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Structural and Raman spectroscopic studies as complementary tools in elucidating the nature of the bonding in polyiodides and in donor-I_2 adducts

Paola Deplano [a,*], John R. Ferraro [b,1],
Maria Laura Mercuri [b], Emanuele F. Trogu [a]

[a] *Dipartimento di Chimica e Tecnologie Inorganiche e Metallorganiche, via Ospedale 72, I-091 24 Cagliari, Italy*
[b] *Argonne National Laboratory, Chemistry and Material Science Divisions, 9700 S. Cass Avenue, Argonne, IL 60439-4831, USA*

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* Corresponding author. Tel.: +39-070-67586678; fax: +39-070-6758670.
E-mail address: deplano@vaxcal.unica.it (P. Deplano)
[1] Also corresponding author.

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Abstract

A large number of examples of polyiodides and donor-I_2 adducts whose structures and Raman spectra are reasonably well-established, have been collected. An empirical method based on structural and Raman data, as complementary tools in elucidating the nature of the iodine moiety, is proposed to remove the arbitrariness in considering discrete/non discrete entities and to provide a unified picture of the bonding in these species. Accordingly polyiodides higher than I_3^- do not exist as discrete entities but are formed by a combination of I^- and/or I_3^- with I_2 through donor–acceptor interactions. The I_3^- moiety represents a crossover, its structural and vibrational features show that it can exist as an I_3^- entity (in accordance with the existence of a covalent bond interaction describable by means of a delocalized three-center four-electron, 3c-4e, bond) or $I^- \cdot I_2$ donor–acceptor adduct. The formal I_2-adducts of donors (D) show structural and Raman features which can be explained considering three types of adducts: $D \cdot I_2$, D–I–I (covalent bond interaction describable by means of a delocalized 3c-4e bond by analogy with the I_3^- entity case) and $(D{-}I)^+ \cdot I^-$, which can be considered as stages along the reaction coordinate between the separated D and I_2 and the salt $[(D{-}I)^+]I^-$. The precautions to be taken in studying these species have been cited. The possibility that some of the Raman attributes in the literature need corrections has been pointed out in regard to the instability inherent in these materials since the decomposition of these species causes spurious peaks to appear in the Raman spectrum.

Keywords: Polyiodides; Donor-I_2 adducts; Raman spectroscopy; X-ray diffraction

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1. Introduction

A large number of polyiodide-containing molecular conductors and superconductors are known [1]. The identification of polyiodides is of crucial importance in electron donor–acceptor materials where I_2 is the acceptor since it can provide an estimate on the extent of the charge-transfer (CT) from the donor to the acceptor. Our aim in this review is to examine a large number of polyiodide examples and donor-I_2 adducts, whose structures are reasonably well-established, and to determine the validity of using X-ray diffraction and Raman data, as complementary tools or individually, to determine the nature of the iodine moiety present. The use of X-ray diffraction as a diagnostic tool is perhaps the most quantitative as it provides bond distances, bond angles and geometry of coordinated I_2 or of the polyiodide. However a single crystal is necessary for the measurements and the availability of single crystals may not be possible. Moreover molecular disorder or the instability of the samples can prevent obtaining accurate structural data.

2. Raman spectra of donor-I_2 adducts and polyiodides-selection rules

Let us consider Raman spectroscopy as a diagnostic tool in lieu of X-ray diffraction or complementing X-ray. The capability of Raman spectroscopy in identifying the iodine moiety in neutral I_2-adducts with donors (D) and polyiodides in salts has been recognized for some time and many references dealing with this topic are available in the literature [2,3]. We can summarize spectral expectations based on selection rules for these compounds as follows: the ν_{I-I} vibration for adducts $D{\cdot}I_2$ where a linear D···I–I (···intermolecular interaction, -intramolecular interaction) arrangement is found, is observed in the region 140–180 cm^{-1} in the Raman spectrum. This frequency is lower than the same vibration for I_2 (solid 180 cm^{-1}, $d(I-I) = 2.715$ Å [4]). The lowered frequency is due to the interaction with donors to form the adduct, which produces a lowered bond order and a consequent increase in the I–I distance in agreement with a molecular orbital description of the adduct, which shows that the donor orbital is mixed with the σ^* antibonding orbital of I_2 [5]. For polyiodides containing the linear symmetrical I_3^- ion, (bond distances elongated to ~ 2.925 Å which correspond to a 0.5 bond order calculated thereof according to Pauling[2] [6]) the Raman active symmetrical stretching mode ν_1 occurs at ~ 110 cm^{-1} (sharp and intense), the antisymmetrical stretching ν_3 and the deformation vibration ν_2, active only in the infrared spectrum, are found near 140 and in the 70–50 cm^{-1} range, respectively, as predicted for a I–I–I three-body system (I_3^- entity). If the I_3^- anion becomes asymmetric due to solid state interactions[3], ν_2 and ν_3 modes can become Raman-active. These results are in accordance with the existence of a covalent bond interaction, and a delocalized three-center four-electron (3c-4e) bond description[4] is consistent with the features of symmetrical I_3^- ions [7]. Higher polyiodides are generally recognized as due to a combination of triiodides and/or iodides with I_2 as a consequence of a typical donor–acceptor interaction, except pentaiodides which have been considered as authentic I_5^- entities (in our opinion incorrectly) and accordingly the assignments of the frequencies have been given (see Section 5.1). Is it possible to find experimental evidence to discriminate whether or not polyiodides are discrete entities?

3. Are polyiodides discrete entities?

It is difficult to ascertain whether or not polyiodides are discrete entities, based on bond distances alone. Does an interiodine distance comprised between the value in gaseous I_2 (2.67 Å [8]) and a van der Waals distance (~ 4.2 Å) constitute a genuine bond? Recently [9], the limit below which an I···I distance may be regarded as bonding was proposed to be in the vicinity of 4 Å for the linear configuration and shorter for the right-angle configuration. However the authors [9] of this proposal recognized that this limit will depend on the particular structure thus the discrete/non discrete assignments will at times be arbitrary.

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[2] The Pauling equation is $d = d_0 - c \log n$, where d and d_0 are I–I distances in coordinated and free I_2 (2.67 Å), c is an empirical constant equal to 0.85 and n is the bond order.

[3] The asymmetry of I_3^- and some of its possible causes are discussed in detail in Ref. [9].

[4] The negative charge is found distributed between the terminal atoms.

In order to achieve a non-arbitrary criterion to discriminate the discrete entities from the non-discrete ones, Raman spectroscopy should be used to help in evaluating the covalency of the interaction. If the polyiodides are discrete entities, spectra in accordance with a multibody system should be observed as occurs in the symmetrical or slightly asymmetrical triiodides case. When they are better described adducts of I^- (or I_3^-) with diiodine, the typical Raman peak due to perturbed I_2 is observed as is found in the neutral CT-adducts (in addition if the donor is a triiodide, its typical peak appears) irrespective of the stoichiometry of the polyiodide but in good correspondence with their structural features. For neutral donor–diiodine adducts, when the interaction gives rise to a covalency comparable to that found in symmetrical triiodides as inferred from the lengthening of the intraiodine distance (~ 2.92 Å, $n \sim 0.5$), the adduct is taken as a discrete entity. Accordingly Raman peaks attributable to the D–I–I vibrations are expected.

We have collected numerous Raman spectra on structurally characterized donor–diiodine adducts and on the basis of the bond distances and of the features of the Raman spectra we have proposed [10] an empirical criterion to assign the prevailing nature of the interaction in these adducts as reported in Table 1.

The proposed criterion based on structural and Raman data provides three types of adducts $D\cdots I_2$ (**1**) D–I–I (**2**), $(D\text{–}I)^+\cdots I^-$ (**3**), which can be considered as stages along the reaction coordinate between the separated D and I_2 and the salt $[(D\text{–}I)^+]I^-$. A reciprocal relationship between the lengthening of an intramolecular interaction with the shortening of an intermolecular interaction is generally observed. Bent ([11]a) has described a hyperbolic curve fitting the experimental distances in triiodides suggesting also that this curve shows approximately the changes between nearest neighbors in the exchange reaction $I_a^- + I_bI_c \rightarrow I_aI_b + I_c^-$. Knop et al. ([11]b) have investigated the more general case of collinear L–Z–L* groups (L, L* atoms of the same elements, Z of the same or of a different element). The inequality of d(L–Z) and d^*(Z–L*), not equivalent by symmetry, is attributed to the trans effect which shortens d and lengthens d^* relative to a reference bond length. The bond-length compensation is believed to be non-linear and the existence of a functional relation between the conjugated bond distances has been demonstrated (for a detailed discussion of the model functions investigated see original

Table 1
Classification of $D\cdot I_2$ adducts on the basis of vibrational and stuctural data

d(I–I) (Å)	n (bond order)	Expected stretching vibrations	$D\cdot I_2$ type[d]
2.72–2.85	>0.6	ν(I–I) 140–180 cm^{-1}	**1** ($D\cdot I_2$)
~ 2.90	~ 0.5	ν_{sym}(D–I–I)[a], ν_{asym}(D–I–I)[b]	**2** (D–I–I)
>3.01	<0.4	ν(D–I)[c]	**3** $[(D\text{–}I)^+\cdot I^-]$

[a] If D = S or Se vibration occurs near 120 cm^{-1}.

[b] If D = S or Se vibration occurs in the 150–200 cm^{-1} range.

[c] If D = P in Ph_3P vibration occurs at 159 cm^{-1}.

[d] The existence of a further coordination mode I–D–I (type **4**) can be proposed, even though strictly speaking this type cannot be considered a complex.

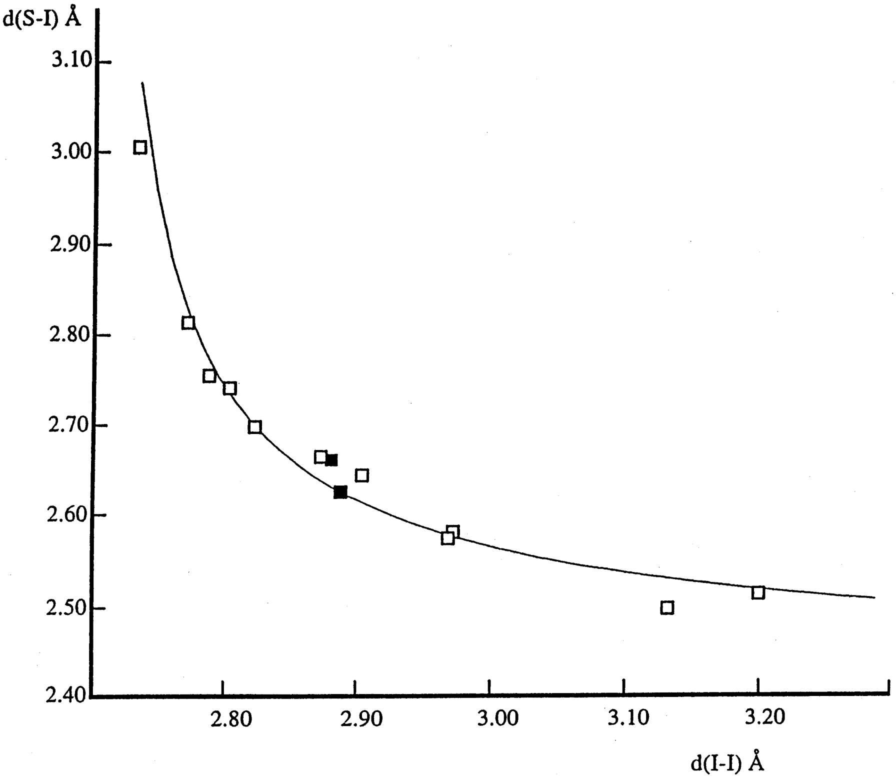


Fig. 1. Plot of d(S–I) vs. d(I–I) for thione–diiodine adducts reported in Refs. [12] (□) and [10] (■).

paper). A reciprocal relationship fitting a hyperbola has been found for thione–diiodine interactions (Fig. 1) [12]. Following our description thione–diiodine adducts of type **1** and type **3** will fall in the almost linear branches of the hyberbola where the intramolecular lengthening can be taken into account considering the acceptor still existing as a discrete molecule [I_2 or $(D-I)^+$] 'perturbed' by the interaction. As a consequence the ν(I–I) or ν(D–I) are still expected to occur, but at lower wavenumbers and the corresponding stretching force constants could be estimated by the simple diatomic Hooke's law approximation from the assigned frequencies. Type **2** adducts instead will fall in the curved branch of the hyperbola where inter- and intra-molecular distances are no longer distinguishable. Thus the D–I–I should be treated as a three-body system, where the D–I and I–I stretching frequencies are expected to be mixed. The borderlines between adduct type Raman spectra could help in assigning the prevailing nature of the complex under investigation.

4. Experimental problems

Before assigning Raman peaks of compounds containing either I_2 or polyiodide, the reliability of the spectra related to experimental problems due to the inherent instability of the samples must be adequately considered. We have previously cited [13] that resonance Raman (RR) spectroscopy and the use of visible excitation sources may induce besides fluorescence, photo-reactions, sample pyrolysis in various solid compounds such as polyiodides. In the case of polyiodides this can be detrimental, as the polyiodide can decompose under the laser beam and cause spurious peaks to appear in the Raman spectrum. With the advent of commercial FT-Raman in the mid-1980s using a near-infrared (NIR) laser excitation, some of the above problems, particularly fluorescence and photo-reactions may be reduced. However, the FT-Raman technique using a Nd:YAG laser excitation may still cause pyrolysis of the sample, unless the laser power is reduced considerably during measurements [14]. In the case of polyiodides some of the I_2 may be lost during measurements (e.g. $I_7^- \rightarrow I_5^- + I_2$; $I_5^- \rightarrow I_3^- + I_2$). The subsequent Raman spectrum may then show scattering from the original polyiodide plus scattering from decomposition products. The use of Raman spectroscopy with either RR- or FT-Raman to identify the nature of polyiodides, must be done with the intrinsic instability of the polyiodides in mind and instability to laser excitation. Additionally it would be advisable to obtain the spectrum of the material in the region where lasers emit their energy in order to determine which laser excitation source would be preferable to use in the Raman experiment to avoid decomposition. This becomes very important in instances where the sample has absorption in the visible and/or the near infrared region. Nevertheless the laser power should be reduced to a minimum; the sample should be encapsulated in a glass capillary for protection from any laser heating, and if possible, the spectrum should be recorded at liquid nitrogen temperature and using the same crystal used in X-ray structural measurements. In addition, the use of Raman spectroscopy alone may be dangerous, and infrared data should be used to support assignments. There has been, in general, a lack of far infrared data accumulated for polyiodides. This is due to the fact that for far infrared measurements the sampling technique involves a mixture of the compound with an inert diluent (e.g. Nujol, CsI or polyethylene) and in most cases grinding is necessary to provide a homogeneous mixture. Under such conditions $D{\cdot}I_2$ complexes and polyiodides may lose their I_2.

5. Results and discussion

5.1. Polyiodides and $D{\cdot}I_2$ adducts describable as $D{\cdots}I_2$ complexes (type **1**)

Table 2 contains a summary of X-ray and Raman data for some polyiodides with significantly longer I···I and shorter I–I distances, which suggest that they can be regarded as adducts of I^- with I_2 (see Table 1 classification). A well-documented example is a triiodide $[(EtNH)_2dtl]I_3$ [13,15] $[(EtNH)_2dtl = $ 3,5-bis(ethylamino)-1,2-

Table 2
Polyiodides and D·I_2 adducts describable as D···I_2 complexes (type **1**)

Iodine containing moiety	Compound	Geometry	d(I–I) (Å)	n (bond order)	Raman data	Refs.
I_3^-: $I^-\cdot I_2$	$[(EtNH)_2dtl]I_3$[a]	Linear asym.	2.74, 3.14	0.83, 0.28	167 s	[13,15]
	CsI_3	Linear asym.	2.842, 3.038	0.63, 0.37	157m, 148s, 137s, 102s, 93s	[16,17]
	$Da2I_3$[b]	Linear asym.	2.793, 3.167	0.72, 0.26	n.a.	[18]
	[1-MethylcytosineH]I_3	Linear asym.	2.794, 3.123	0.71, 0.29	n.a.	[19]
	$[NH_4]I_3$	Linear asym.	2.797, 3.114	0.71, 0.30	n.a.	[20]
I_4^{2-}: $2I^-\cdot I_2$	$[(C_5H_7N_2Se\text{-})_2]$ $I_3\cdot 1/2I_4$	Linear	2.819, 3.405	0.67, 0.13	155s	[21]
	AuI_2 (μ_2-I_4)		2.709, 3.387	0.90, 0.15	n.a.	[22]
I_5^-: $I^-\cdot 2I_2$	$UrPrI_5$[c]	L-shaped	2.829, 2.793, 2.804, 2.776 3.060, 3.117, 3.096, 3.153	0.65–0.75 0.35–0.27	164s, 142m, 110m, 100m	[23,24]
	$UrBuI_5$[c]		n.a.		163s, 149s, 143s, 100sh	[24]
	$UrBuI_5$ after decomposition				126vw, 112s	[24]
	$[(Mn(modtc)_3]I_5$[d]	L-shaped	2.810, 2.827, 2.750, 2.759, 3.117, 3.031, 3.186, 3.216	0.65–0.80 0.23–0.38	165sh, 143s	[13,25]
	Me_4NI_5	L-shaped	2.81, 3.17	0.68, 0.26	155s, 144s	[13,26]
	Me_4NI_5				153s,br	[27]
	Me_4NI_5				157s, 147s, 112w (λ_{exc} 647.1 nm)	[28]
	Me_4NI_5				143m, 113s (λ_{exc} 488.0 nm)	[28]
	Pr_4NI_5		2.830, 3.502	0.65, 0.11	164s	[27,29]
	Bu_4NI_5				160m, 156m, 150s, 134m, 105w	[24]

Table 2 (Continued)

Iodine containing moiety	Compound	Geometry	d(I–I) (Å)	n (bond order)	Raman data	Refs.
	Bu_4NI_5				165s, 159vw, 149vs, 136w, 105w	[30]
I_5^-: $I^-\cdot 2I_2$	[(Trimesic acid)$_{10}$H]I_5	Linear	2.74 3.186, 3.216	0.83 0.25, 0.23	160s, 107w	[17]
I_7^-: $I^-\cdot 3I_2$	[(*N*-Methylbenzothiazole)$_2$I] I_7	Pyramidal	2.771, 2.766, 2.746 3.237, 3.260, 3.242	0.76–0.72 0.22–0.20	175m, 157s	[31]a
	[H_3O^+18-crown-6]I_7	Infinite saw-horse array	2.764, 2.748, 2.735 3.426, 3.249, 3.252	0.78–0.84 0.13–0.21	n.a.	[32]
	[PPh_4]I_7	Pyramidal	2.738, 2.730 2.814 3.295, 3.281, 3.057	0.68–0.85 0.18–0.35	178m, 166m, 152ms, 113s	[33]
	UrPrI_7^{c}	Pyramidal	2.735, 2.751 2.836 3.385, 3.374, 3.040	0.84–0.64 0.14–0.37	176m, 170s, 145vw, 111wsh, 102s	[23]
I_8^{2-}: $I^-\cdot I_2\cdot I_2\cdot I^-\cdot I_2$	$[(CH_2)_8N_4CH_3]_2I_8$	Outstretched Z-shaped	2.830, 3.038 2.773, 3.386	0.65, 0.37 0.76, 0.14	n.a.	[34]
I_9^-: $(I^-\cdot 2I_2)\cdot 2I_2$	Me_4NI_9	Twisted h	2.67 (×2), 2.90, 3.18, 2.91, 3.24 (×2), 3.43	1.00, 0.54, 0.25, 0.52, 0.21, 0.12	180vs, 150–140 w,br	[35,13]
					190w, 157mw, 145mw, 108mw	[28]
I_{12}^{2-}: $I_2\cdot 2(I^-\cdot 2I_2)$	$[Ph_2Me_2N]_2I_{12}$	I_2 bridging two V-shaped I_5^-	2.738, 3.481, 3.339, 2.751, 3.153, 2.780	0.83, 0.11, 0.16, 0.80, 0.27, 0.74	n.a.	[36]

Table 2 (Continued)

Iodine containing moiety	Compound	Geometry	d(I–I) (Å)	n (bond order)	Raman data	Refs.
I_{13}^{3-}: $I_2 \cdot I^- \cdot 2(I^- \cdot 2I_2)$	$[Ph_2Me_2N]_3I_{13}$	Zig-zag chains $I_2 \cdot I^-$ interacting with two V-shaped I_5^-	2.827, 3.351, 3.606, 2.781, 3.190, 3.069, 2.813	0.65, 0.16, 0.08, 0.74, 0.24, 0.34, 0.68	n.a.	[36]
$D \cdot I_2$	$dtt \cdot I_2$[e]	Linear	2.823	0.66	145s	[39]
	$dtlt \cdot I_2$[f]	Linear	2.843	0.63	143s	[40]
	$Modto \cdot 2I_2$[g]	Linear	2.751, 2.805	0.80–0.69	170s, 150sh, 111m (I_3^-)	[41]
	$Et_4todit \cdot 2I_2$[h]	Linear	2.822	0.66	147s	[41]

[a] $(EtNH)_2dtl$ = 3,5-bis(ethylamino)-1,2-dithiolylium.

[b] Da = 1,4-diazoniabicyclo[2.2.2]octane.

[c] UrR = *N*-alkylurotropinium.

[d] modtc = morpholinecarbodithioato.

[e] dtt = 1,3-dithiolane-2-thione.

[f] dtlt = 1,3-dithiole-2-thione.

[g] Modto = bis(morpholino)dithiooxamide.

[h] Et_4todit = 4,5,6,7-tetrathiocino[1,2-b:3,4-b′]diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione.

dithiolylium] (see Table 2 and Fig. 2) where the presence of one Raman peak at 167 cm^{-1} is in complete accordance with this description. Other very asymmetric triiodides, where the distance between terminal atoms (~ 5.85 Å) is typical of triiodides, are reported in Table 2. Raman spectra where only the peak due to a perturbed iodine molecule of the $I^- \cdot I_2$ adduct are expected. The Raman spectrum of CsI_3 [16,17] is not easily explained due to the presence of several peaks in the region of the intraiodine vibrations which suggests that the sample used for the Raman measurements may be contaminated by the presence of different polyiodide anions. In tetraiodides one short and two long distances are observed [21,22]. Bond orders thereupon calculated are again in accordance with the formulation $2I^- \cdot I_2$ and the reported Raman spectrum for a typical tetraiodide shows only one strong peak near 155 cm^{-1} attributable to the perturbed I_2 as a consequence of the interaction with the two iodide donors. Examples of polyiodides with I_5^- stoichiometry, describable as a combination of I^- with two I_2 are illustrated in Table 2. No I_3^- emission is observed at ~ 110 cm^{-1} in $[Mn(modtc)_3]I_5$ (modtc = morpholinecarbodithioato) [13], and this is in accordance with the X-ray data [25]. The other examples of pentaiodides in Table 2 are presented to indicate how a visible excitation source may induce sample pyrolysis and the formation of triiodide. Spurious peaks can result and this may cause wrong assignments to be made. For instance Resonance Raman (RR) spectra on Me_4NI_5 by using several separate excitation lines have been reported [28] and on going from λ_{exc} 647.1 to 488.0 nm the spectra were significantly different. In particular a strong peak at 113 cm^{-1} for

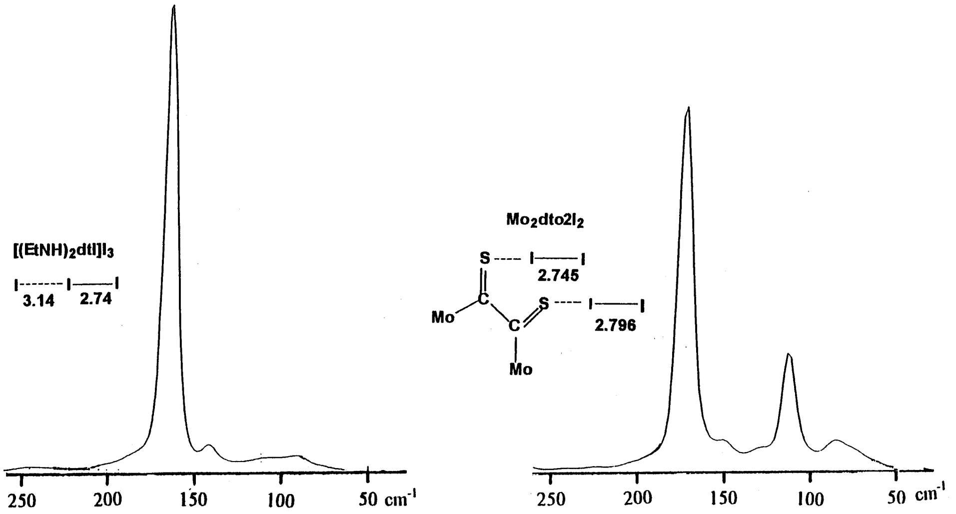


Fig. 2. FT-Raman spectrum of $[(EtNH)_2dtl]I_3$ [$(EtNH)_2dtl$ = 3,5-bis(ethylamino)-1,2-dithiolylium], where the triiodide is describable as type **1** adduct ($I^- \cdot I_2$, $\nu_{I-I} = 167$ cm^{-1}). The FT-Raman spectrum ($\nu_{I-I} = 170$ cm^{-1}) of the neutral adduct $Modto \cdot 2I_2$ [Modto = bis(morpholino)dithiooxamide] showing a similar intraiodine elongation is reported for comparison (the peak at 111 cm^{-1} is due to decomposition to triiodide).

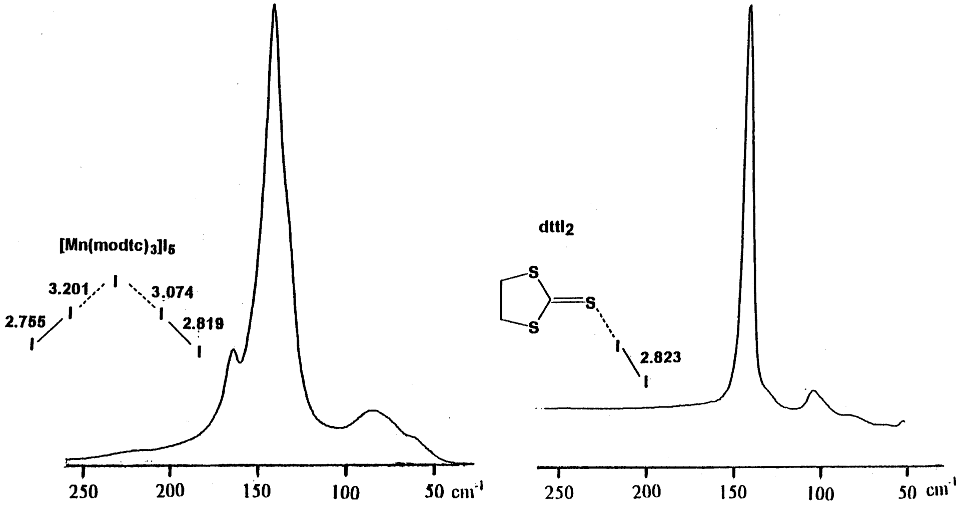


Fig. 3. FT-Raman spectrum of [(Mn(modtc)$_3$]I$_5$ [modtc = morpholinecarbodithioato] where pentaiodide is describable as $I^-\cdot 2I_2$ ($\nu_{I-I} = 143$ cm^{-1}). The FT-Raman spectrum ($\nu_{I-I} = 145$ cm^{-1}) of the neutral adduct dtt·I$_2$ [dtt = 1,3-dithiolane-2-thione] showing a similar intraiodine elongation is reported for comparison.

λ_{exc} 488.0 nm, absent in the spectrum obtained at λ_{exc} 647.1 nm, was assigned to the inner symmetrical stretch ν_2. This peak is also absent in our FT-Raman spectrum of Me_4NI_5, which is simpler than predicted for a multibody system and shows instead peaks at 155 and 144 cm^{-1}. Thus original assignments [28] which seemed to support the pentaiodide as an authentic I_5^- (discrete) unit, were based on spurious peaks (the peak at 113 cm^{-1} should be assigned to the presence of I_3^-).

Similarly the different Raman spectra on the same samples (Bu_4NI_5, $UrPrNI_5$, Ur = urotropinium) reported in Table 2 show that they are affected by spurious peaks, as also suggested in Ref. [24].

Also, in the linear pentaiodide of the trimesic acid example [17] the weak Raman peak observed at 104 cm^{-1} is likely ascribable to almost ubiquitous triiodide present as impurity or decomposition of the pentaiodide.

We conclude that experimental results on the pentaiodides presented in Table 2 are better understood considering these anions as $I^-\cdot 2I_2$ adducts rather than discrete entities (see Fig. 3).

Similarly, structural data of the I_7^- salts [31–33], reported in the Table 2, suggest that they are describable as $I^-\cdot 3I_2$ adducts. Raman data are in complete accordance with this description in the [(*N*-methylbenzothiazole)$_2$I]I$_7$ case. The presence of a peak near 110 cm^{-1} in the other reported examples of heptaiodide, must be carefully verified in order to rule out that this can be due to ubiquitous I_3^- impurities.

X-ray results of the octaiodide $[(CH_2)_8N_4CH_3]_2I_8$ indicate that the iodine moiety may be described as an $(I^-\cdot I_2\cdot\ I_2\cdot\ I^-\cdot I_2)$ dianion [34].

The enneaiodide in Me_4NI_9 is represented by $I^- \cdot 2I_2 \cdot 2I_2$. Our Raman data from FT-Raman results of the material in a glass capillary to prevent decomposition show a broad weak envelope at 150–140 cm^{-1} and a strong absorption at 180 cm^{-1} consistent with the presence of I_2 molecules in an adduct $(I^- \cdot 2I_2)$ and I_2 as guest molecules [13]. X-ray results by James et al. [35] are in general agreement even though the data are old, and too qualitative to allow a meaningful correlation. The original Raman spectrum is in doubt because of possible decomposition [28].

Other cases of polyiodides which are built up by a sequence of I^- and I_2 are tridecaiodides $(I_{13}^{-3} = I_2 \cdot I^- \cdot 2I_5^-)$ [36], dodecaiodides $(I_{12}^{-2} = I_5^- \cdot I_2 \cdot I_5^-)$ [36,37] and hexadecaiodides $(I_{16}^{-2} = I_7^- \cdot I_2 \cdot I_7^-)$ [38]. In these examples I_5^- and I_7^- are represented by $I^- \cdot 2I_2$ and $I^- \cdot 3I_2$, respectively, but Raman data are unavailable.

Finally some examples of neutral I_2 adducts are reported in Table 2 to show that similar elongations in the perturbed diiodine produce spectra similar to the polyiodides.

Figs. 2 and 3 show the similarity of the Raman spectra of a very asymmetric triiodide as well as a pentaiodide with neutral I_2 adducts where as a consequence of the $D \cdot I_2$ and $I^- \cdot nI_2$ interactions similar elongation of the interiodine distances are found. Instead Fig. 4 shows the difference between the spectra of two pentaiodides both bent but showing different elongations of I–I distances.

5.2. Polyiodides and $D \cdot I_2$ adducts describable as D–I–I complexes (type **2**)

Table 3 contains a summary of X-ray and Raman data for some symmetrical and slightly asymmetrical triiodides where intraiodine distances are comparable, as well as donor–diiodine complexes where the lengthening of the intraiodine distance as a

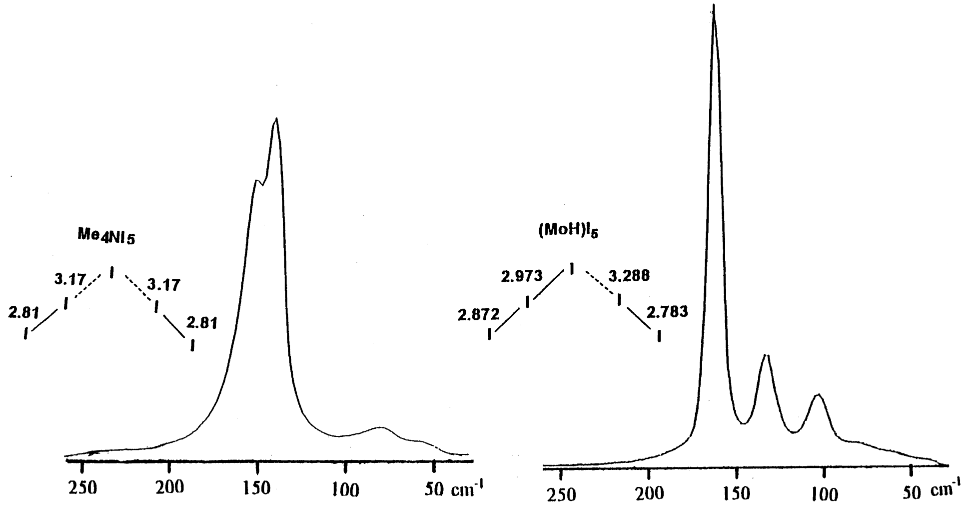


Fig. 4. Comparison of FT-Raman spectra of two bent pentaiodides: Me_4NI_5, describable as $I^- \cdot 2I_2$ ($\nu_{I-I} = 155$, 144 cm^{-1}) and $(MoH)I_5$ describable as $I_3^- \cdot I_2$ (ν_3 and ν_1 135 and 106, $\nu_{I-I} = 164$ cm^{-1}).

Table 3
Triiodides and covalent D·I_2 adducts describable as D–I–I complexes (type **2**)

Iodine containing moiety	Compound	Geometry	*d*(I–I) (Å)	*n* (bond order)	Raman data	Refs.
I_3^-: I–I–I	Ph_4AsI_3	Linear symmetric	2.92	0.50	118 vs	[16,17]
	$UrEtI_3$[a]	Linear symmetric	2.906	0.53	112vs, 163w	[42,24]
	$UrBuI_3$[a]	Linear asymmetric	2.935, 2889	0.49, 0.55	112vs, 113vs, 128w	[42,24]
	Me_3SI_3	Linear asymmetric	2.946, 2.915	0.47, 0.51	110vs	[43]
	β-$(ET)_2I_3$[b]	Linear symmetric	2.904	0.53	118s, 143w	[44]
	β-$(DMPEDTTTF)_3$ I_3[c]	Linear symmetric	2.921, 2.952	0.51, 0.47	109vs	[45]
	$[(C_6H_5CONH_2)_2H]$ I_3	Chain of I_3^- units	2.924, 2.934, 2.935, 2.930	0.50–0.49	113s	[46]
D·I_2: S–I–I	mbit·$2I_2$[d]	Linear asymmetric	2.897	0.54	125vs, 180–194ms	[10]
	ebit·$2I_2$[e]	Linear asymmetric	2.903	0.53	121vs, 199s	[10]
	dtz·I_2[f]	Linear asymmetric	2.918	0.51	112–121s, 191s	[12]
D·I_2: Se–I–I	mbis·$2I_2$[g]	Linear asymmetric	2.912	0.52	125vs, 151s	[47]

[a] UrR = *N*-alkylurotropinium.
[b] ET = bis(ethylenedithio)tetrathiafulvalene.
[c] DMPEDTTTF = dimethylpyrazinoethylenedithiotetrathiafulvalene.
[d] mbit = 1,1′-methylenebis(3-methyl-4-imidazoline-2-thione).
[e] ebit = 1,1′-ethylenebis(3-methyl-4-imidazoline-2-thione).
[f] dtz = dithizone.
[g] mbis = 1,1′-methylenebis(3-methyl-4-imidazoline-2-selone).

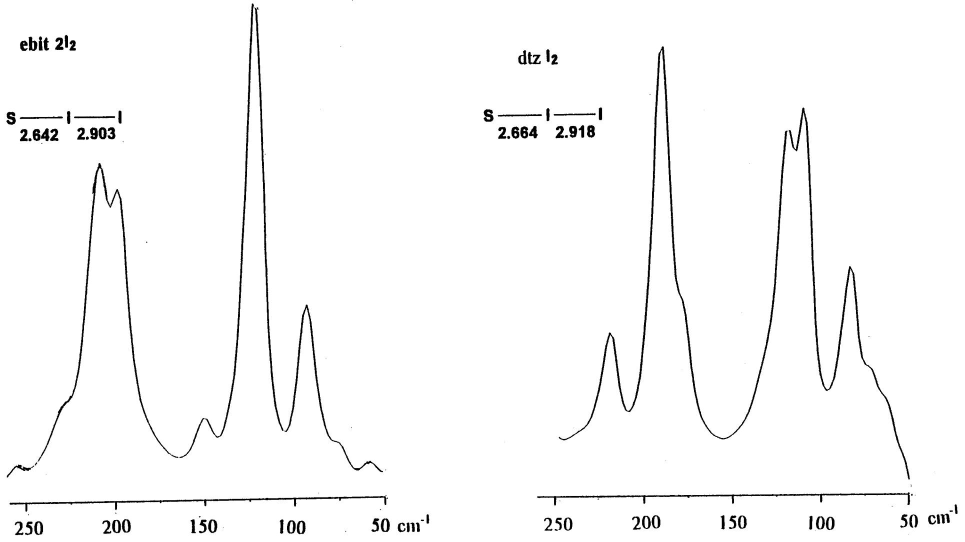


Fig. 5. Examples of FT-Raman spectra of type **2** adducts ebit·$2I_2$ [ebit = 1,1′-ethylenebis(3-methyl-4-imidazoline-2-thione)] and dtz·I_2 (dtz = dithizone), where two groups of bands occur near 200 and 120 cm^{-1} and are assigned to the antisymmetrical and symmetrical stretching of the S–I–I moiety, respectively.

consequence of the interaction is similar to that found in triiodides (*d*(I–I) ~ 2.92 Å). Many examples of symmetrical or slightly asymmetrical triiodides in accordance with the above are reported in the literature [2,3,24], and some typical examples interesting in the field of molecular conductors are reported in Table 3. In the structures of the conductors β-$(PEDTTTF)_3I_3$ and β-$(DMPEDTTTF)_3I_3$ (PEDTTTF = pyrazinoethylenedithiotetrathiafulvalene, DMPEDTTTF = dimethylpyrazinoethylenedithiotetrathiafulvalene) [45] the I_3^- is disordered, so the presence of I^- and I_2 instead would not be ruled out if the Raman results showing the characteristic peak of I_3^- anions at 109 cm^{-1} were not available. Also some examples of neutral donor–diiodine adducts: mbit·$2I_2$; ebit·$2I_2$ [10] (see Fig. 5); mbis·$2I_2$ [47] [mbit = 1,1′-methylenebis(3-methyl-4-imidazoline-2-thione); ebit = 1,1′-ethylenebis(3-methyl-4-imidazoline-2-thione); mbis = 1,1′-methylenebis(3-methyl-4-imidazoline-2-selone]; where the values of the intraiodine distance are comparable to those found in symmetrical or slightly asymmetrical triiodides and correspond to a ~ 0.5 bond order are reported. Analogously to the molecular orbital scheme proposed for the 22 electron I_3^- ion, we have previously proposed [47] to describe this kind of adducts as being formally formed by the combination of the linear three-coordinated 22 electron groups $[D–I–I]^{2-}$ (D = S or Se) with an empty sp^2 hybrid orbital of the carbon atom of the imidazoline ring. The orbital involved in the bonding would be one of the degenerate pair of the npπ* MOs mainly located on the D atom. The remaining MO orbitals are essentially unchanged. The presence in the Raman of two bands support the existence of a molecular three-body system, analogously describable as the asymmetrical triiodide entity. Due to the asymmetry of these systems both the symmetrical and antisymmetrical stretching should be active in the Raman and accordingly the observed peaks have been assigned. It is noteworthy that Se–I–I groups and I_3^- give similar vibrational spectra. Thus the Se–I and I–I vibrations seem to involve similar energies. This fact can produce confusion when Se-donors are reacted with diiodine, since the presence of a triiodide may be erroneously invoked in the presence of neutral derivatives. Examples of the Raman spectra of a neutral derivative containing the I–Se–I group and a triiodide [48] are reported in Fig. 6, and illustrate the above point.

5.3. Polyiodides describable as a sequence of $I^- \cdot I_2$ and $I_3^- \cdot I_2$ complexes

Table 4 tabulates polyiodides described as adducts of the donors I^- and I_3^- with I_2. The resulting polyiodides give rise to Raman spectra in accordance with their structural features. The ν(I–I) scattering has increased intensity in the Raman relative to ν_{as}(I–I–I), thus the two vibrations can be observed. The case of Cs_2I_8 [17] is interesting since structural data may be in agreement either with a description $I^- \cdot I_2 \cdot I_2 \cdot I^- \cdot I_2$ or $I^- \cdot I_2 \cdot I_2 \cdot I_3^-$ (intraiodine distances are 2.84, 3.00 Å [49], bond orders 0.63, 0.41 in the triiodide moiety), but Raman results (171s, 150m, 110s) suggest that the latter is preferable. Similarly in the case of [ebis]I_8 [ebis^{2+} = $(C_5H_7N_2Se\text{-})_2^{2+}$ is the dication of ebis = 1,1′-ethylenebis(3-methyl-4-imidazoline-2-selone] structural (unpublished) data [52] of the triiodides are at the borderline of our classification between type **1** and **2**, but Raman results agree with the existence of the I_3^- entity ($I_3^- \cdot I_2 \cdot I_3^-$, Fig. 7).

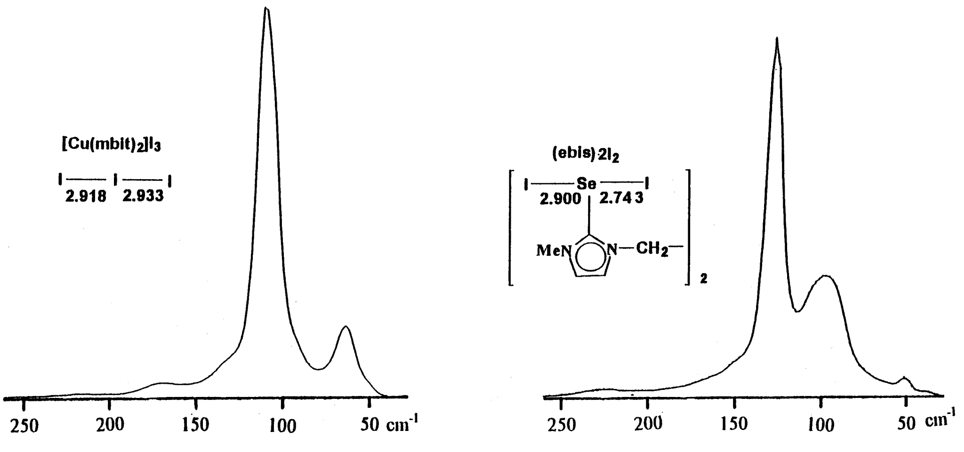


Fig. 6. Comparison of FT-Raman spectra of the triiodide ($\nu_1 = 110$ cm^{-1}) in [Cu(mbit)$_2$]I_3, [mbit = 1,1′-methylenebis(3-methyl-4-imidazoline-2-thione)] and of the I–Se–I group ($\nu = 128$ cm^{-1}) in ebis·2I_2 [ebis = 1,1′-ethylenebis(3-methyl-4-imidazoline-2-selone].

Table 4
Polyiodides describable as a sequence of $I_3^- \cdot I_2$ and $I^- \cdot I_2$

Iodine containing moiety	Compound	Geometry	d(I–I) (Å)	n (bond order)	Raman data	Refs.
I_5^-: $I_3^- \cdot I_2$	$[MoH]I_5$[a]	L-shaped	2.78, 2.877,2.973	0.74, 0.58, 0.44	164s, 135m,106mw	[13,50]
	$(Phenacetin)_2HI_5$	Zig-zag chains	2.748, 2.907	0.83, 0.53	178vs, 150w, 110ms	[2,51]
I_7^-: $I_2 \cdot I_3^- \cdot I_2$	Et_4NI_7	Zig-zag chains	2.76, 3.47, 2.91	0.78, 0.11, 0.52	178s, 114w	[13]
					179vs, 108vs	[24]
					182ms, 134vw, 108vs	[28]
I_8^{2-}: $I_3^- \cdot I_2 \cdot I_3^-$	$[(C_5H_7N_2Se\text{-})_2]I_8$	Z-shaped	2.758, 2.849, 2.988 2.839, 2.965	0.82, 0.62–0.42 0.63–0.44	155s, 144m, 110m	[52]
I_{16}^{4-}: $[I_3^- \cdot I_2 \cdot I^- \cdot I_2]_2$	$[(mottl)_2]I_{16}$[b]	Chain	2.741, 2.858, 2976 3.018, 2.827	0.83, 0.60–0.44 0.39–0.65	174s, 161m, 139w, 112m	[13,53]

[a] MoH^+ = morpholinium.

[b] $mottl^{2+}$ = [3,5-di(morpholinio)-1,2,4-trithiolano].

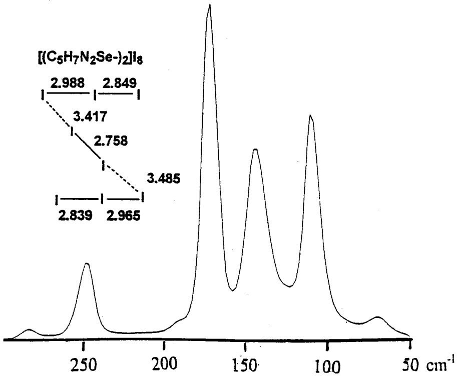


Fig. 7. Example of a FT-Raman spectrum of an octaiodide in $[(C_5H_7N_2Se\text{-})_2]I_8$, describable as asymmetrical I_3^- ions (ν_3 and ν_1 144 and 110 cm^{-1}) interacting with I_2 ($\nu_{I-I} = 172$ cm^{-1}).

Recently the most iodine-rich polyiodide compound Fc_3I_{29} (Fc^+ = ferrocenium ion) has been reported [54] The I_{29}^{3-} belongs to the class of polyiodides having general formula I_{6i-1}^{3-} and is the first example with $i = 5$. This anion shows a rather confusing structure (see original paper and figures for a detailed description). An asymmetrical triiodide interacts with a pentaiodide and with two iodine molecules giving rise to a formal dodecaiodide. The pentaiodide, which forms chains and lies on a mirror plane, is cross linked over an I_2 lying between the mirror planes to form a layer. A further I_2 lies between the mirror planes. A third I_2 bridge forms a three dimensional network. Vibrational spectra of this anion have been reported but regarded meaningless due to the high iodine content, its possible loss and the complicated structure. However the reported bands (213w, 172.5m and 115.5m cm^{-1} Raman, and 139s, 133s and 106s cm^{-1} IR) seem to agree with our view that despite the complicated structure only the presence of a triiodide (115.5 cm^{-1} R, 106 and 133s cm^{-1} IR) and of perturbed diiodine molecules (172.5 cm^{-1} R, less perturbed I_2, 139 cm^{-1} IR more perturbed I_2 of the I_5^- group) could be recognized (the peak at 213 cm^{-1} may be assigned to I_2 in the vapour phase, due to diiodine loss).

5.4. $D{\cdot}I_2$ adducts describable as $D\text{–}I^+{\cdot}I^-$ complexes (type **3**)

Table 5 shows $D{\cdot}nI_2$ adducts as type **3** $D\text{–}I^+{\cdot}I_{2n-1}^-$ complexes. Dihalogen adducts $R_3P{\cdot}X_2$ of tertiary phosphines have been discussed on the basis of the following two alternative structures: molecular complexes [55] or halophosphonium halides ([56]a,b). The solid state structures of $Ph_3P{\cdot}I_2$ by McAuliffe et al. [55] and $Bu^t_3P{\cdot}I_2$ by du Mont et al. ([56]a) have shown that both compounds exhibit the four-coordination around the P atom and the linear P–I–I arrangement. The I–I distances are considerably lengthened (3.16 and 3.32 Å, respectively) with respect to that in molecular I_2 (2.67 Å) but significantly shorter than the sum of the van der Waals radius of iodine (~4.2 Å). On these basis these compounds have been

Table 5
$D\cdot nI_2$ adducts describable as $D\text{–}I^+\cdot I^-_{2n-1}$ complexes (type **3**)

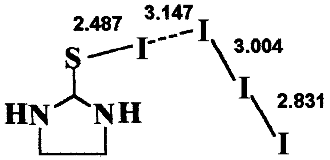
Iodine containing moiety	Compound	Geometry of the D–I–I group	d(I–I) (Å)	n (bond order)	Raman data	Refs.
$[DI]^+\cdot I^-$	$Ph_3P\cdot I_2$	Linear	3.161	0.27	159s	[55]
$[DI]^+\cdot I_3^-$	$Ph_3P\cdot 2I_2$	Linear	3.551	0.09	n.a.	[58]
	etu$\cdot 2I_2$[a]	Linear	3.147	0.27	n.a.	[12]
$[DI]_2^+\cdot 2I_5^-\cdot I_2$	$(dtz)_2\cdot 7I_2$[b]	Linear	3.215	0.23	n.a.	[12]

[a] etu = ethylenethiourea-.

[b] dtz = dithizone.

interpreted as molecular CT adducts of I_2 by McAuliffe et al. [55]; du Mont et al. ([56]a) suggested instead that the structure $Bu^t_3P{\cdot}I_2$ can be regarded also as ionic $Bu^t_3PI^+I^-$. A reinvestigation of the nature of the bonding taking into account geometrical features, conductometric, UV–vis, $^{31}P\{^1H\}$-NMR and Raman studies of the adducts allowed us to conclude that they are neither iodophosphonium iodides nor molecular CT adducts of R_3P with I_2 but CT adducts of the donor I^- with the acceptor $R_3P{-}I^+$ [57]. A qualitative MO scheme for the CT interaction has been proposed where the donor orbital is mixed with the σ^* antibonding orbital of the P–I bond [57]. Accordingly, this interaction should produce an elongation of the P–I distance, which undergoes a shift depending on the donating power of the donor. Donors such as a triiodide where the charge can be delocalized on more centers produce lower elongation ($[Ph_3PI]{\cdot}I$: $d(P{-}I) = 2.481$, $[Ph_3PI]{\cdot}I_3$: $d(P{-}I) = 2.395$ Å [58]). Therefore a peak at higher frequencies with respect to 159 cm^{-1} assigned to $\nu(P{-}I)$ in ($[Ph_3PI]{\cdot}I$ should be observed. In order to attempt a more significant correlation, a wider range of structural and Raman data is required.

Similar cases are found in adducts of thione donors with diiodine [12]. For example structural data of ethylenethiourea-bis(diiodine) summarized in the figure below show that the adduct can be described as $(D{-}I)^+{\cdot}I^-{\cdot}I_2$. The sum of single bond for covalent radii for S and I is 2.37 Å [6]. The observed lengthening of this distance as well as the geometrical features (linear arrangement of the S–I–I group) are thus in accordance with a CT interaction between the $(D{-}I)^+$ acceptor and a polyiodide donor, as previously proposed [12].



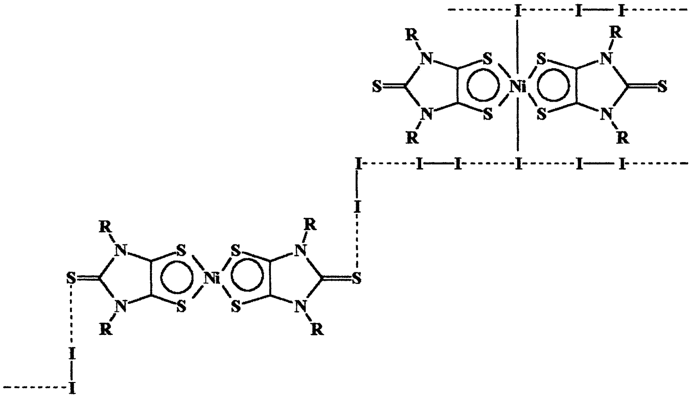
Instead in the $dtz{\cdot}I_2$ (dtz = dithizone) adduct case where S–I and I–I distances are 2.664 and 2.918 Å, respectively, we do not agree with the suggested $(D{-}I)^+I^-$ formulation [12] and prefer to classify it as type **2** adduct on the basis of its structural features. Raman spectra support this classification (Table 3, Fig. 5).

5.5. Iodine chains

The ordered iodine chains are unusual. Recently, a very interesting compound $(Me_4Sb)_3I_8$ has been reported [59]. In this compound linear sequences of iodine atoms with slightly alternating distances of 3.283 ($n = 0.19$) and 3.299 Å ($n = 0.18$) are found. As expected no Raman peaks in the region of the interiodine vibrations are observed. Doubts if these linear sequences should be considered as iodine chains can be raised on the basis of the results of an ab initio optimization of the equilibrium geometries of several X_n^{m-} (X = Br, I) anions [7,60].

5.6. Strongly absorbing samples

In the case of the new class of nickel-dithiolenes [Ni(R_2timdt)$_2$] (R_2timdt is the monoanion of 1,3-dialkylmidazolidine-2,4,5-trithione) (**1**) recently synthesized [61], the characteristic long-wavelength electronic band typical of nickel-dithiolenes [62] falls approximately at 1000 nm, with a remarkably high extinction coefficient ($\varepsilon \sim 80000$ dm^3 mol^{-1} cm^{-1}). Reaction of **1** for R = Pr^i with different amount of I_2 leads (depending on the donor to acceptor molar ratio) to [Ni(Pr$^i_2$timdt)$_2$]·2I_2·1/2I_2 (**2**) [a neutral adduct in which two I_2 molecules interact with the peripheral thione sulfur atoms of **1** (d(I–I) = 2.815 Å) and the remaining I_2 is present as a guest] and [Ni(Pr$^i_2$timdt)$_2$]·2I_2[Ni(I)$_2$(Pr$^i_2$timdt)$_2$]·3I_2 (**3**), a mixed-valence compound in which the neutral adduct **2** and the octahedral complex [Ni(I)$_2$(R_2timdt)$_2$]·3I_2 (the ligand in neutral form) are held together by diiodine molecules, as shown below:



The intraiodine distances for I_2 vicinal to thione groups are 2.790 and 2.815 Å, and of those vicinal to I^- 2.783 and 2.786 Å, respectively.

The FT-Raman spectra of **2** and **3** have been previously recorded and since these compounds strongly absorb at the wavelength of the excitation source (Nd:YAG laser, $\lambda = 1064$nm) even at a power of 20 mW, peaks cannot be assigned unambiguously for the intraiodine vibrations. Using a He–Ne laser ($\lambda = 632$ nm) and recording the spectra of a single crystal of **2**, a very strong peak at 142 cm^{-1}, assigned to the coordinated I_2, and a peak at 192 cm^{-1}, assigned to I_2 present as a guest, are observed (Fig. 8a). By using a single crystal of **3** a broad peak centered at 159 cm^{-1} occurs. This peak is assigned to the contribution of the slightly different I_2 present in the compound. The iodine molecules interacting mainly with thione sulfurs are not discernible by those mainly interacting with I^- (formal polyiodide) as expected being the corresponding elongations very similar. Moreover if a long exposure time to the laser beam is used the sample decomposes and loses I_2 as can be seen in Fig. 8(b), where its Raman spectrum is reported. Far-IR measurements on these samples agree with these assignments.

In the absence of different excitation sources or also in the cases where fluorescence does not provide satisfactory Raman spectra, Far-IR measurements can be used to assign the intraiodine vibrations. In Fig. 9 the NIR–FT-Raman spectrum of [Pc$_2$Nb]·1/2(I$_8$)·7/2(ClNP), (Pc = phtalocyanine, ClNP = α-chloronaphtalene) [63] is reported. The peak at 167 cm^{-1} which appears over the fluorescence peak produced by ClNP is likely due to an intraiodine vibration. The IR spectrum is also reported in Fig. 9 and shows the presence of a strong peak at 144 cm^{-1}. The structural features of this I$_8^{2-}$ anion show the existence of a central I$_2$ (bond distance 2.771 Å, bond order 0.76) weakly and symmetrically interacting (3.407 Å) with two asymmetrical triiodides (short and long distances 2.806 and 3.004 Å and corresponding bond order 0.69 and 0.40, respectively). Thus we conclude that this anion can be described as (I$_2$·I$^-$)·I$_2$·(I$_2$·I$^-$), and that while the symmetrical central I$_2$ gives rise to the peak active in the Raman (the other expected peak of lower intensity probably falls under this very strong one), the triiodide seems to give an IR active band likely related to the perturbed intraiodine vibration of the adduct (I$_2$·I$^-$).

Other cases of strongly absorbing samples are the molecular conductors which strongly absorb up to the near infrared region.

The Raman spectrum of a single crystal of β-(ET)$_2$I$_3$ (ET = bis(ethylenedithio)tetrathiofulvalene) using a He–Ne laser (λ = 632 nm) shows a strong absorption at 118 cm^{-1}, indicative of an I$_3^-$ entity [44]. A very weak band, present also in the Far-IR, is observed at 143 cm^{-1} and may be assigned to the antisymmetric I–I–I vibration. The X-ray data show an average bond distance at 2.90 Å. The Raman data are consistent with a slightly asymmetric I$_3^-$ entity at room temperature.

5.7. Summary of Raman spectra expectations for polyiodides, and D·I$_2$ adducts

Based on the agreement between X-ray and Raman data, it is concluded that in polyiodides belonging to one of the classes: I$^{n}_{2m+n}$ (I$_4^{2-}$,.. I$_{16}^{4-}$); I$^{3-}_{6i+1}$ (I$^{3-}_{13}$) and I$^{3-}_{6i-1}$

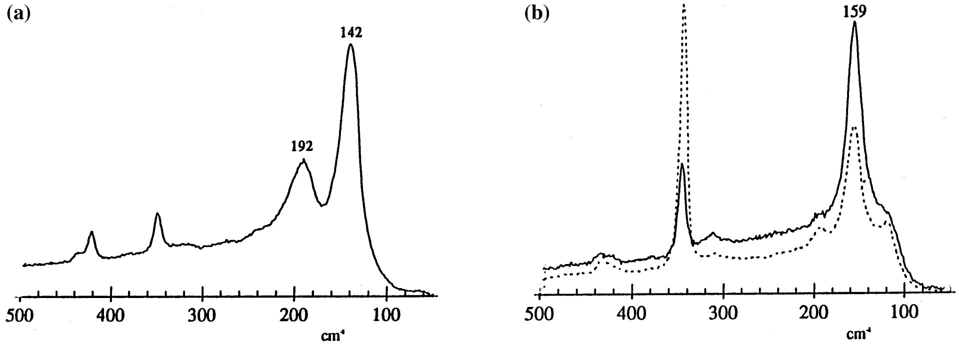


Fig. 8. (a) Raman spectrum of a single crystal of [Ni(Pr$^i_2$timdt)$_2$]·2I$_2$·1/2I$_2$ by using a He–Ne laser source (λ = 632 nm). (b) Raman spectrum of a single crystal of [Ni(Pr$^i_2$timdt)$_2$]·2I$_2$[Ni(I)$_2$(Pr$^i_2$timdt)$_2$]·3I$_2$ by using a He–Ne laser source (λ = 632 nm). The dotted line is the spectrum of the same crystal and shows loss of I$_2$ ($\nu_{\text{I–I}}$ at 159 cm^{-1} becomes lower in intensity) after a long exposure time (~ 3 h) to the laser beam.

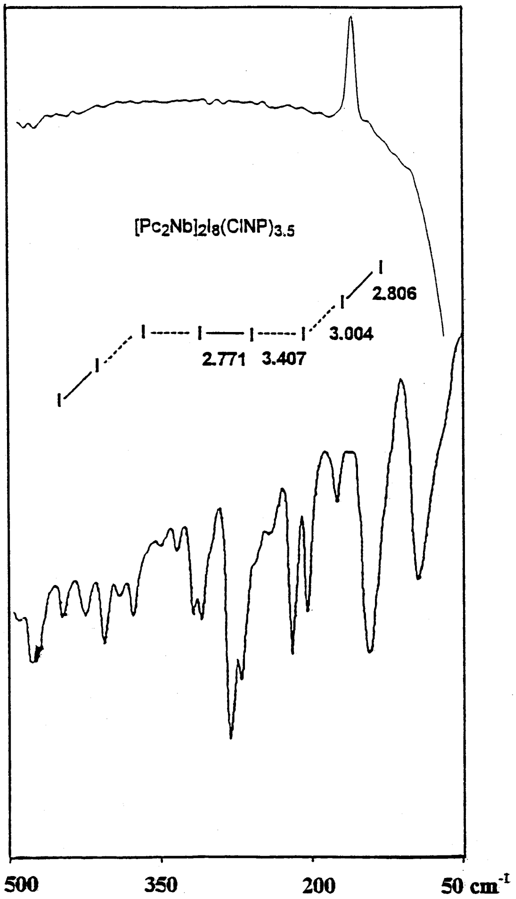


Fig. 9. Comparison of the FT-Raman (upper, $\nu_{I-I} = 167$ cm^{-1} assigned to the less elongated I_2) and Far-IR spectra (lower, $\nu_{I-I} = 144$ cm^{-1} assigned to the more elongated I_2) of $[Pc_2Nb]\cdot 1/2(I_8)\cdot 7/2(ClNP)$, (Pc = phtalocyanine, ClNP = α-chloronaphtalene).

(I_{29}^{3-}), and each stoichiometry offering a wide range of structures in many instances, the polyiodide moiety does not exist as an authentic entity but can be best described as derived from the interaction involving I_3^- and/or I^- (donors) with I_2 (acceptor), as it happens in type **1** adducts of neutral donors with I_2. On the other side $D\cdot I_2$ adducts of type **2** exist as an authentic entity as it happens in the case of symmetrical triiodides. Table 6 summarizes the Raman spectra expected for various iodine containing moieties in polyiodides, and in $D\cdot I_2$ adducts.

Our proposed unified classification of polyiodides and I_2 adducts is based on experimental results and seems to agree with theoretical studies recently reported [64] which describe the bonding in trihalides and in donor–acceptor compounds with a unified picture.

Table 6
Raman scattering predicted for various polyiodides and $D{\cdot}I_2$ adducts

Possible iodine-containing moieties	Predicted Raman scattering (cm^{-1})	Assignments
I_3^- $(I–I–I)^-$	110	$\nu_{I–I–I(sym)}$
I_{2m+n}^{n-} $(nI^- mI_2)$	140–180	$\nu_{I–I}$
I_3^- $(I^-{\cdot}I_2)$; I_4^{2-} $(2I^-{\cdot}I_2)$; I_5^- $(I^-{\cdot}2I_2)$; I_7^- $(I^-{\cdot}3I_2)$; I_8^{2-} $(I^-{\cdot}I_2{\cdot}I_2{\cdot}I^-{\cdot}I_2)$; I_9^- $(I^-{\cdot}2I_2{\cdot}2I_2)$		
$I_{2m+n}^{n-}[xI_3^-{\cdot}(m-x)I_2{\cdot}(n-x)I^-]$	140–180, 110	$\nu_{I–I}$, $\nu_{I–I–I(sym)}$
I_5^- $(I_3^-{\cdot}I_2)$; I_7^- $(I_3^-{\cdot}2I_2)$; I_8^{2-} $(I_3^-{\cdot}I_2{\cdot}I_3^-)$; I_{16}^{4-} $2(I_3^-{\cdot}I_2{\cdot}I^-{\cdot}I_2)$		
$I_{(6i+1)}^{-3}$, $i=2$: I_{13}^{-3} $(I_2{\cdot}I^-{\cdot}2I_5^-)$, $(I_5^- = I^-{\cdot}2I_2)$	140–180	$\nu_{I–I}$
$I_{(6i-1)}^{-3}$, $i=5$: I_{29}^{-3} $\{[I_5^-{\cdot}2I_2]\ [I_{12}^{2-}{\cdot}2I_2]{\cdot}2I_2\}$, $(I_{12}^{2-} = I_3^-{\cdot}I_5^-{\cdot}2I_2)$	140–180, 110	$\nu_{I–I}$, $\nu_{I–I–I(sym)}$
Iodine chains (I_8^{3-})[a]	No signal	
$D{\cdot}I_2$	140–180	$\nu_{I–I}$
D–I–I	120, 150–200	$\nu_{D–I–I(sym)}$, $\nu_{D–I–I(asym)}$; D = S or Se
$D–I^+{\cdot}I^-$	159	$\nu_{P–I}$; D = P

[a] I···I distances greater than 3.2 Å.

6. Conclusions

(1) An empirical method based on X-ray and Raman data to classify adducts and polyiodides, which attempt to provide a unified picture of the bonding in these species and to remove the arbitrariness in considering discrete/non discrete entities is proposed.

(2) General agreement is observed between X-ray and Raman data. These data have indicated that in going from I_4^{2-} to I_{29}^{3-} moieties, no discrete entities exist. These moieties are adducts of I^- and/or I_3^- with I_2. The I_3^- moiety represents a crossover, and it can exist as a real I_3^- entity or an $I^-{\cdot}I_2$ adduct.

(3) The precautions to be taken in studying polyiodides have been cited. Due to the instability inherent in these materials it is possible that some of the Raman results in the literature may be wrong.

(4) Infrared data can be useful when experimental restraints (strongly absorbing samples in the NIR region) prevent to obtain satisfactory Raman spectra and when triiodides demonstrate asymmetry. To avoid grinding the sample and the use of a matrix effects in the infrared sampling technique, microspectroscopy is preferred as no grinding or a matrix is required.

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