Low-frequency Vibrational Spectra of Some 4-Benzylpiperidinium and *N*-Benzylpiperazinium Pentahalogenoantimonates(III) and Pentahalogenobismuthates(III). Partial Crystal Structure Determination of 4-Benzylpiperidinium Pentachloroantimonate(III)

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Some compounds of the type $[bzpipn]_2[MX_5]$ and $[bzpipzn][MX_5]$ (bzpipn = 4-benzylpiperidinium cation; bzpipzn = *N*-benzylpiperazinium dication; M = Sb or Bi; X = Cl or Br) have been prepared and characterized by means of Raman and far-i.r. spectroscopy. The crystal data, although poor, of the $[bzpipn]_2[SbCl_5]$ compound show that the antimony atom is surrounded by six chlorine atoms. Five of these are strictly bonded to the metal atom (2.5 Å), forming a square-pyramidal $SbCl_5^{2-}$ unit, and another chlorine atom of an adjacent $SbCl_5^{2-}$ unit completes the octahedral co-ordination around the metal atom through a weak interaction (3.2 Å), giving rise to infinite chains running along the *c* axis. The molecular structures of the complexes depend more on the halogen atoms than on the counter-cation dimensions and hydrogen-bonding abilities. In fact the vibrational spectra of all the chloro-anions may be interpreted on the basis of the crystal structure of the $[bzpipn]_2[SbCl_5]$ compound, while those of the bromo-anions suggest the presence of a distorted octahedron of bromine atoms around the metal with two bromine bridges that link adjacent metal atoms.

OUR interest in the chemical behaviour of halogeno-complexes derives from the fact that their geometries are greatly affected by many factors,[1] among which are interactions due to crystal-packing forces and hydrogen bonding to cations.

By using counter cations like the 4-benzylpiperidinium and *N*-benzylpiperazinium cations (bzpipn and bzpipzn respectively), which have similar dimensions and therefore similar size effects, the effect of hydrogen bonding alone may be investigated. In this paper we report on the influence of this effect on the co-ordination geometries of the halogenoantimonate(III) and halogenobismuthate(III) ions.

The choice of these metals is due to the fact that, because of the electronic structure of the Group 5B atoms, the species $M^{III}X_5^{2-}$ may present some particularly interesting stereochemical possibilities, depending on the role of the lone pair.

EXPERIMENTAL

The hydrohalide salts were prepared as previously described.[2] All the complexes were prepared by mixing ethanolic solutions or methanolic solutions of the metal halides and of the hydrohalide salts in metal-to-ligand molar ratios of 1 : 2 or 1 : 1.

All the compounds were recrystallized from methanol.

Analytical data are reported in Table 1 and are in agreement with the cited formulae, within experimental error. All the compounds are crystalline, stable in air, and insoluble in non-polar organic solvents. Nitrogen, carbon, and hydrogen were analysed with a Carlo Erba elemental analyser instrument, model 1104. The halogens were directly determined from aqueous solutions of the complexes by the Volhard method.

TABLE 1

Analytical data

Compound	Analysis (%) *				
	C	H	N	Cl	Br
$[bzpipn]_2[SbCl_5]$	44.8 (44.2)	6.00 (5.55)	4.20 (4.30)	27.1 (27.2)	
$[bzpipn]_2[SbBr_5]$	32.8 (32.95)	4.15 (4.15)	3.20 (3.20)		45.7 (45.75)
$[bzpipn]_2[BiCl_5]$	39.2 (39.0)	4.95 (4.90)	3.85 (3.80)	23.85 (24.0)	
$[bzpipn]_2[BiBr_5]$	30.0 (29.95)	3.90 (3.75)	2.95 (2.90)		42.0 (41.6)
$[bzpipzn][SbCl_5]$	28.0 (27.7)	3.70 (3.60)	5.35 (5.90)	37.3 (37.25)	
$[bzpipzn][SbBr_5]$	18.85 (18.9)	2.90 (2.45)	3.55 (4.00)		57.3 (57.2)
$[bzpipzn][BiCl_5]$	23.3 (23.45)	3.55 (3.05)	4.65 (4.95)	31.5 (31.45)	
$[bzpipzn][BiBr_5]$	16.2 (16.8)	2.55 (2.20)	3.30 (3.55)		50.85 (50.85)

* Calculated values are given in parentheses.

Determination and Refinement of the Crystal Structure.—Great difficulties were experienced in obtaining single crystals suitable for *X*-ray analysis. After recrystallization of the compounds, the best crystals, although not completely satisfactorily, were obtained for 4-benzylpiperidinium pentachloroantimonate(III).

Crystal data. $C_{24}H_{36}Cl_5N_2Sb$, $M = 651.521$, Triclinic, $a = 16.655(6)$, $b = 24.335(9)$, $c = 7.497(4)$ Å, $\alpha = 89.97(8)$, $\beta = 77.02(7)$, $\gamma = 85.69(7)°$, $U = 2\,952.1$ Å^3, D_m (flotation) = 1.48 g cm^{-3}, $Z = 4$, $D_c = 1.466$ g cm^{-3}, $F(000) = 1\,320$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 73.9 cm^{-1}, space group $P\bar{1}$ (C_i^1, no. 2).

The selected crystal (0.21 × 0.08 × 0.07 mm), sealed on a glass fibre, was directly mounted on a Philips PW 1100 automatic diffractometer. Cell data were obtained from the least-squares refinement of the setting angles of 22 strong high-angle reflections, by using the standard control program of the PW 1100 system for a randomly oriented crystal and graphite-monochromated Mo-K_α radiation. Intensities were collected in the θ—2θ scan mode, $3 < \theta < 22°$. The scan width was 1.0° and the scan speed 2.4° min^{-1}, while background counts were taken at the extremes of the scan for a time equal to 10 s.

A total of 7 174 independent reflections ($\pm h$, $\pm k$, $+l$) were measured, but, because of the small crystal size, only 1 570 had $I > 2\sigma(I)$ [$\sigma(I)$ = (peak counts + total background counts)$^{\frac{1}{2}}$] and were considered observed. Two standard reflections, monitored every 180 reflections, showed no changes in intensities. No absorption correction was applied.

A three-dimensional Patterson map provided the approximate locations of two Sb and ten Cl atoms, and a least-squares refinement of their positional and isotropic thermal parameters converged to a conventional R factor of 0.256.* But at this stage neither difference- nor observed-Fourier syntheses provided clear evidence for the locations of the remaining 52 C and N atoms. Thus, considering the quality of intensity data and their limited quantity, and in view of the large number of independent atoms in the structure, the X-ray analysis was interrupted at this stage; results are summarized in Figure 1.

* Major calculations were performed on the CYBER 76 computer of Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale at Bologna by using the 'SHELX-76' system of programs (G. M. Sheldrick, 'SHELX-76 Program for Crystal Structure Determination,' Cambridge, 1976). An E map calculated from the most probable set of signs, produced by the 'SHELX-76' direct methods program, provided the same solution obtained from the Patterson map.

Interatomic distances and angles are given in Table 2 and positional and thermal parameters in Table 3. The observed and calculated structure factors are available in Supplementary Publication No. SUP 22993 (12 pp.).†

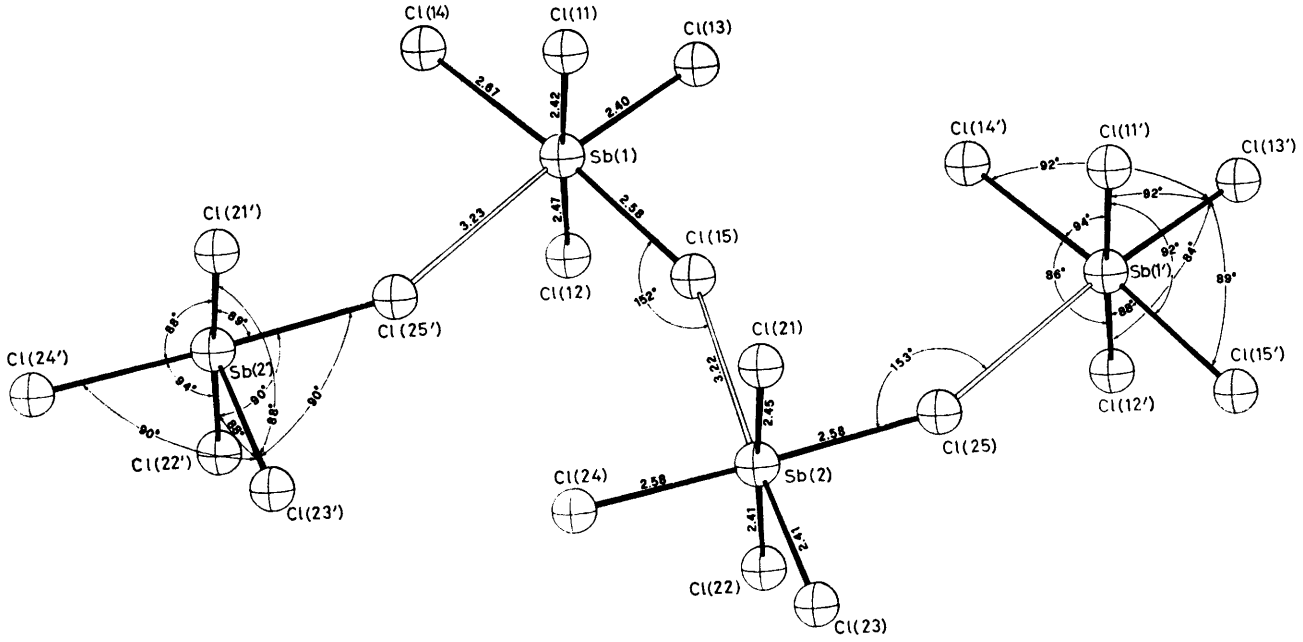

FIGURE 1 Perspective view of the structure along the c axis

Physical Measurements.—Infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer in Nujol mull on Polythene. Raman spectra were recorded for solid samples on a CODERG PHO spectrophotometer equipped with krypton and argon lasers.

TABLE 2

Interatomic distances (Å) and angles (°) for $[bzpipn]_2[SbCl_5]$ with estimated standard deviations in parentheses

(*a*) Distances

Sb(1)–Cl(11)	2.42(7)	Sb(2)–Cl(21)	2.45(7)
Sb(1)–Cl(12)	2.47(6)	Sb(2)–Cl(22)	2.41(8)
Sb(1)–Cl(13)	2.40(4)	Sb(2)–Cl(23)	2.41(4)
Sb(1)–Cl(14)	2.67(4)	Sb(2)–Cl(24)	2.58(5)
Sb(1)–Cl(15)	2.58(4)	Sb(2)–Cl(25)	2.58(5)
Sb(1)–Cl(25')	3.23(4)	Sb(2)–Cl(15)	3.22(4)

(*b*) Angles

Cl(11)–Sb(1)–Cl(12)	176(2)	Cl(21)–Sb(2)–Cl(22)	176(2)
Cl(11)–Sb(1)–Cl(13)	92(2)	Cl(21)–Sb(2)–Cl(23)	88(2)
Cl(11)–Sb(1)–Cl(14)	94(1)	Cl(21)–Sb(2)–Cl(24)	88(2)
Cl(11)–Sb(1)–Cl(15)	92(2)	Cl(21)–Sb(2)–Cl(25)	89(2)
Cl(11)–Sb(1)–Cl(25')	91(1)	Cl(21)–Sb(2)–Cl(15)	93(2)
Cl(12)–Sb(1)–Cl(13)	84(2)	Cl(22)–Sb(2)–Cl(23)	88(2)
Cl(12)–Sb(1)–Cl(14)	86(2)	Cl(22)–Sb(2)–Cl(24)	94(2)
Cl(12)–Sb(1)–Cl(15)	88(2)	Cl(22)–Sb(2)–Cl(25)	90(2)
Cl(12)–Sb(1)–Cl(25')	93(1)	Cl(22)–Sb(2)–Cl(15)	91(2)
Cl(13)–Sb(1)–Cl(14)	92(1)	Cl(23)–Sb(2)–Cl(24)	90(1)
Cl(13)–Sb(1)–Cl(15)	89(1)	Cl(23)–Sb(2)–Cl(25)	90(1)
Cl(13)–Sb(1)–Cl(25')	175(2)	Cl(23)–Sb(2)–Cl(15)	176(2)
Cl(14)–Sb(1)–Cl(15)	173(2)	Cl(24)–Sb(2)–Cl(25)	177(2)
Cl(14)–Sb(1)–Cl(25')	92(1)	Cl(24)–Sb(2)–Cl(15)	94(1)
Cl(15)–Sb(1)–Cl(25')	86(1)	Cl(25)–Sb(2)–Cl(15)	86(1)
Sb(1)–Cl(15)–Sb(2)	152(1)	Sb(2)–Cl(25)–Sb(1')	153(2)

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

RESULTS AND DISCUSSION

Crystal Structure of $[bzpipn]_2[SbCl_5]$.—Although the crystal data were poor, the structure nevertheless clearly consists of chloroantimonate(III) anions and 4-benzylpiperidinium cations. As shown in the perspective view of the molecule (Figure 1), the antimony is surrounded by six chlorine atoms, five of which are strictly bonded to it

TABLE 3

Positional and thermal parameters of the Sb and Cl atoms for $[bzpipn]_2[SbCl_5]$

Atom	*x*	*y*	*z*	B/Å^2
Sb(1)	0.084 1(9)	0.311 9(4)	0.141 8(14)	2.4(2)
Cl(11)	0.201 0(48)	0.244 0(20)	0.083 1(71)	5.5(1.3)
Cl(12)	−0.029 6(37)	0.385 3(15)	0.186 1(56)	3.6(8)
Cl(13)	0.156 7(41)	0.373 9(17)	−0.075 3(62)	3.9(9)
Cl(14)	0.128 5(39)	0.359 7(16)	0.421 0(58)	4.0(9)
Cl(15)	0.024 5(40)	0.272 5(17)	−0.116 4(61)	4.7(9)
Sb(2)	−0.084 1(11)	0.188 3(4)	−0.272 8(17)	3.3(3)
Cl(21)	0.029 7(45)	0.116 1(19)	−0.334 7(66)	4.4(1.0)
Cl(22)	−0.198 8(52)	0.257 2(22)	−0.231 9(77)	6.2(1.2)
Cl(23)	−0.164 0(39)	0.128 8(17)	−0.409 2(61)	4.0(9)
Cl(24)	−0.135 2(46)	0.144 1(19)	0.041 7(68)	5.4(1.1)
Cl(25)	−0.025 8(45)	0.228 0(19)	−0.590 2(65)	5.2(1.0)

(mean distance 2.5 Å) and the sixth completing the distorted octahedral co-ordination around it through a weak interaction (3.2 Å). This interaction, being 0.8 Å less than the sum of the van der Waals radii,[3] may be considered as a bonding interaction. Two adjacent antimony atoms are bridged by one chlorine atom so that the anions are linked through weak interactions (3.2 Å) forming infinite chains along the *c* axis.

This type of structure is unusual for antimony(III). In fact, among the very few antimony(III) chloride structures reported in the literature, $SbCl_3$ exhibits a trigonal-pyramidal structure[4] while in $[NH_4]_2[SbCl_5]$ the chlorine atoms are arranged in a square-pyramidal geometry around the antimony atom,[5] the assumed stereochemically active unshared electron pair occupying the sixth position of co-ordination. The anion $SbCl_6^{3-}$ forms perfect octahedra in $[Co(NH_3)_6][SbCl_6]$[6] while the $SbCl_5^{2-}$ anion in $K_2[SbCl_5]$ displays a distorted square-planar configuration;[7] in this structure some type of weak interaction between the $SbCl_5^{2-}$ anions is possible. In fact in the sixth position of hypothetical octahedral co-ordination, the antimony atom of the $SbCl_5^{2-}$ anion links to a chlorine atom of a different $SbCl_5^{2-}$ anion at a distance of 0.02 Å lower than the sum of the van der Waals radii.[3] The $SbCl_4^-$ anion in $[C_5H_5NH][SbCl_4]$ forms an infinite chain by means of chlorine bridges,[8] each bridging chlorine being 2.64 Å from one antimony and 3.12 Å from the next. The presence of two bridging chlorines in the $SbCl_4^-$ unit causes each antimony to possess a distorted octahedral environment.

Vibrational Spectra of the $[bzpipn]_2[MX_5]$ (M = Sb *or* Bi; X = Cl *or* Br) *Complexes*.—As reported above, the antimony atom in $[bzpipn]_2[SbCl_5]$ has a distorted octahedral co-ordination (C_{4v} symmetry), there being one longer Sb–Cl bond. Consequently, two types of Sb–Cl stretching vibrations may be expected, one type corresponding to the stretches of the $SbCl_5^{2-}$ unit, having a square-pyramidal structure, and the other to the stretch of the longer Sb–Cl bond. In particular, the former stretching mode might appear at a higher wavelength than the latter type.

For the first type of Sb–Cl stretch in C_{4v} symmetry we

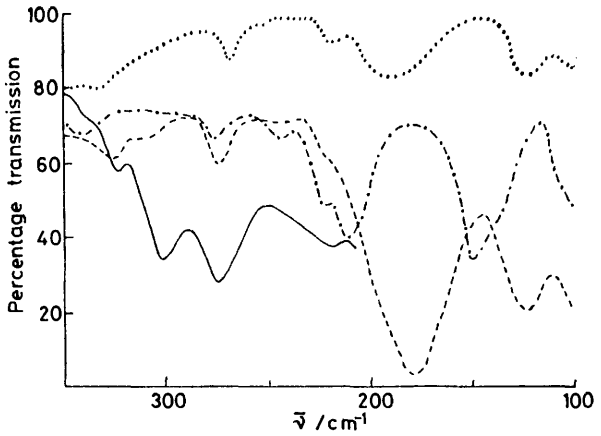

FIGURE 2 I.r. spectra (Nujol mulls) of $[bzpipn]_2[SbCl_5]$ (——), $[bzpipn]_2[SbBr_5]$ (– – –), [bzpipn]Cl (– · –), and [bzpipn]Br (· · ·)

can expect vibrational modes: $2A_1 + E$ (all i.r. and Raman active) $+B_1$ (Raman active only). For the second type of Sb–Cl stretch we expect one A_1 vibration (i.r. and Raman active). The shape and positions of the bands in the observed i.r. and Raman spectra of the complex, shown in Figures 2 and 3, agree well with these predictions. The most probable assignments of the Sb–Cl stretching frequencies are reported in Table 4.

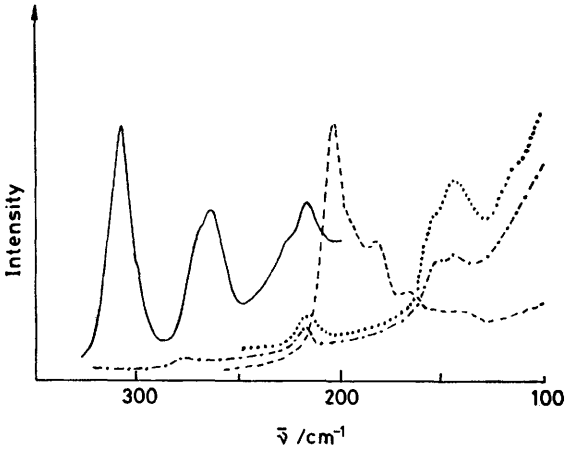

FIGURE 3 Raman spectra of solid $[bzpipn]_2[SbCl_5]$ (——), $[bzpipn]_2[SbBr_5]$ (– – –), [bzpipn]Cl (– · –), and [bzpipn]Br (· · ·)

The assignment of the longer Sb–Cl bond stretching frequency (3.2 Å) to the band appearing at 219 cm^{-1} in the Raman spectrum, corresponding to a shoulder in the i.r. spectrum, cannot be conclusive since in the same spectral region a ligand band is present.

As support for our assignments, we note that the

Sb–Cl stretching frequencies found at higher energies strongly resemble those reported in the literature [2,9] for square-pyramidal $SbCl_5^{2-}$ anions.

The i.r. and Raman spectra of the $[bzpipn]_2[BiCl_5]$ complex in the region of the M–Cl stretching vibrations show trends similar to those of the corresponding antimony(III) complex and to those of square-pyramidal $BiCl_5^{2-}$ anions.[2,9,10] Consequently, for this complex a distorted-octahedral arrangement of halogen atoms around the metal ion, similar to that found for the parent antimony(III) complex, or square-pyramidal co-ordination, in which the stereochemically active unshared electron pair occupies the sixth co-ordination position, may be suggested. The lack in the spectra of a band assignable to the stretch arising from the longer M–Cl bond makes it impossible to choose between these two suggestions.

The i.r. and Raman spectra of the $[bzpipn]_2[SbBr_5]$ compound (Figures 2 and 3) strongly resemble those of the structurally known compound $[pipn]_2[SbBr_5]$ (pipn = piperidinium),[2,11–13], for which a bridged polymeric structure, containing antimony atoms at the centres of distorted octahedra and two halogens bridging two adjacent antimony atoms, may be suggested. In this situation there should be no effect of the 'lone pair' upon co-ordination. The symmetry around the antimony atom would be C_{2v} with two possible A_1, one B_1, and one B_2 stretching vibrations for the Sb–Br terminal bonds and one A_1 and one B_1 stretching vibrations for the Sb–Br bridging bonds. These stretching vibrations are all i.r. and Raman active.

Possible assignments for the Sb–Br stretches in our compound are given in Table 5. The values of these vibrations agree with those reported for many other $R_2[SbBr_5]$ compounds, for which a structure similar to that of $[pipn]_2[SbBr_5]$ has been hypothesized.[14]

For the $[bzpipn]_2[BiBr_5]$ compound, co-ordination of the type proposed for the corresponding antimony compound may be hypothesized. In fact, its i.r. and Raman spectra (Table 5) are similar to those reported for some $R_2[BiBr_5]$ complexes [12,15] having molecular structures of the type found for $[pipn]_2[BiBr_5]$, which is isostructural with $[pipn]_2[SbBr_5]$.[16] Therefore for the $[bzpipn]_2[BiBr_5]$ complex there is little evidence for any influence of the bismuth 'lone pair' on co-ordination around the metal ion.

TABLE 4

Vibrational stretching frequencies (cm^{-1}) of $SbCl_5^{2-}$ and $BiCl_5^{2-}$ complexes *

$R_2[SbCl_5]$			$R_2[BiCl_5]$			
R = bzpipn		R_2 = bzpipzn	R = bzpipn		R_2 = bzpipzn	Assignment
I.r.	Raman	I.r.	I.r.	Raman	I.r.	
	309 (10)			266 (10)		A_1
301s	300 (sh)	300m	240 (sh)			A_1
274vs	270 (sh)	268vs	224vs		230vs	E
	266 (5)			221 (3)		B_1
220 (sh)	219 (3)					A_1

* Relative Raman intensities are given in parentheses: s = strong, m = medium, v = very, sh = shoulder.

Vibrational Spectra of $[bzpipzn][MX_5]$ *Complexes* (M = Sb *or* Bi; X = Cl *or* Br).—The results of the vibrational spectra of these complexes are incomplete since the complexes altered on laser irradiation. Nevertheless their i.r. spectra agree closely with those of the corresponding 4-benzylpiperidinium salts, for which a C_{4v} symmetry is suggested for the chloro-anions, while a C_{2v} symmetry is suggested for the bromo-anions.

TABLE 5

Vibrational stretching frequencies (cm^{-1}) of $SbBr_5^{2-}$ and $BiBr_5^{2-}$ complexes *

$R_2[SbBr_5]$			$R_2[BiBr_5]$			
R = bzpipn		R_2 = bzpipzn	R = bzpipn		R_2 = bzpipzn	Assignment
I.r.	Raman	I.r.	I.r.	Raman	I.r.	
	206 (10)			171 (10)		A_1 Terminal
	197 (sh)		156s		156vs	B_1 stretching
	184 (4)			150 (5)		A_1 modes
178vs	170 (sh)	180vs				B_2
	140w		118s	120w		A_1 Bridging
125s,br		120s,br	130vs,br		130m,br	B_1 stretching modes

* Relative Raman intensities given in parentheses: s = strong, m = medium, v = very, sh = shoulder, br = broad.

Conclusions.—This main conclusion drawn from this work is as follows. The molecular structure of the complexes depend on the halogens more than on the dimension or hydrogen-bonding ability of the counter cation. In the chloro-complexes, the metal ion sits in an octahedral co-ordination environment arising from five equivalent metal–chlorine bonds and one longer metal–chlorine bond. Therefore, we think it possible to describe their structures approximately as containing the square-pyramidal MCl_5^{2-} anion, slightly perturbed by a sixth very long metal–chlorine bond, due to the interaction with another MCl_5^{2-} anion. On the other

hand, in the bromo-derivatives, as in the $[pipn_2][MBr_5]$ (M = Sb or Bi) complexes, the anion shows a distorted octahedron of Br atoms around the metal atom with two Br bridges that link adjacent metal atoms.

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REFERENCES

[1] D. W. Smith, *Coord. Chem. Rev.*, 1976, **21**, 93.
[2] F. Cariati, G. Marcotrigiano, L. Menabue, F. Morazzoni, G. C. Pellacani, and G. M. Zanderighi, *Spectrochim. Acta, Part A*, 1978, **34**, 801.
[3] L. Pauling, 'Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.
[4] I. Lindquist and A. Niggli, *J. Inorg. Nucl. Chem.*, 1956, **2**, 345.
[5] M. Webster and S. Keats, *J. Chem. Soc. A*, 1971, 298.
[6] D. R. Schroeder and R. A. Jacobson, *Inorg. Chem.*, 1973, **12**, 210.
[7] R. K. Wismer and R. A. Jacobson, *Inorg. Chem.*, 1974, **13**, 1678.
[8] S. K. Porter and R. A. Jacobson, *J. Chem. Soc. A*, 1970, 1356.
[9] R. A. Walton, *Spectrochim. Acta, Part A*, 1968, **24**, 1527.
[10] R. A. Work and M. L. Good, *Spectrochim. Acta, Part A*, 1973, **29**, 2547.
[11] G. C. Allen and R. F. McMeeking, *Inorg. Chim. Acta*, 1977, **23**, 285.
[12] M. A. Hooper and D. W. James, *Aust. J. Chem.*, 1973, **26**, 1401.
[13] H. A. Abdel-Rehim and E. A. Meyers, *Cryst. Struct. Commun.*, 1973, **2**, 45.
[14] P. W. Jagodzinski and J. Laane, *J. Raman Spectrosc.*, 1980, **9**, 22.
[15] J. Laane and P. W. Jagodzinski, *Inorg. Chem.*, 1980, **19**, 44.
[16] W. G. McPherson and E. A. Meyers, *J. Phys. Chem.*, 1968, **72**, 532.