296 cm^{-1} for $SbCl_5 \cdot POCl_3$ and at 345 cm^{-1} for $NbCl_5 \cdot POCl_3$ are assigned to the asymmetric stretching modes of the A′ species. Considering the observed frequencies, the MCl_5 moiety can be treated to have a C_{4v} local symmetry. The tendency in each moiety to maintain the degeneracy, C_{4v} for MCl_5 and C_{3v} for $POCl_3$, probably can be related to a weak metal–ligand interaction.

The PCl_3 deformation of the A′ species is assigned to the band at about 295 cm^{-1} for both complexes.

TABLE II
Approximate description of symmetry coordinates of $MCl_5 \cdot POCl_3$

νMCl_{eq}	S_1, S_3, S_4, S_{21}
νMCl_{ax}	S_2
νMO	S_5
νPO	S_6
$\nu_s PCl_3$	S_7
$\nu_a PCl_3$	S_8, S_{22}
δMOP	S_9
$\delta ClMCl$	$S_{10}, S_{11}, S_{12}, S_{13}, S_{14}, S_{24}, S_{25}, S_{26}$
$\delta OMCl$	$S_{15}, S_{16}, S_{17}, S_{23}$
$\delta_s PCl_3$	S_{18}
$\delta_a PCl_3$	S_{20}, S_{28}
$\rho OPCl_3$	S_{19}, S_{27}

This band is accidentally degenerated with the lowest MCl stretching band in the antimony complex. This assignment is reasonable comparing with that made for $SnCl_4 \cdot 2POCl_3$, $TiCl_4 \cdot 2POCl_3$[17a] and $(TiCl_4 \cdot POCl_3)_2$[17b], *i.e.*, 294, 290 and 280 cm^{-1} respectively. The other two $POCl_3$ deformation modes are assigned to the bands at about 380 and 210 cm^{-1}. These bands show a high frequency shift from those of free $POCl_3$.

TABLE III
Urey-Bradley force constants (mdyn/Å)

	Sb	Nb
1. $K(MCl)_{eq}$[a]	1.694	2.093
2. $K(MCl)_{ax}$[a]	1.880	2.278
3. K(MO)	0.434	0.390
4. K(PO)	7.499	7.942
5. K(PCl)	2.888	2.896
6. H(ClPCl)	0.215	0.216
7. F(Cl··P··Cl)	0.170	0.170
8. H(OPCl)	0.159	0.163
9. F(O··P··Cl)	0.340	0.340
10. H(MOP)	0.029	0.024
11. F(M··O··P)	0.050	0.050
12. H(OMCl)	0.113	0.116
13. F(O··M··Cl)	0.200	0.200
14. H(ClMCl)	0.084	0.083
15. F(Cl··M··Cl)	0.100	0.100
16. κ[b]	0.450	0.450
17. $I(MCl,MCl)_{trans}$[c]	0.142	0.266
18. $I(MO,MCl)_{trans}$[c]	0.076	0.045
19. $I(PCl,PCl)$[c]	0.296	0.319

[a] eq and ax correspond to equatorial and axial positions.
[b] unit is in mdyn Å.
[c] stretch-stretch interaction force constants.

TABLE IV
Observed and calculated frequencies and PED for $SbCl_5 \cdot POCl_3$.

	Obs.	Calc.	PED
A′	1158	1158	$97S_6$
	622	624	$87S_8$
	524	525	$85S_7$
	383	390	$35S_{19} + 20S_{15} + 15S_5$
	363	359	$104S_4$
	355	355	$97S_2$
	334	321	$41S_1 + 41S_3$
	296	306	$52S_1 + 52S_3$
	296	290	$69S_{18}$
	209	215	$68S_{20} + 17S_{15}$
	180	167	$54S_{14} + 32S_{11} + 21S_{10}$
	150	155	$79S_{16}$
	144	140	$26S_{12} + 26S_{13} + 18S_{15} + 15S_{19}$
	124	127	$50S_{14} + 30S_{11} + 19S_{10}$
	113	108	$46S_{19} + 28S_5 + 23S_{20}$
	101	102	$28S_5 + 23S_{15}$
	36	30	$88S_9$
	622	620	$88S_{22}$
	363	365	$39S_{27}$
	355	358	$97S_{21}$
	209	212	$65S_{28} + 18S_{24}$
	168	161	$100S_{26}$
	150	154	$53S_{24} + 43S_{23} + 19S_{25}$
	144	137	$49S_{25} + 29S_{27} + 21S_{28} + 16S_{24}$
	101	105	$40S_{23} + 30S_{27} + 29S_{25} + 15S_{28}$

The six $OMCl_5$ deformation modes for C_{4v} local symmetry, including three degenerate ones, are expected below 210 cm^{-1}. The observed data show that in this region the mass effects on the frequencies are very small. If we assume the same values of force constants for both complexes and carry out the normal coordinate calculations, it is found that the mass effects on frequencies are only about 5%. The bands which can be assigned rather tentatively to $OMCl_5$ deformation modes are those at about 180, 150, 144, 124, 110 and 100 cm^{-1}. Since the donor-acceptor bond strength is expected to be weak, the band of the MOP deformation may be below 100 cm^{-1}.

Normal Coordinate Treatments

Normal coordinate calculations were carried out for the modified Urey-Bradley force field. The geometric parameters were taken from those of ref. 13 using an average value: $SbCl_5 \cdot POCl_3$ (Sb–Cl = 2.33 Å, Sb–O = 2.17 Å, P–O = 1.47 Å, P–Cl = 1.95 Å and ∠SbOP = 145°) and $NbCl_5 \cdot POCl_3$ (Nb–Cl = 2.30 Å, Nb–O = 2.16 Å P–O = 1.45 Å P–Cl = 1.94 Å and ∠NbOP = 149°). The geometry of $OMCl_5$ was considered as octahedral and that of $POCl_3$ as tetrahedral.

Approximate description of symmetry coordinates are given in Table II.

TABLE V
Observed and calculated frequencies and PED for $NbCl_5 \cdot POCl_3$.

	Obs.	Calc.	PED
A′	1188	1188	$97S_6$
	622	622	$87S_8$
	527	528	$85S_7$
	409	409	$102S_4$
	398	404	$97S_2$
	387	388	$32S_{19} + 18S_{15}$
	356	356	$42S_1 + 42S_3$
	345	345	$52S_1 + 52S_3$
	295	291	$72S_{18}$
	212	214	$66S_{20} + 21S_{15}$
	182	177	$53S_{14} + 32S_{11} + 21S_{10}$
	155	159	$73S_{16}$
	145	142	$21S_{12} + 21S_{13} + 19S_{19} + 18S_{15} + 17S_{20}$
	130	129	$50S_{14} + 30S_{11} + 20S_{10}$
	104	107	$44S_{19} + 23S_{20} + 20S_5$
	98	103	$39S_5 + 17S_{15}$
	31	28	$90S_9$
A″	622	620	$88S_{22}$
	409	409	$104S_{21}$
	368	367	$42S_{27} + 15S_{24}$
	212	213	$64S_{28} + 19S_{24}$
	168	162	$100S_{26}$
	155	158	$47S_{24} + 43S_{23} + 27S_{25}$
	145	139	$41S_{25} + 32S_{27} + 25S_{26} + 23S_{24}$
	104	106	$38S_{23} + 31S_{27} + 30S_{25} + 16S_{28}$

The final set of force constants calculated by the least squares method is presented in Table III. Torsional force constants were assumed to be zero in numerical calculations. The calculated frequencies are given in Table IV and V, with the potential energy distributions (PED).

DISCUSSION

The separation of bond stretching force constants into $K(MX)_{ax}$ and $K(MX)_{eq}$ appears to be reasonable taking into account of a trans influence. As shown in Table III, the values of $K(MCl)_{ax}$ are larger than those of $K(MCl)_{eq}$ and this tendency may be related to the interatomic bond distances.[13] Similar results are obtained with other complexes, namely: $TiCl_4 \cdot 2POCl_3$ ($K(MX)_{ax}$ = 1.467 mdyn/Å and $K(MX)_{eq}$ = 1.379 mdyn/Å); $SnCl_4 \cdot 2POCl_3$ ($K(MX)_{ax}$ = 1.694 mdyn/Å and $K(MX)_{eq}$ = 1.619 mdyn/Å)[17a]; ($(TiCl_4 \cdot POCl_3)_2$ ($K(MX)_{ax}$ = 1.761 mdyn/Å and $K(MX)_{eq}$ = 1.506 mdyn/Å)[17b]; $TiCl_4 \cdot 2NCCH_3$ ($K(MX)_{ax}$ = 1.620 mdyn/Å and $K(MX)_{eq}$ = 1.403 mdyn/Å) and $SnCl_4 \cdot 2NCCH_3$ ($K(MX)_{ax}$ = 1.707 mdyn/Å and $K(MX)_{eq}$ = 1.497 mdyn/Å)[18]. For these mentioned complexes, the X-ray studies show slightly different bond distances.[19 21]

Compared with those of the free $POCl_3$,[22,23] the value of K(PO) of the complexes is smaller and that of K(PCl) larger, and these tendencies of force constants also give a result that the coordination is formed through the oxygen atom. The electron density drift is along the Cl -P O M bonds in the direction of the metal.[10]

The obtained values of K(SbO) and K(NbO) show a slight tendency to be higher than those obtained for $MCl_4 \cdot 2POCl_3$ (K(TiO) = 0.379 mdyn/Å and K(SnO) = 0.375 mdyn/Å) and for $(TiCl_4 \cdot POCl_3)_2$ (K(TiO) = 0.353 mdyn/Å). This observed trend probably can be correlated with the higher oxidation number in Sb and Nb atoms, since the coordination numbers are the same in all these complexes. The values of these force constants are reasonable considering the nature of weak donor-acceptor bond strength, which is arised from the low effective charge on the oxygen atom of $POCl_3$,[24] and consequently from the weak donation of an electron lone pair. These constants K(MO) are smaller than K(MN) of $TiCl_4 \cdot 2NCCH_3$ and $SnCl_4 \cdot 2NCCH_3$,[18] *e.g.*, 0.794 and 0.668 mdyn/Å, and this tendency is supported by difference of the donicity between $POCl_3$ and CH_3CN.[25]

ACKNOWLEDGMENTS

We wish to thank FINEP (Financiadora de Estudos e Projetos) for financial support and O.L.A. is also indebted to FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for a fellowship.

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