Preparation and Infrared Spectra of Hexamethylenetetramine–Di-iodine (1/1, 1/2, and 1/3)

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The i.r. spectra (50—1 350 cm^{-1}) of the solid 1 : 1 and 1 : 2 adducts of hexamethylenetetramine with iodine are discussed with reference to the recently determined crystal structures for these compounds. The preparation of the solid 1 : 3 adduct is reported for the first time, and its i.r. spectrum is analyzed. The spectrum is consistent with a C_{3v} structure in which three iodine molecules are bound to three of the four available nitrogen donor sites in the amine. The preparative method used in a previously reported ^{129}I Mössbauer study of the 1 : 1 adduct has been reinvestigated, and it is shown that the compound studied was probably the 1 : 2 adduct.

THE addition compounds which result from the interaction of amines with halogens and interhalogens have been the subject of considerable research in recent years.[1-5] The main aim of these studies has been to obtain information about the structure and bonding in these compounds, and vibrational spectroscopy has been particularly useful in this respect.[4]

In a previous study of some addition compounds of iodine with hexamethylenetetramine (1,3,5,7-tetra-azatricyclo[3.3.1.1]decane), $C_6H_{12}N_4$, we showed by means of i.r. and Raman spectroscopy that the solid 1 : 1 adduct can exist in a molecular form, hexamethylenetetramine–di-iodine, hx·I_2, and in an ionic form, bis(hexamethylenetetramine)iodine(I) tri-iodide, $[I(hx)_2][I_3]$, and that the molecular form is spontaneously transformed into the ionic form on standing.[6] The structures of both forms of the 1 : 1 adduct have recently been determined by *X*-ray crystallography,[7,8] and the preparation and crystal structure of the 1 : 2 adduct, hx·$2I_2$ have also been reported.[8]

Adducts of hexamethylenetetramine are particularly interesting because they provide an opportunity to examine the degree of interaction between the donor sites in this tetrabasic amine (*i.e.* the extent to which complex formation at one site influences the donor properties of the uncomplexed sites). A previous spectrophotometric study of the hexamethylenetetramine–iodine system indicated that adducts of no higher than 1 : 2 stoicheiometry form in methylcyclohexane solution.[9] The reported observation that the solid 1 : 2 adduct loses iodine very quickly in air,[8] while the 1 : 1 adduct is stable with respect to loss of iodine, might suggest that solid adducts of higher than 1 : 2 stoicheiometry cannot be prepared. We have found, however, that a 1 : 3 adduct hx·$3I_2$ can be easily prepared, and we report here its characterization, and a comparison of the i.r. spectrum with those of the 1 : 1 and 1 : 2 adducts. The conditions under which these compounds are formed from solution are investigated, and it is shown that the stoicheiometry of the product is not always that which would be expected on the basis of the mol ratio of the reagents. It is possible that failure to recognize this fact has led to the assumption of incorrect stoicheiometries in previous work on these compounds,[10] and this question is examined further in the present study.

EXPERIMENTAL

Preparation of Compounds.—Hexamethylenetetramine–di-iodine(1/1) *and bis*(*hexamethylenetetramine*)*iodine*(I) *tri-iodide*. These were prepared by previously described methods.[6]

Hexamethylenetetramine–di-iodine(1/2). A solution of hexamethylenetetramine (0.38 g, 2.7 mmol) in water

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(100 cm^3) was added to a solution of iodine (1.38 g, 5.4 mmol) in ethanol (150 cm^3). The solution was allowed to stand for *ca.* 15 min, and the orange crystalline product was collected and dried *in vacuo* over phosphorus pentaoxide (Found: C, 11.4; H, 1.8; I, 78.1; N, 8.6. Calc. for $C_6H_{12}I_4N_4$: C,11.1; H, 1.9; I, 78.6; N, 8.6%).

Hexamethylenetetramine–di-iodine(1/3). (*a*) *From* hx·$2I_2$ *and iodine.* Hexamethylenetetramine–di-iodine(1/2) (0.409 7 g, 0.632 mmol) was placed in an open weighing bottle in a vacuum desiccator containing a small beaker of powdered iodine. The desiccator was evacuated and allowed to stand for a few days. The mass of the sample increased to 0.571 2 g and remained constant at this value after 2 d. The mass increase of 0.161 5 g corresponds to 0.636 mmol of iodine, or 1.01 mol of iodine per mol of hx·$2I_2$ [Found: I (by iodimetry), 84.4. Calc. for $C_6H_{12}I_6N_4$: 84.5%].

(*b*) *From* $[I(hx)_2][I_3]$ *and iodine.* Bis(hexamethylenetetramine)iodine(I) tri-iodide (0.4505 g, 0.572 mmol) was placed in an open weighing bottle in a vacuum desiccator containing a small beaker of powdered iodine. The desiccator was evacuated and allowed to stand for several days. The mass of the sample increased to 1.033 g and remained constant at this value after 6 d. The mass increase of 0.582 g corresponds to 2.293 mmol of iodine, or 4.01 mol of iodine per mol of $[I(hx)_2][I_3]$. The i.r. spectrum of this product was identical to that of the product obtained in (*a*).

(*c*) *From hexamethylenetetramine and iodine.* A solution of hexamethylenetetramine (0.20 g, 1.4 mmol) in water (100 cm^3) was added to a solution of iodine (1.1 g, 4.3 mmol) in ethanol (10 cm^3). The product separated immediately as a brown precipitate and was collected and dried *in vacuo* over P_4O_{10}. Its i.r. spectrum indicated that it was mainly hx·$3I_2$, with a small amount of hx·$2I_2$ as impurity. The solvents used in this preparation are important. When ethanol was used instead of water as the solvent for the amine only the 1 : 2 adduct was obtained, even when the mol ratio of iodine to amine was increased to 6 : 1.

The 1 : 3 adduct loses iodine on standing in the air. The presence of weak bands due to the 1 : 2 adduct in the i.r. spectra of the pure 1 : 3 adduct indicates that dissociation takes place to a small extent in the mulls. This dissociation was completely suppressed by adding a small amount of iodine to the mulls during their preparation.

Investigation of the Previously Reported Method for Preparing hx·I_2.[10]—(*a*) A solution of hexamethylenetetramine (0.56 g, 4.0 mmol) in water (30 cm^3) was added to a solution of iodine (1.0 g, 3.9 mmol) in ethanol (30 cm^3) at room temperature (294 K). An orange precipitate formed, which turned brown within a few seconds. It was collected and dried *in vacuo*. The i.r. spectrum of this product showed that it was $[I(hx)_2][I_3]$.

(*b*) Same as (*a*), except that the solutions were warmed to 313 K prior to mixing. The i.r. spectrum of the orange product showed that it was mainly hx·$2I_2$.

(*c*) Same as (*a*), except that the concentrations of the solutions were reduced by a factor of five. The i.r. spectrum of the product showed that it was hx·$2I_2$.

Spectroscopy.—Infrared spectra in the range 400—4 000 cm^{-1} were obtained using a Shimadzu IR-27G spectrometer. Spectra were run on Nujol mulls between KBr plates, and were calibrated using the spectrum of polystyrene. The far-i.r. spectra (50—400 cm^{-1}) were obtained using a Grubb–Parsons Cube MKII interferometer fitted with a 6.25-μm Mylar-film beamsplitter. Spectra in this range were run on petroleum jelly mulls between Polythene plates, and were calibrated using the spectrum of water vapour. The far-i.r. spectra were run at room temperature (293 K), and at low temperature (*ca.* 125 K) using the Grubb–Parsons GRM 01 low-temperature cell cooled with liquid nitrogen.

RESULTS AND DISCUSSION

The i.r. spectra in the range 50—1 350 cm^{-1} are listed in the Table. Bands at >1 350 cm^{-1} were obscured by Nujol absorption, and were not examined in this work. The far-i.r. spectra run at *ca.* 125 K are shown in the Figure. The low-temperature spectra were better resolved, and showed band shifts to higher wavenumber of up to 5 cm^{-1} relative to the room-temperature spectra. Apart from these differences, the spectra run at the two temperatures are very similar.

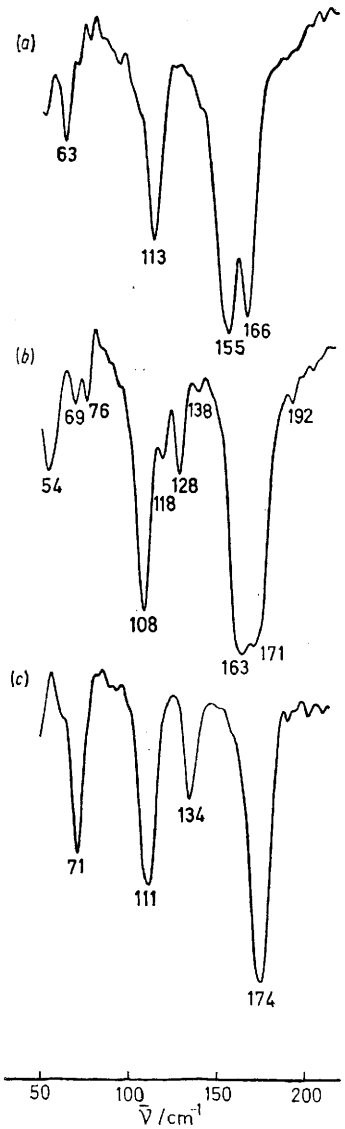
Infrared spectra (50—1 350 cm^{-1}). Spectra at <400 cm^{-1} were run at *ca.* 125 K

hx·I_2	hx·$2I_2$	hx·$3I_2$	Assignment *
1 340vw	1 345vw	1 336w	ν_8 (*E*), ν_{13} (T_1)
1 330w	1 335vw	1 325vw	
1 315w	1 327vw	1 309w	
	1 317vw		
	1 310vw		
1 237s (sh)	1 244s	1 243s	ν_{21} (T_2)
1 230s	1 234s	1 223m	
	1 225m		
1 051m	1 056w	1 058m	ν_3 (A_1), ν_{16} + ν_{24} (T_2), $2\nu_{25}$ (T_2), ν_{22} (T_2)
1 037w (sh)	1 048m	1 036vw	
1 032w	1 030w (sh)	1 023s	
1 016vs	1 021vs	1 009vs	
996vs	1 000vs	983vs	
	989vs		
914m	928w (sh)	922m	ν_{15} (T_1)
	923w		
820s	830m	838m	ν_{23} (T_2), ν_4 (A_1)
815s	811m	829w	
795m	786vs	792s	
764vs	774vs	776s	
746m (sh)	752vw	759w	
698vs	707s	697vs	ν_{24} (T_2)
661vs	679s	663m	
	657m		
516m	527m	522m	ν_{25} (T_2)
507m	515m	505w	
500m	506w		
374vw	384vw		ν_{16} (T_1)
	374vw		
	192vw		?
166vs	171vs	174vs	ν(I–I), ν(N–I)
155vs	163vs		
113s	138vw	134m	
	128m	111s	
	118w		
	108s		
63m	76vw	71s	?
	69vw		
	54m		

*Assignments for hexamethylenetetramine vibrations from ref. 11.

The crystal structures of the 1 : 1 and 1 : 2 adducts show that they contain almost linear N–I–I groups with the iodine atoms lying in the direction of the nitrogen lone-pair orbitals.[8] The approximate local symmetry is therefore C_{3v} for the 1 : 1 and C_{2v} for the 1 : 2 adduct. Free hexamethylenetetramine has T_d symmetry, and its normal co-ordinates transform as $4A_1 + A_2 + 5E +$

$6T_1 + 9T_2$.[11] The expected changes in the vibrational spectrum of hexamethylenetetramine on formation of the 1 : 1 and 1 : 2 adducts can be determined from correlation tables for the point groups T_d, C_{3v}, and C_{2v}.[12]



Far-i.r. spectra at *ca.* 125 K of (*a*) hx·I_2, (*b*) hx·$2I_2$, and (*c*) hx·$3I_2$

The main changes expected in the i.r. spectra are a splitting of the i.r.-active T_2 modes, and activation of the A_1, E, and T_1 modes. The assignments given in the Table for the vibrations of the hexamethylenetetramine molecule in its adducts are based on those previously determined for the uncomplexed molecule,[11] and on the observed intensities and splitting patterns. These assignments differ in some respects from those made in earlier studies of similar compounds,[6,13] and it has not been possible to uniquely assign all the bands because of overlap of the regions concerned. However, bands arising from the T_2 fundamentals ν_{21}, ν_{24}, and ν_{25} and the T_1 fundamentals ν_{15} and ν_{16} have been identified. The T_2 modes provide the best indication of the symmetry of the adduct, as these are expected to split into two components ($A_1 + E$) for C_{3v} symmetry and into three components ($A_1 + B_1 + B_2$) for C_{2v} symmetry. The expected splitting is observed for most of the T_2 modes in the 1 : 1 and 1 : 2 adducts, and is most clearly seen in the ν_{24} (CNC deformation) region at *ca.* 700 cm^{-1} (Table). In the 1 : 1 adduct the ν_{25} fundamental at *ca.* 500 cm^{-1} shows a splitting into three components (Table). This is consistent with the lower site symmetry (C_s) of the adduct molecules in the crystal.[8]

By analogy with the known structures of the 1 : 1 and 1 : 2 adducts, the 1 : 3 adduct would be expected to have a structure in which three iodine molecules are bound to three of the four available nitrogen donor sites of the amine, yielding a structure of C_{3v} symmetry. Such a structure is consistent with the observed splitting of the hexamethylenetramine T_2 fundamentals ν_{21}, ν_{24}, and ν_{25} into doublets (Table). As in the case of the 1 : 1 and 1 : 2 adducts, bands arising from ν_{22} and ν_{23}, the only other T_2 fundamental in the range studied, could not be unambiguously assigned because of the occurrence of other bands in the same region. The presence of a single band at 922 cm^{-1} arising from the inactive T_1 mode ν_{15} of the free amine is also consistent with the proposed structure. In contrast to the 1 : 1 adduct, there is no evidence of further splitting which might indicate lower than C_{3v} symmetry in the solid, although this does not prove that the site symmetry is C_{3v}.

The far-i.r. spectra show bands in the 100—200 cm^{-1} region which arise from I–I and N–I stretching modes. It is not possible to rigorously identify I–I and N–I stretching modes separately, since these internal coordinates are expected to be extensively mixed in the normal modes concerned. It is clear, however, that the 1 : 1 and 1 : 2 adducts show more than the expected number of bands in this region, and it can be shown that the number of bands is less than that expected on the basis of factor-group analysis.[12,14] An additional complication concerns the presence of bands at <100 cm^{-1}. These could be due to intramolecular bending modes or lattice modes, but it is also possible that these involve some N–I and I–I stretching. Thus the far-i.r. region is not as useful as one might hope in providing structural information.

The ^{129}I Mössbauer spectrum of an adduct of hexamethylenetetramine with iodine has been reported by Ichiba *et al.*[10] The compound was obtained by mixing solutions containing equimolar quantities of the amine and iodine, and the Mössbauer spectrum shows the presence of two chemically inequivalent iodine sites in the adduct. Apparently, only the radioactive ^{129}I compound

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was prepared, and no analytical figures were reported, but these workers assumed that the compound studied was the 1 : 1 adduct, hx·I_2. This is now open to question, however, since we have shown that this compound is unstable with respect to its ionic form, and that its preparation requires special conditions.[6] The method used by the above workers differs from that reported by us in the use of water rather than chloroform as the solvent for the amine, and possibly also in the concentrations and temperatures of the solutions. No details of the latter variables were given by these workers, so it is not possible to reproduce their preparation exactly. However, we have found that this method results in the formation of the ionic 1 : 1 adduct $[I(hx)_2][I_3]$, the molecular 1 : 2 adduct hx·$2I_2$, or a mixture of both these compounds, depending on the concentrations and temperatures of the reacting solutions (see Experimental section). The pure 1 : 2 adduct is obtained when the concentrations of both solutions are below *ca.* 3×10^{-2} mol dm^{-3}, in spite of the fact that the mol ratio of the reagents is 1 : 1. For the more concentrated solutions, where mixtures of $[I(hx)_2][I_3]$ and hx·$2I_2$ are formed, the proportion of the latter compound is increased if the solutions are warmed to 313 K prior to mixing. However, we could find no conditions under which hx·I_2 could be isolated using this method.

It is therefore possible that the compound studied in the Mössbauer work was either $[I(hx)_2][I_3]$ or hx·$2I_2$. However, only the second possibility is consistent with the presence of only two chemically inequivalent iodine sites. Moreover, the ^{127}I quadrupole coupling constants determined from the Mössbauer spectrum do not agree with those determined by n.q.r. spectroscopy for two of the three chemically inequivalent iodine sites in $[I(hx)_2]$-$[I_3]$.[15] Thus, the compound studied by Ichiba *et al.* was probably the 1 : 2 adduct.

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