

## The Influence of $\pi$ -Bonding and Steric Factors on Hexahalogeno-metallates

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### Abstract

A comparison of the asymmetric stretching frequency  $\nu_3$  and unit cell length  $a_0$  for a series of hexahalogeno-metallates  $A_2MX_6$  [ $A = K^+, Rb^+, Cs^+$  and  $NH_4^+$ ,  $M = Ru, Os, Sn$  and  $Te$  and  $X = Cl, Br$ ] has been made. Trends observed for the tellurium and tin compounds may be related to steric factors whereas possible  $M \rightarrow X$   $d_{\pi}-p_{\pi}$  bonding may explain the opposite trend found for ruthenium and osmium compounds.

It has often been reported that for the transition metal hexahalogeno complexes the asymmetric stretching frequency  $\nu_3$  (in the infrared) increases as the size of the cation decreased.<sup>1,2</sup> This has been attributed to variations in the  $M-X$   $\pi$ -bonding.

In order to investigate this effect a range of compounds have been studied and attempts made to relate the infrared data to the structural parameters of the metal complexes.

The complexes  $A_2MX_6$  [ $A = K^+, Rb^+, Cs^+$  and  $NH_4^+$ ;  $M = Ru, Os, Sn$  and  $Te$ ; and  $X = Cl$  and  $Br$ ] all exhibit the cubic  $K_2PtCl_6$  structure. Up to 12 lines on the X-ray powder diffractograms were measured and calculation of the cell parameter  $a_0$  was carried out by least-squares refinement. The results are listed in Table 1.

The space available in the unit cell for the halogens can be estimated in a variety of ways. One such is to calculate the quantity  $a_0/\sqrt{2} - 2r_A$ . It is clear from the figures in Table 1 that as the cation size increases there is, overall, less space available for the halogen and hence for the hexahalogeno anions  $MX_6^{2-}$ . (A similar calculation for the ammonium salts is possible, but less reliable because of the possibility of hydrogen bonding influencing the unit cell size.) The constraint arising from an increase in cation size could be expected to lead to a rise in the metal-halogen stretching frequency. This is observed for the tellurium compounds, while the tin complexes show little or no significant change with cation. It is probable that the tin complexes are normal and the tellurium compounds abnormal. For the latter element the influence of the lone pair is to lengthen the  $Te-X$  bond significantly. This is reflected in the low values of the asymmetric stretching mode  $\nu_3$ . Since the  $Te-X$  bond is longer than expected for a normal covalent bond it is probably more susceptible to constraints imposed in the solid state.

<sup>1</sup> Adams, D. M., 'Metal-Ligand and Related Vibrations' (Edward Arnold: London 1967).

<sup>2</sup> Adams, D. M., Gebbie, H. A., and Peacock, R. D., *Nature*, 1963, **199**, 278.

The same lattice compression occurs for the hexahalogeno complexes of ruthenium and osmium, but the trend in  $\nu_3$  is in the opposite direction (Table 1), viz. the frequency decreases with increase in cation size. Clearly some other factor becomes important for the transition metals. The principal difference between the transition metals and the metals of the p-block is the ability of the transition metal to donate d electrons to

Table 1. X-ray powder diffractogram data

$a_0$  is in Å and is  $\pm 0.001$ – $\pm 0.004$  Å;  $\nu_3$  is in  $\text{cm}^{-1}$  and is  $\pm 2$ – $\pm 3$   $\text{cm}^{-1}$ ;  $r_A$  is the radius of the alkali metal cation:  $\text{K}^+$  1.33,  $\text{Rb}^+$  1.48,  $\text{Cs}^+$  1.69 Å

Compound	$a_0$	$\nu_3$	$a_0/\sqrt{2}-2r_A$	Compound	$a_0$	$\nu_3$	$a_0/\sqrt{2}-2r_A$
$\text{K}_2\text{TeCl}_6$	10.147	230	4.52	$\text{K}_2\text{RuCl}_6$	9.772	338 <sup>B</sup>	4.25
$(\text{NH}_4)_2\text{TeCl}_6$	10.201	241		$(\text{NH}_4)_2\text{RuCl}_6$	9.875	332	
$\text{Rb}_2\text{TeCl}_6$	10.248	245	4.29	$\text{Rb}_2\text{RuCl}_6$	9.925	333	4.06
$\text{Cs}_2\text{TeCl}_6$	10.478	250	4.03	$\text{Cs}_2\text{RuCl}_6$	10.208	327	3.84
$\text{K}_2\text{TeBr}_6$	10.670	188	4.89	$\text{K}_2\text{RuBr}_6$	10.309	263	4.63
$(\text{NH}_4)_2\text{TeBr}_6$	10.733	197		$(\text{NH}_4)_2\text{RuBr}_6$	10.383	248	
$\text{Rb}_2\text{TeBr}_6$	10.771	198	4.66	$\text{Rb}_2\text{RuBr}_6$	10.452	246	4.43
$\text{Cs}_2\text{TeBr}_6$	10.927	200	4.35	$\text{Cs}_2\text{RuBr}_6$	10.615	243	4.13
$\text{K}_2\text{SnCl}_6$	9.998	315	4.41	$\text{K}_2\text{OsCl}_6$	9.780	325 <sup>C</sup>	4.26
$(\text{NH}_4)_2\text{SnCl}_6$	10.054	313 <sup>A</sup>		$(\text{NH}_4)_2\text{OsCl}_6$	9.889	319	
$\text{Rb}_2\text{SnCl}_6$	10.125	318	4.20	$\text{Rb}_2\text{OsCl}_6$	9.976	320	4.10
$\text{Cs}_2\text{SnCl}_6$	10.375	311	3.96	$\text{Cs}_2\text{OsCl}_6$	10.230	314 <sup>D</sup>	3.86
$\text{K}_2\text{SnBr}_6$		220		$\text{K}_2\text{OsBr}_6$	10.348	227	4.66
$(\text{NH}_4)_2\text{SnBr}_6$		220		$(\text{NH}_4)_2\text{OsBr}_6$	10.395	224	
$\text{Rb}_2\text{SnBr}_6$		221		$\text{Rb}_2\text{OsBr}_6$	10.434	219	4.42
$\text{Cs}_2\text{SnBr}_6$		215		$\text{Cs}_2\text{OsBr}_6$	10.662	218	4.16

<sup>A</sup> Our results agree with those of Hiraishi, J., Nakagawa, I., and Shimanouchi, T., *Spectrochim. Acta*, 1964, **20** 819, and Beattie, I. R., McQuillan, G. P., Rule, L., and Webster, M., *J. Chem. Soc.*, 1963, 1514.

<sup>B</sup> A value of  $346\text{ cm}^{-1}$  has been reported by Adams, D. M., and Gebbie, H. A., *Spectrochim. Acta*, 1963, **19**, 925.

<sup>C</sup> For values similar to ours see ref. 1, p. 64.

<sup>D</sup> For the same result see Woodward, L. A., and Ware, M. J., *Spectrochim. Acta*, 1964, **20**, 711.

the ligand in a  $\pi$ -bond  $\text{M}(\text{d}_\pi) \rightarrow \text{X}(\text{d}_\pi)$ . It is suggested that this is the reason for the observed trend in  $\nu_3$  with  $a_0$  for the ruthenium and osmium complexes. The reason for the increase in  $\nu_3$  with decrease in size of the cation is probably the stronger polarizing influence of smaller cations on the halogen, which assists in the electron donation from transition metal to halogen.

If the  $\text{M}(\text{d}_\pi) \rightarrow \text{X}(\text{d}_\pi)$  bond is important it could be expected to increase in strength across the transition metal series. The data<sup>3–5</sup> listed in Table 2 indicate that this is so. Data presented by Brown, McDugle and Kent<sup>6</sup> show a similar trend in  $\nu_3$  across the third transition metal series for the  $\text{MCl}_6^{2-}$  species; however, they do not specify the counter cation. The trend in  $a_0$  is as expected; but the change is small compared with the change in  $a_0$  with alkali metal cation. Hence compression of the lattice will be

<sup>3</sup> Edwards, A. J., Peacock, R. D., and Said, A., *J. Chem. Soc.*, 1962, 4643.

<sup>4</sup> Kennedy, C. J., and Peacock, R. D., *J. Chem. Soc.*, 1963, 3392.

<sup>5</sup> Fergusson, J. E., and Scaife, D. E., *Aust. J. Chem.*, 1971, **24**, 1325.

<sup>6</sup> Brown, T. L., McDugle, W. G., and Kent, L. G., *J. Amer. Chem. Soc.*, 1970, **92**, 3645.

small but significant. The change in  $\nu_3$  is in accord with the lattice compression but, the increase in the stretching frequency is greater than expected for a small change in  $a_0$ .

Table 2. Changes across the transition metal series

Compound	$a_0$	$\nu_3$	$a_0/\sqrt{2}-2r_A$	Compound	$a_0$	$\nu_3$	$a_0/\sqrt{2}-2r_A$
$\text{Cs}_2\text{MoCl}_6$	10.27 <sup>3</sup>	325 <sup>2</sup>	3.88	$\text{K}_2\text{WCl}_6$	9.88 <sup>4</sup>	324 <sup>2,4</sup>	4.33
$\text{Cs}_2\text{TcCl}_6$	10.26 <sup>A</sup>	315	3.88	$\text{K}_2\text{ReCl}_6$	9.855	318	4.31
$\text{Cs}_2\text{RuCl}_6$	10.208	327	3.84	$\text{K}_2\text{OsCl}_6$	9.780	325	4.28
$\text{Cs}_2\text{RhCl}_6$	10.24	330	3.86	$\text{K}_2\text{IrCl}_6$	9.765 <sup>5</sup>	331 <sup>5</sup>	4.25
$\text{Cs}_2\text{PdCl}_6$	10.17	334	3.81	$\text{K}_2\text{PtCl}_6$	9.748 <sup>5</sup>	344 <sup>5</sup>	4.23

<sup>A</sup> Estimated.

We suggest this is due to an increase in the degree of  $\text{M} \rightarrow \text{X} \pi$ -bond as the number of d-electrons increase.

### Experimental

The complexes were prepared by standard methods described in the literature, and analysed for halogen.

The infrared spectra were obtained with a R.I.I.C. FS720 Fourier spectrometer, and the powder diffraction data obtained on a Phillips 1010/30 automatic diffractometer. The powder data were calibrated with NaCl; an  $a_0$  value of 5.639 Å was used.

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