

Resonance Raman spectrum of triiodide complex formed in the reaction of iodine with 1,4,8,11-tetraazacyclotetradecane

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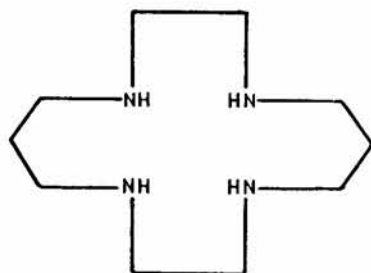
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The resonance Raman spectrum of the solid complex formed in the reaction of 1,4,8,11-tetraazacyclotetradecane (TACTD) with iodine exhibits characteristic bands of the triiodide ion, I_3^- at 147, 108 and 85 cm^{-1} assignable to $\nu_{as}(I-I)$, $\nu_s(I-I)$ and $\delta(I_3^-)$ modes, respectively. The formed complex is best described as $[(TACTD)]^+ \cdot I_3^-$.

The solid complexes formed between iodine and several types of electron donors have attracted considerable attention¹⁻⁷, in view of their good electrical conductivity. Recently, the bis(tetrathiotetradecene)triiodide, $(TTT)_2I_3$ is reported³ to be among the best of the presently known organic conductors.

In previous works^{6,7} vibrational spectroscopy was successfully used in the structural elucidation of a number of iodine compounds. We report herein the formation of the triiodide ion, I_3^- , in the reaction of iodine with 1,4,8,11-tetraazacyclotetradecane (TACTD). The formula and structure of triiodide complex are discussed.



(TACTD)

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Experimental

All chemicals were of AR grade.

The Raman spectra of the triiodide complex were recorded using a Cary model 82 spectrophotometer and a Coherent Radiation Innova 12 argon ion laser. In order to prevent the photochemical and thermal decomposition of the sample by the laser beam, ~2% by weight of the complex in KBr was examined in a rotating solid disk of conventional design. Sodium sulphate was added as an internal standard. The electronic absorption spectra of the reactants and the complex in $CHCl_3$ were obtained using a Perkin-Elmer spectrophotometer model 552.

Preparation of triiodide complex

A solution of iodine ($5 \times 10^{-2} M$) in ethanol (50 ml) was added to an equal volume of a solution of TACTD ($1 \times 10^{-2} M$) in ethanol. The dark brown complex which separated out was filtered and washed several times with ethanol. The use of iodine in excess was checked following the electronic absorption band of the free iodine. The iodide complex analysed for $C_{10}H_{24}N_4I_4$ (Found: C, 15.85; H, 3.35; N, 7.75; I, 73.05. Required: C, 16.90; H, 3.38; N, 7.90; I, 71.82%).

Results and discussion

The Raman spectra of the complex were recorded using laser lines of 514.5 and 488.0 nm with power < 200 mw and resonance enhancement was observed with each excitation line. The assignments of the Raman bands are shown in Table 1. The spectrum can be explained entirely by the presence of the triiodide ion, I_3^- . The three bands at 85, 108 and 147 cm^{-1} are characteristic of this ion⁷⁻¹⁰ and are assigned to $\delta(I_3^-)$, $\nu_s(I-I)$ and $\nu_{as}(I-I)$, respectively. Their Raman activities suggest that the I_3^- ion is non-linear, otherwise, the symmetric stretching

Table 1—Resonance Raman frequencies† (cm^{-1}) of $(TACTD)I_3^-$ complex

$\lambda_{ex} = 488.0 \text{ nm}$	$\lambda_{ex} = 514.5 \text{ nm}$	Assignments
85 m	83 m	$\delta(I_3^-)$
108 s	108 m	$\nu_s(I-I)$
147 s	147 s	$\nu_{as}(I-I)$
220 w		$2 \nu_s(I-I)$
317 w		$3 \nu_s(I-I)$

†s = strong; m = medium; w = weak

mode would only be Raman active. Nevertheless, the appearance of strong resonance Raman band due to $\nu_{as}(I-I)$ does not completely rule out the possibility of I_3^- ion being linear but non-centrosymmetric. The existence of the I_3^- ion in this solid iodine complex is also supported by its electronic absorption spectrum which displays bands characteristic^{8,9} for this ion at 290 ($\epsilon = 4.22 \times 10^{-4} M^{-1} cm^{-1}$) and 360 nm ($\epsilon = 2.42 \times 10^{-4} M^{-1} cm^{-1}$). However, photometric titration measurements in various solvents clearly indicate that the TACTD: I_2 ratio is 1:2. These results along with the elemental analyses indicate that the triiodide complex of iodine with TACTD may be described as $[(TACTD)I]^+ \cdot I_3^-$. This structure is similar to that reported by Bowmaker and Knappstein¹¹ for the complex $[(HMTA)I]^+ \cdot I_3^-$ formed in the reaction of hexamethylenetetramine with iodine in 1:2 molar ratio.

In the light of the foregoing discussion, a general mechanism is proposed for the I_2 -TACTD reaction as follows:

- (i) $TACTD + I_2 = [(TACTD)I]^+ \cdot I^-$
 (ii) $[(TACTD)I]^+ \cdot I^- + I_2 = [(TACTD)I]^+ \cdot I_3^-$

The results presented herein clearly demonstrate the diversity of structures of iodine compounds in the solution and solid states.

Acknowledgement

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References

- 1 Robin M B, *J chem Phys*, 40 (1964) 3369.
- 2 Gabes W & Stufkens D J, *Spectrochim Acta*, 30A (1974) 1835.
- 3 Trotter P J & White P A, *Appl Spectrosc*, 32 (1978) 323.
- 4 Mizuno M, Tanaka J & Harada I, *J phys Chem*, 85 (1981) 1789.
- 5 Kim H, *Biopolymers*, 21 (1982) 2083.
- 6 Nour E M, Chen L H & Laane J, *J phys Chem*, 90 (1986) 2841.
- 7 Nour E M, Chen L H & Laane J, *J Raman Spectrosc*, 17 (1986) 467.
- 8 Kiefer W & Bernstein H J, *Chem phys Lett*, 16 (1972) 5.
- 9 Kaya K, Mikami N, Udagawa Y & Ito M, *Chem phys Lett*, 16 (1972) 151.
- 10 Parrett F W & Taylor N J, *J inorg nucl Chem*, 32 (1970) 2458.
- 11 Bowmaker G A & Knappstein R J, *J chem Soc Dalton*, (1977) 1928.