

The Raman Spectra of Bis(hexamethylenetetramine)-iodine(I) and -bromine(I) Perchlorates

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Abstract

The low-wavenumber ($< 200\text{ cm}^{-1}$) Raman spectra of bis(hexamethylenetetramine)iodine(I) perchlorate and bis(hexamethylenetetramine)bromine(I) perchlorate have been measured, and the nitrogen-halogen symmetric stretching mode of the cation has been assigned for each compound. The nitrogen-halogen bond stretching and interaction force constants for the cations have been calculated, and these are found to be very similar to those for the corresponding bis(pyridine)halogen(I) cations.

Introduction

We have previously reported the infrared and Raman spectra of the solid 1 : 1 addition complexes of hexamethylenetetramine, $(\text{CH}_2)_6\text{N}_4$ (hx), with iodine¹ and with bromine.² It was shown that the iodine complex can exist in a molecular form, hexamethylenetetramine-1-diiodine, $\text{hx}\cdot\text{I}_2$, and in an ionic form, bis(hexamethylenetetramine)iodine(I) triiodide, $[(\text{hx})_2\text{I}] \text{I}_3$,¹ while the bromine complex apparently only exists in the ionic form bis(hexamethylenetetramine)bromine(I) tribromide, $[(\text{hx})_2\text{Br}] \text{Br}_3$.² The structures of both forms of the iodine complex have recently been determined by X-ray crystallography,^{3,4} and the $(\text{hx})_2\text{I}^+$ ion in $[(\text{hx})_2\text{I}] \text{I}_3$ was shown to have an almost linear N-I-N arrangement with equal N-I bond lengths.³

Assuming centrosymmetric structures for the $(\text{hx})_2\text{X}^+$ ions ($\text{X} = \text{Br}, \text{I}$), we would expect these ions to give rise to symmetric (ν_s) and antisymmetric (ν_a) N-X stretching vibrations, active in the Raman and infrared spectra respectively. We made tentative assignments for these modes in the compounds $[(\text{hx})_2\text{I}] \text{I}_3$ and $[(\text{hx})_2\text{Br}] \text{Br}_3$, and used the resulting frequencies to calculate values for the N-X bond stretching and interaction force constants for the $(\text{hx})_2\text{X}^+$ ions. The values obtained were greater than those for the corresponding bis(pyridine)halogen(I) ions, $(\text{py})_2\text{X}^+$, and this led us to suggest that the N-X bonds in the $(\text{hx})_2\text{X}^+$ ions might be stronger than those in $(\text{py})_2\text{X}^+$.^{1,2} This was not supported by the crystal structure results, which showed that the N-I bond length in $(\text{hx})_2\text{I}^+$ (230 pm) is significantly greater than that in $(\text{py})_2\text{I}^+$ (216 pm).³

¹ Bowmaker, G. A., and Hannan, S. F., *Aust. J. Chem.*, 1971, **24**, 2237.

² Bowmaker, G. A., and Hannan, S. F., *Aust. J. Chem.*, 1972, **25**, 1151.

³ Pritzkow, H., *Acta Crystallogr., Sect. B*, 1975, **31**, 1505.

⁴ Pritzkow, H., *Acta Crystallogr., Sect. B*, 1975, **31**, 1589.

The main uncertainty in the force constant calculations arises from uncertainty in the assignment of $\nu_s(\text{N-X})$. These assignments can be checked by studying the perchlorate salts, since these are more suitable for study by Raman spectroscopy (they are colourless, and contain no anion bands in the low-wavenumber region). We report here the results of such measurements. While this work was in progress the Raman spectrum of $[(\text{hx})_2\text{I}]\text{ClO}_4$ was reported by other workers,⁵ and their results are in good agreement with ours.

Experimental

Preparation of Compounds

Bis(hexamethylenetetramine)iodine(i) perchlorate and bis(hexamethylenetetramine)bromine(i) perchlorate were prepared by previously described methods.^{1,2}

Spectroscopy

Raman spectra were obtained by means of an RCA LD 2140 argon ion laser (514.5 nm line) coupled to a Spex 1401 double monochromator. Samples were examined as powdered solids in glass capillary tubes.

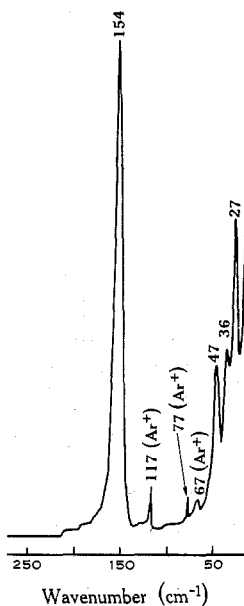


Fig. 1. Low-wavenumber Raman spectrum of $[(\text{hx})_2\text{Br}]\text{ClO}_4$ (514.5 nm excitation).

Results and Discussion

The low-wavenumber Raman spectrum of $[(\text{hx})_2\text{Br}]\text{ClO}_4$ is shown in Fig. 1. This spectrum is very similar to that previously obtained for $[(\text{hx})_2\text{Br}]\text{Br}_3$.² The main feature is a very strong band at 154 cm^{-1} which has no counterpart in the vibrational spectrum of uncomplexed hexamethylenetetramine (the lowest wavenumber fundamental of the hexamethylenetetramine molecule occurs at 378 cm^{-1} ⁶). This can be assigned to $\nu_s(\text{N-Br})$ of the $(\text{hx})_2\text{Br}^+$ ion. The Raman spectrum of

⁵ Jander, J., and Maurer, A., *Z. Anorg. Allg. Chem.*, 1975, **416**, 251.

⁶ Bertie, J. E., and Solinas, M., *J. Chem. Phys.*, 1974, **61**, 1666.

$[(\text{hx})_2\text{I}]\text{ClO}_4$ in the region below 200 cm^{-1} showed only a single band at 138 cm^{-1} , and this can be assigned to $\nu_s(\text{N-I})$ of the $(\text{hx})_2\text{I}^+$ ion.

The N-X stretching frequencies ν_s and ν_A for the $(\text{hx})_2\text{X}^+$ ions are listed in Table 1, together with those for the corresponding $(\text{py})_2\text{X}^+$ ions.⁷ A decrease in $\nu_s(\text{N-X})$ from $\text{X} = \text{Br}$ to $\text{X} = \text{I}$ is observed for both types of ion.

Table 1. Nitrogen-halogen stretching frequencies and force constants for some bis(amine)halogen(i) cations

Ion	ν_s (cm^{-1})	ν_A (cm^{-1})	k (N m^{-1})	k' (N m^{-1})	Ref.
$(\text{py})_2\text{I}^+$	181	172	107	46	^A
$(\text{hx})_2\text{I}^+$	138	165	114	44	^B
$(\text{py})_2\text{Br}^+$	193	170	110	64	^A
$(\text{hx})_2\text{Br}^+$	154	182	128	68	^B

^A Ref. 7. ^B Refs 1 and 2 and this work, from results for the perchlorate salts.

The difference between the $\nu_s(\text{N-X})$ values obtained here for the perchlorates and those previously obtained for the $[(\text{hx})_2\text{X}]\text{X}_3$ compounds^{1,2} is probably due to misassignment of these bands in the latter cases. The Raman spectrum of $[(\text{hx})_2\text{Br}]\text{Br}_3$ shows a strong band at 155 cm^{-1} which we assigned in our previous study to $\nu_s(\text{Br-Br})$ of the tribromide ion, Br_3^- .² It now seems likely that $\nu_s(\text{N-Br})$ for $(\text{hx})_2\text{Br}^+$ and $\nu_s(\text{Br-Br})$ for Br_3^- accidentally occur at the same wavenumber in this complex, thus accounting for the presence of only one strong Raman band in the $100\text{--}200\text{ cm}^{-1}$ region. No such explanation can be given in the case of $[(\text{hx})_2\text{I}]\text{I}_3$, however, since this showed two strong Raman bands at 110 and 155 cm^{-1} . The assignment of the 110 cm^{-1} band to $\nu_s(\text{I-I})$ of I_3^- seems reasonable, but the remaining band at 155 cm^{-1} does not agree well with the value $\nu_s(\text{N-I}) = 138\text{ cm}^{-1}$ found for $[(\text{hx})_2\text{I}]\text{ClO}_4$. It has been suggested that the 155 cm^{-1} band might be due to a laser-induced decomposition product.⁵

Using the more reliable wavenumbers obtained for the perchlorate salts, we have recalculated values for the N-X bond stretching and interaction force constants k and k' . For these calculations the cations are regarded as linear Y-X-Y systems in which the amine molecules behave as point masses Y.^{1,2} The results, together with those for the $(\text{py})_2\text{X}^+$ ions,⁷ are given in Table 1. The values for the $(\text{hx})_2\text{X}^+$ ions are very close to those for the corresponding $(\text{py})_2\text{X}^+$ ions, and the differences cannot be regarded as significant, in view of the approximations involved in the calculations.

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⁷ Haque, I., and Wood, J. L., *J. Mol. Struct.*, 1968, **2**, 217.