CHEMICAL REVIEWS

Volume 103, Number 5

Synthesis, Structure, and Bonding in Polyiodide and Metal Iodide–Iodine Systems

Per H. Svensson and Lars Kloo*

Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Received July 10, 2002

Contents

I. Introduction and Background

Iodine was discovered in 1811 by the French chemist Curtois during the process of manufacturing potassium nitrate, with which he supplied the Napoleon armies.[1] While washing seaweed ashes (used to conserve potash in the process) with sulfuric acid, he noticed violet fumes that condensed on his copper equipment and caused corrosion. Later, Gay-Lussac

10.1021/cr0204101 CCC: $44.00

Per H. Svensson was born in Lessebo, Sweden, in 1969. In 1998 he received his Ph.D. at Lund University, where he under the guidance of Professor Kloo worked on polyiodide chemistry. During 1999–2001 he carried out research on high nuclearity clusters together with Professor Giuliano Longoni at Bologna University. Following this postdoctoral time in Italy he conducted research at the Royal Institute of Technology in Stockholm. He also studied economy at the Stockholm School of Economics, before he in 2002 received a position at Sanofi-Synthélabo in Strasbourg, France, where he currently works on structure-based drug design.

Lars Kloo received his Ph.D. in Inorganic Chemistry at Lund University, Sweden, in 1990. He continued as research associate, lecturer and research fellow at Lund University until 1998, when he moved to his current position as Professor in Inorganic Chemistry at the Royal Institute of Technology in Stockholm. During 1991–95 he was in shorter or longer periods also visiting scientist in the laboratories of Prof. Brian T. Heaton, Liverpool University, UK, Prof. Roald Hoffmann, Cornell University, USA and Prof. Peter Schwerdtfeger, Auckland University, New Zealand. His interest in polyiodide chemistry started through the co-operation with Dr. Harald Stegemann, Greifswald University, Germany, in the end of the 1980's concerning the development of new electrolytes for pacemaker batteries.

and Davy recognized it as a new element and named it after the Greek word for violet (Greek: $\iota\omega\delta\eta\varsigma$).[2] Shortly after, polyiodide chemistry was discovered when Pelletier and Caventou showed that the addition of iodine to strychnine resulted in the crystalline compound strychnine triiodide, which they named "hydroiodure ioduré".[3] The reaction between metal halides and iodine, as well as the increased solubility of iodine in different solvents on the addition of potassium iodide also attracted early attention. Several investigators considered the increase in solubility a consequence of the formation of triiodide ions. However, many researchers were reluctant to accept this explanation. The first systematic investigation was initiated in 1839 by Jörgensen.[4] He proposed that polyiodide alkaloids contain iodide as well as iodine.

Figure 1. Tincture of iodine.

Even at an early stage in their history, polyiodides found applications in several areas. The blue starch–iodine complex (believed to consist of polyiodide fragments[5]) was discovered already in 1814, and in that same year was employed as a sensitive analytical test for iodine.[6] A more unusual application for polyiodides was found during the extermination of stray dogs undertaken by the Paris police in 1830.[4,7] They used strychnine-containing derivatives, and it was not long before an antidote was requested. Donne found that a solution of iodine in potassium iodide (potassium triiodide) was an appropriate antidote for the poisoning.[7] The same mixture (tincture of iodine; Figure 1) has also been applied to the treatment of goiter.[8]

Polyiodides have earned much deserved attention because of their fascinating structural chemistry. Examples of everything from very simple discrete units to one-dimensional chains and complicated two- and three-dimensional networks all occur. Already in 1933, the first complete structural determination of a polyiodide, ammonium triiodide [$(NH_4)I_3$], was reported.[9] Up until now, a large number of polyiodide ions have been structurally characterized and anions in the range from I_2^- to I_{29}^{3-} have been established. The great variety of possible polyiodide structures is a consequence of the ability of iodine to catenate through donor–acceptor interactions combined with the influence of counterions. These features have been rationalized and utilized in template synthesis, as well as in molecular and crystal engineering, where different cations are used to achieve special structural features.[10] Apart from cation variation, it is also possible to substitute the polyiodide building blocks for other donor and acceptor species in order to modify the structural properties.[11] Polyiodides are hypervalent, and many large polyiodide structures cannot be explained by simple covalent bonding models. The nature of the bonding in polyiodides has therefore been the object of much theoretical speculation.[12] The interest in polyiodides has also been focused on mixed-valence, donor–acceptor materials (organic metals) where iodine is used as the acceptor. These materials often exhibit unusually high electrical conductivity.[13] Several of these mixed-valence compounds have been found to be superconductors with a T_c typically at 2–8 K.[14] The use of iodine to dope conjugated polymers (where polyiodides are formed via charge transfer) to form conducting polymers has been an area of great interest, and the 2000 Nobel Prize in Chemistry to A. J. Heeger, A. G. MacDiarmid, and H. Shirakawa was awarded for research in this area.[15]

Room-temperature, molten polyiodides show high electrical conductivity, and the reason for this behavior has been the subject of several investigations.[16] A mechanism of conductivity similar to the Grotthus one for protons in water has been suggested.[17]

Many of the properties mentioned above suggest potential technical applications in a great variety of areas. Indeed, polyiodides have found such applications in electronics, fuel cells, batteries, solar cells, optical devices, etc.[18]

II. Synthesis and Characterization

Even though the number of known polyiodides is large, it is possible to rationalize their synthesis and chemical properties. This section covers the general principles of synthesis and characterization of polyiodides.

II.1 General Considerations

The Lewis acid acceptor iodine and the Lewis base donors I^- or I_3^- can be regarded as the fundamental “building blocks” of polyiodides. However, as will be described later, there also exist “guest” building blocks (e.g., metal iodides and donor species of Groups 15 and 16). The building blocks catenate easily and a large variety of polyiodides can be synthesized (e.g., I_4^{2-}, I_5^-, and I_7^-; see Figure 2) with geometric features such as linear chains ${}^1_\infty[I^-{\cdot}I_2]$, quadratic networks ${}^2_\infty[I^-{\cdot}I_2]$ or ${}^3_\infty[I^-{\cdot}I_2]$ cubic 3D networks.[13a−b,19] Since polyiodides are usually diamagnetic, the possible combinations of the building blocks can be described by the following formulas (Scheme 1 and Figure 2). For the rationalization of the formal composition in some extended polyiodides also noninteger values of n may be employed.

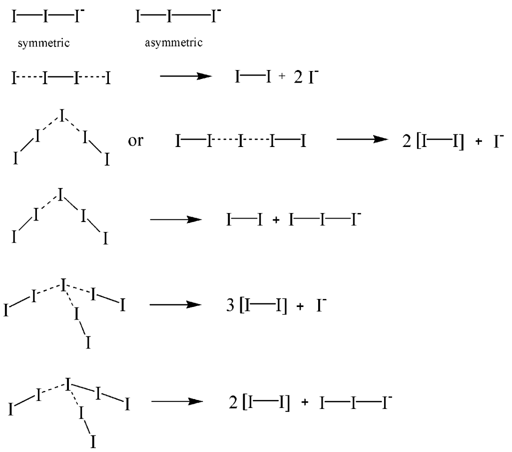


Figure 2. Construction of I_4^{2-}, I_5^-, and I_7^- ions from the polyiodide building blocks.

Scheme 1

$$m\,I_2 + n\,I^- \longrightarrow I_{2m+n}^{\;n-} \text{ (m and n integers > 0, n = 1 - 4)}$$

The variable m is equal to the number of iodine molecules, and n is equal to the number of iodide ions. The upper limit of n is set to 4, since this is the highest charge presently known for polyiodides. The formula does not contain the triiodide as a variable but it is included indirectly since the triiodide is formed from an iodide ion and an iodine molecule. A less general polyiodide classification according to $I^-_{1+2i+2j/k}$ (where i, j, and k integers, $0 \leq i$, $0 < j \leq k$, k = ionic charge) has also been proposed.[20] Under special conditions it is possible to form ions such as I_2^-, I_4^-, and I_6^- as well as polyiodonium cations (e.g., I_2^+, I_3^+, I_4^{2+}, and I_5^+) by violating the formula in Scheme 1.[21] Generally, the stability of polyiodides is very dependent on the size, shape, charge, and symmetry of the cation used. Large cations with a high symmetry can be employed to obtain large and thermally stable polyiodides.[13a−b,19] In general, an increase in iodine content destabilizes the resulting polyiodide. Polyvalent cations usually lead to significant increase in triiodide asymmetry.[13a−b,19,22,23] Recently, the polyvalent complex crown ether cations have been shown to be useful in the synthesis of polyiodides.[10a−d] Evidence has been found for the presence of polyiodides in solution, with the triiodide ion the predominant species in water (Scheme 2).[24] However, higher polyiodides (e.g., I_4^{2-} and I_5^-) have also been reported in solution.[24,25] Recent investigations indicate that I_3^- is the only isolated polyiodide that exists in aqueous solution, whereas larger polyiodide species are stabilized by H^+ ions.[26] In most nonaqueous solvents, polyiodides show a dramatic increase in stability.[19,25] Polyiodides are readily soluble in solvents such as acetone and ethanol.

Scheme 2

$$I_2(s) + I^-(aq) \longrightarrow I_3^-(aq) \quad K \approx 723 \pm 10 \;\; (25°C)$$

All polyiodides decompose to some extent into iodine and iodide at room or higher temperatures. The color of polyiodides is a direct function of the amount of iodine present. As the iodine content increases, the color becomes darker and darker. Higher polyiodides usually exhibit a characteristic metallic luster.

II.2 Synthesis and Model Polyiodide Systems

II.2.1 Synthesis

To date, several hundreds of polyiodides have been reported in the literature. They have very different structural and physical properties. However, the syntheses used can in general terms and with few exceptions be described simply as the addition of iodine to an iodide in an appropriate reaction medium.[19,25] This procedure can of course be varied in many different ways depending on how the iodine and iodide are mixed, the solvent used and the cation associated with the iodide. There is a multitude of possible cations (e.g., onium, metal, crown ether, cryptand, and heterocyclic nitrogen cations) that can be used in the synthesis of polyiodides. All of them exert a specific influence on the resulting polyiodide structure. One modification of the general synthetic route is to react iodine with an existing polyiodide thus obtaining a polyiodide with a higher I_2 content. Metathesis reactions have also been reported.[27] In some cases, when the polyiodide has a high iodine content, it is important to employ a solvent that is inert and possesses poor solvating properties with respect to iodine.

The reaction of nucleophiles (e.g., phosphine selenides/sulfides and unsaturated nitrogen heterocycles) with iodine can also result in the formation of polyiodide species (see section III). This is a consequence of a charge-transfer interaction between the two species resulting in a charge separation. Generally, all the synthetic routes mentioned above are performed in a single phase. However, examples of two-phase synthetic routes are also described in the literature.[28] Here, a water−organic solvent mixture, where the polyiodides are extracted from the organic phase are used.

The reaction of metal iodides (and donor species in general) with polyiodides constitutes a special synthetic route, since the metal iodide in such systems causes the iodine to compete for the iodide ions. This mechanism enables the insertion of guest atoms into the polyiodide networks. In these complexes, the metal iodides can be regarded as substituting for the negative ions I^- and I_3^- in the pure polyiodide networks. Thus, the metal iodides can be considered new polyiodide building blocks. It is possible to distinguish between two classes of metal iodide−iodine complexes, where the polyiodide is incorporated into the coordination sphere: Complexes with other stabilizing ligands (e.g., amine, cyclopentadienyl, phenyl, and phosphine), and complexes with only iodide ligands (binary metal iodide−iodine systems). The former is quite well-known in polyiodide chemistry and several examples will be given in section III.

The majority of all polyiodides exist in the solid state, although polyiodide melts have been synthesized also. It is possible to distinguish between two types of molten polyiodide systems: Pure liquid iodine melts at elevated temperatures, and room temperature polyiodide melts. The formation of room temperature molten polyiodides and melts in general are facilitated by (a) monovalent cation and anion, (b) voluminous cation or anion, and (c) charge delocalization or good ligand screening [viz. $Pt(NH_3)_4^{2+}$].[29]

II.2.2 Model Systems

There are two main approaches to the systematic study of polyiodides each of which exhibits some limitations. In the first, the liquid model systems, it is possible to study nonextended structural units. In this case, either solutions of iodine dissolved in organic solvents or polymers, pure liquid iodine or room temperature polyiodide melts are studied. The problem with the second, solid polyiodide model systems is that to obtain a good understanding of the relationship between structure and physical properties, it is important to be able to exercise synthetic control. This requires the synthesis of series of compounds with systematic changes in composition and structure. But because of the multitude of small effects strongly influencing the exact structure and composition of solid polyiodides precipitating from a specific synthetic batch, such control is virtually impossible. The problem with using I_2-based liquid model systems, on the other hand, is due to the use of $I_2(l)$ as solvent. In addition to its hazardous nature, molten iodine has several undesirable properties; it is corrosive, has a high vapor pressure, and because of its low dielectric constant, it is a rather poor solvent for inorganic electrolytes such as metal iodides. The obvious problem with using a two-component system is the influence of a second component such as another solvent or polymer. The solubility of inorganic electrolytes in organic solvents is low and several of them are known to promote heterolytic cleavage of I_2.

The gas phase is a potential third model system. However, to date, it is used implicitly only in theoretical approaches.

II.3 Characterization

Several techniques have been employed to characterize the nature of polyiodide systems. In addition to X-ray based methods the most powerful methods used to obtain structural information are Mössbauer spectroscopy and vibrational spectroscopy. Other methods such as NMR, ESR, ESCA, and UV/vis spectroscopy, as well as electrochemical measurements have also been applied. This section will focus on spectroscopic methods, while X-ray diffraction and scattering data will be discussed in section III.

II.3.1 Vibrational Spectroscopy

Raman and far-IR spectroscopy are powerful methods for the characterization of polyiodides in both the liquid and solid state. They are especially valuable when the compounds investigated are noncrystalline. When compounds crystallize, additional structural information is obtained. In the following survey of the vibrational properties of polyiodide systems, iodine is discussed separately from I_3^- and the higher polyiodides.

II.3.2 Iodine

Although solid iodine has a Raman-active mode at 180 cm^{-1}, ν_1, no spectral features are seen in the IR spectra as a result of the symmetry selection rules.[30] The ν_1 symmetric mode for molten and gaseous iodine are at 194 and 213 cm^{-1}, respectively.[31,32] Spectral features for molten iodine indicating the presence of I_3^- and $(I_2)_n$ cluster formation has also been detected.[31] As I_2 becomes coordinated to a donor, the force constant is reduced and the ν_1 mode moves to lower wavenumbers.[10c,33] This is a consequence of electron density donation into the σ^* antibonding orbital of iodine. Usually, coordination to the donor species also lowers the symmetry of iodine. As a result the ν_1 mode becomes IR-active. Classical examples of this type of donor−acceptor interaction are solutions of iodine in different organic solvents (e.g., alcohols, pyridine, etc.).[34] Other examples are found for iodine compounds with alkenes/alkynes, and iodine intercalated into fullerenes or superconductors.[35–37]

The paramagnetic, molecular ion I_2^- (with alkali metal cations) has also been investigated using Raman spectroscopy and the frequency of the ν_1 band was reported to be 115 cm^{-1}.[38] Measurements were made in liquid helium because of the instability of the ion.

Vibrational spectroscopy studies have proven useful in the study of iodine-doped organic, polymeric conducting compounds (organic metals). Such studies have provided information about the nature of the iodine species present, charge-transfer interactions, as well as the conductivity mechanism.[13a,13b,39] As a tool for the characterization of iodine, Deplano et al. have suggested an empirical correlation between the ν_1 frequency of I_2 and the intramolecular iodine distance, d(I−I), applicable to weak or medium-strength, charge-transfer compounds.[33,40] They also suggest that for strong interactions between iodine and the acceptor (I_2 bond order < 0.6), the complex cannot be regarded as a two-body system. Hence, this has to be taken into account in the interpretation of the vibrational spectra.

II.3.3 Triiodides and Higher Polyiodides

The centrosymmetric (D_{ih}) triiodide has a Raman-active (symmetric stretch) band ν_1 and two IR-active bands. These are the doubly degenerate bending and asymmetric stretch modes, ν_2 and ν_3, respectively. If the symmetry is lower than D_{ih}, then all three modes become both Raman- and IR-active. In general, for a symmetrical I_3^- ion the bands from the ν_1, ν_2, and ν_3 modes can be expected at approximately 110, 50−70, and 130−140 cm^{-1}, respectively.[13b,33d,40−42] The Raman spectrum of (dbqr)I_3 shows the characteristic ν_1 mode at 110 cm^{-1}.[43] The ν_3 mode is found at 125 cm^{-1}, whereas in the far-infrared spectrum the ν_2 modes are at approximately 50 cm^{-1}.

Deviation from the selection rules have been found for several triiodide systems. Gabes et al. point out that effects such as factor-group splitting and site symmetry splitting have to be taken into account in the solid state to correctly interpret spectra.[44]

For solutions of triiodides, the selection rules for D_{ih} have been found to be violated. For example, $(Me_4N)I_3$ dissolved in either nitrobenzene and ethanol, as well as KI_3 dissolved in water or methanol show spectral features deviating from the expected D_{ih} symmetry.[10c,45] They suggest that such deviations from D_{ih} symmetry are a consequence of symmetry lowering. This can result from either (a) anion−anion interaction, (b) complex formation with the solvent, or (c) the relative instability of the linear symmetric structure compared to a slightly asymmetric structure.[44] The explanations (a) and (c) may also arise due to the presence of higher polyiodides.

In a more recent investigation, Milne suggests that spectral effects, Raman enhancement and Fermi resonance, all have to be taken into account to achieve a complete interpretation of the spectral features.[33] He applied this theory to the HI/I_2 system in aqueous solution. Here, extra spectral features in the Raman spectra were found at 150 and 172 cm^{-1}. The 150 cm^{-1} band was assigned to Fermi resonance between ν_1 and $2\nu_2$, while the 172 cm^{-1} band was assigned to the I−I stretch of the ion-pair $[H^+]I_3^-$.

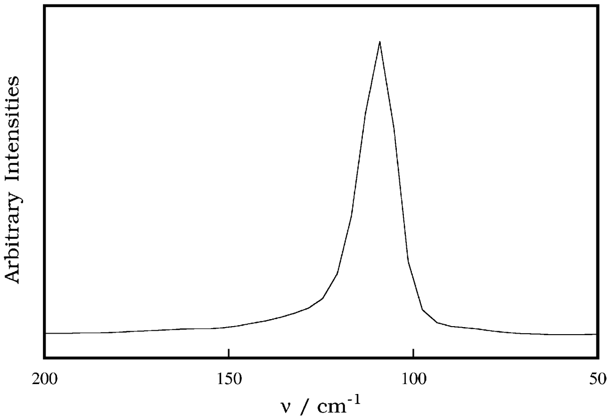


Figure 3. Raman spectra of (dbqr)I_3.

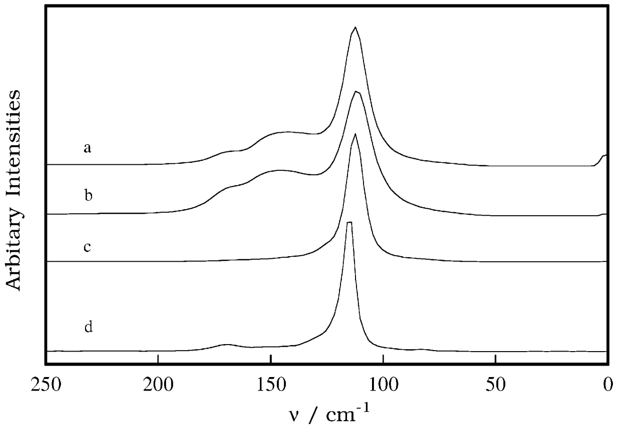
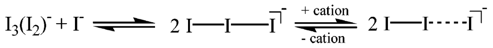


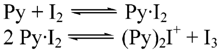
Figure 4. Raman spectra of (a) molten $(Et_3S)I_3$ at room temperature, (b) molten $(Me_3S)I_3$ at approximately 40 °C, (c) solid $(Me_3S)I_3$ at room temperature (mp = 37 °C), (d) Quenched Et_3SI_3 (196 °C). *J. Chem. Soc., Dalton Trans.* **2000**, 2449. Reprinted with permission of the Royal Society of Chemistry. Copyright 2000.

The vibrational spectra of the $(R_3S)I_3$(l) polyiodides (R = Me or Et) show unexpected (for D_{ih} symmetry) spectral features at 145 and 170 cm^{-1} (cf. Figure 3).[42,46] However, solid $(Me_3S)I_3$ and $(Et_3S)I_3$ are found to follow the selection rules for D_{ih} (Figure 4).[42,46] Polarization experiments showed that the 170 cm^{-1} peak originates from a symmetric vibrational mode. The addition of excess I^- causes the peak at 170 cm^{-1} to disappear, while the peak at 145 cm^{-1} is invariant. In addition to the above explanations hot bands, dynamic process, solvent effects, and redox reactions have all been suggested as possible explanations for the spectral features observed. Another explanation using liquid X-ray scattering (LXS) data of a formal $(Et_3S)I_2$ melt together with Raman spectra of the Br_3^- and Br_2I^- ions suggests that the Raman band at 145 cm^{-1} is caused by the existence of asymmetric I_3^- in solution, whereas the additional spectral feature at 170 cm^{-1} is a result of the I_2 ν_1 mode in a pentaiodide configuration; $[(I^-)\cdot 2I_2]$ or $[(I_3^-)\cdot I_2]$. The major contribution to the lowering of the I_3^- symmetry is probably cation interaction. The formation of I_5^- can

Scheme 3



Scheme 4



Scheme 5

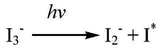


Table 1. Calculated Vibrational Frequencies for Pentaiodides

mode	frequency linear[49] (cm^{-1})	frequency linear[50] (cm^{-1})	frequency V-shaped[49] (cm^{-1})	frequency V-shaped[50] (cm^{-1})
ν_1	154−162	165	157−164	157
ν_2	67−75	55	113−130	90
ν_6	145−163	146	137−157	143
ν_7	90−128	114	77−100	110

be seen as arising from the disproportionation $(n+1)I_3^- \rightarrow I_3(I_2)_n^- + nI^-$ ($n = 1$). Thus, the system can be understood in terms of a coupled equilibrium initiated by the liquidification of a triiodide system (Scheme 3). The presence of symmetric and asymmetric triiodides and pentaiodides gives rise to vibrational features compatible with the ones observed experimentally.

Pentaiodides have two principal geometries, either linear (D_{ih}) or V-shaped (C_{2v}, $[(I^-)\cdot 2I_2]$). The latter, which is the most common, also has a distorted variant in the L-shaped $[(I_3^-)\cdot I_2]$ pentaiodide. The first of several investigations of pentaiodides using vibrational spectroscopy was an attempt by Parret et al. to assign the spectral bands.[41,47,48] However, these assignments are not very detailed. A more comprehensive assignment was made by Nour et al. in 1984.[49] More recently, Sharp and co-workers used ab initio calculations to make assignments.[50] These show that the V-shaped pentaiodide has nine vibrational modes (four stretching and five bending modes), while the linear pentaiodide has seven vibrational modes (four stretching modes and three doubly degenerate bending modes). The four stretching modes of the V-shaped polyiodide can be divided into inner/outer symmetrical stretches (ν_2/ν_1) and inner/outer asymmetrical stretches (ν_7/ν_6). These four stretching modes are the ones usually observed as a fingerprint. The linear pentaiodide has corresponding modes. As seen from Table 1 it is not easy to separate the linear and V-shaped pentaiodides using the frequencies alone. However, Sharp and co-workers point out that since the linear pentaiodide will have a substantially higher ν_6/ν_7 ratio in the far-IR spectrum it is possible to distinguish between the two configurations.

The L-shaped pentaiodide configuration displays a weak coupling between the I_2 and I_3^- unit and the vibrational features can be interpreted as originating from the two discrete units.[51] A typical Raman spectrum for the L-shaped pentaiodide is found for (dbcr)I_5 (Figure 5). The peaks at 112 and 168 cm^{-1} correspond to the ν_1 of a triiodide and a weakly coordinated iodine, respectively. The presence of an asymmetric triiodide is revealed by the peak at 143 cm^{-1}.

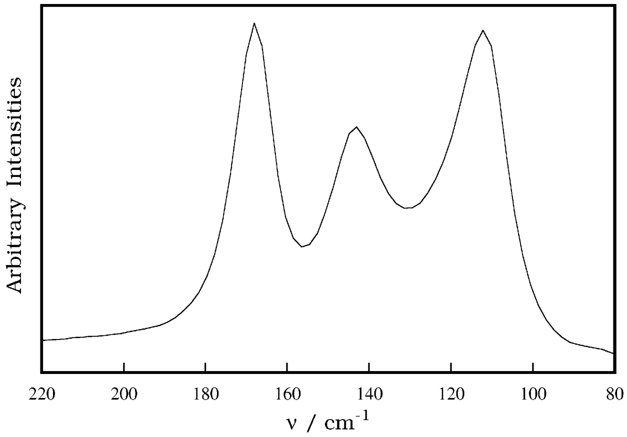


Figure 5. Raman spectrum of (dbqr)I_5.

No theoretical calculations have been reported to support the assignments for heptaiodides. However, the interpretation of heptaiodide vibrational features can be rationalized if it is assumed that they originate from combinations of I^-, I_2, and I_3^- $\{[(I^-)\cdot 3I_2]$, $[(I_3^-)\cdot 2I_2]$), or $[(I_5^-)\cdot I_2]\}$.[10c,47−51] Deplano et al. have recently suggested that even the I_5^- spectroscopic features can be described using the fundamental polyiodide building blocks. Although this interpretation seems promising, there is still a substantial lack of vibrational spectroscopic data (mostly IR) for the liquid and solid states needed to confirm this hypothesis. Theoretical investigations have shown that significant covalent interaction appear to be present for distances as long as 4 Å, leading to the conclusion that spectral features may be even more difficult to interpret.

The assignment of vibrational features for the higher polyiodides can be based on the same principles as those applied to the heptaiodide. However, as the iodine content increases there is little to distinguish the vibrational features from the lower polyiodides, and without supporting data from other methods the assignments become very speculative.

A valuable extension of traditional Raman spectroscopy is resonance Raman spectroscopy (RRS).[52] In this method, the sample is irradiated with a laser whose frequency lies within an electronic absorption band region, and as a consequence the Raman emission is greatly enhanced. This Raman enhancement is of course important when the sample size is limited and is a weak scatterer. With RRS, it is possible to distinguish between an asymmetric and a symmetric triiodide.[53] This results from an increase in the low-energy absorption in the asymmetric triiodide, while the symmetric triiodide absorbs strongly at higher energies.

However, RRS suffers from the disadvantage that the visible laser can induce not only melting of the sample, but also fluorescence, sample pyrolysis, and photoreactions.[40] Despite this, the method has been successful in the investigation of conducting mixed-valence complexes of halogens and several polyiodide systems.[19a−b,40,54]

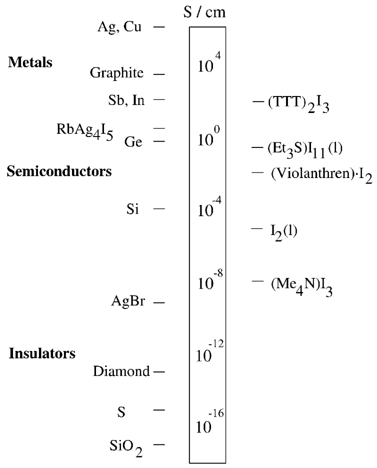


Figure 6. Conductivity of some polyiodides and iodine-doped compounds.

II.3.4 Conductivity Measurements

The investigation of the electrical conductivity of iodine was initiated well before 1900 and already in 1906 the first quantitative data were reported.[55] In the 1930s, it was noticed that the addition of iodine to pyridine drastically enhances the conductivity.[56] However, the system was poorly understood. During the 1950s, the presence of triiodide in pyridine/iodine systems was confirmed by UV/vis spectroscopy and Mulliken proposed a reaction sequence where Py·I_2 is heterolytically dissociated into PyI^+ and I^- .[57,58] The I^- thus formed then reacts with the iodine present to form I_3^- and higher polyiodides. This model was later slightly modified, when the iododipyridinium ion $(Py)_2I^+$ was identified in the system[59] (Scheme 4).

During the 1950s and early 1960s investigations of the electrical conductivity in charge-transfer complexes, with iodine as acceptor, were also performed.[60] Several of these compounds (e.g., iodine-doped violanthrene and pyrene) display large electrical conductivity enhancements. Since then, iodine has been used in a wide number of investigations to improve conductivity in polycyclic aromatic hydrocarbons, graphite, stacked inorganic systems and polymers. In many of these mixed-valence systems, which are often low-dimensional, polyiodides have been shown to be present. They usually occupy channels between stacks of planar, cationic structural elements. The conductivity of these compounds spans a wide range (Figure 6). Several superconducting charge-transfer complexes have also been reported [e.g., K(BEDT-TTF)$_2$I$_3$, (DMET)$_2$I$_3$, and (BEDT-TTF)I$_3$].[61]

The mechanism of conductivity in the mixed-valence systems is believed to be associated with the cationic stacks, but there is some suggestion that polyiodides are also involved in the conduction process. Even though the polyiodides play an important role in these systems, few studies of the conductivity of pure polyiodide systems have been reported.

Crystalline, organic polyiodides [e.g., $(Me_3PhN)I_3$ and $(MePy)I_3$] were investigated by Kusabayashi et al. They concluded that although the conductivity is quite low as the iodine content is increased the conductivity also increases.[62] In 1987, Stegemann et al. measured the conductivity of *N*-alkylurotropinium polyiodides and reported that the cation has no significant effect on the conductivity and that the charge transport is predominantly electronic. They also showed that the conductivity increases for the higher polyiodides (i.e., with larger iodine content).

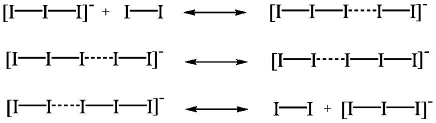


Figure 7. Schematic illustration of the Grotthus mechanism.

Liquid polyiodides would be expected to have high electrical conductivity as a consequence of translational ion movement in the melts. Thus, the addition of iodine ought to decrease the conductivity since it is an insulator and because its coordination to I^- and I_3^- ions in the melt would increase the physical size of the charge carrier. In such a model, larger polyiodides should have less ionic mobility. However, the molten polyiodides $(R_3S)I_x$ and $(R_4N)I_x$ show an increase in conductivity with increasing iodine content. Consequently, an ionic conductivity mechanism does not seem applicable. Conductivity in analogous systems has been explained by radical formation, delocalized electrons, or conduction via a Grotthus mechanism.[29] Stegemann and co-workers suggest that the latter option should be applicable to polyiodide melts (Figure 7). The Grotthus mechanism, also referred to as a relay mechanism, produces a net transport of charge without any net transport of mass. This mechanism is favored by a high iodine packing density which results in advantageous electronic interactions between the donor and acceptor.

Hence, the conductivity enhancement with increasing iodine content is a consequence of an increase in connectivity and the reduced distance between donors and acceptors. Stegemann et al. also reported that the activation of charge-carrier transport is of the same magnitude as for solid proton conductors with an established Grotthus mechanism.[29]

II.3.5 UV/vis Spectrophotometry

Dissolved iodine gives rise to a broad spectrum of colors. In aliphatic solvents, the color is violet, while in alcohols, ethers, and benzene it is brown or reddish-brown. The use of UV/vis spectrophotometry for the characterization of polyiodides is therefore appropriate. Gabes et al. have performed numerous UV/vis investigations of polyiodides, and they report that the triiodide ion has two absorption bands at 290 and 367 nm (in the solid state and in CCl_4).[63] The blue starch−iodine complex was also investigated, and the band at approximately 600 nm was assigned to the pentaiodide ion.[64,65] The absorption band for pentaiodides has also been reported as occurring at about 700 nm.[66] Higher polyiodides, such as I_7^- and I_9^-, have been reported to show the same spectral features as the triiodide and pentaiodide ions.[19e] An increasing I_2 content seems to extend the tail of the absorption bands to larger wavelengths (Figure 8).

II.3.6 Other Methods

Nuclear quadrupole resonance spectroscopy (NQR) of iodine (^{127}I, spin 5/2) in polyiodides provides the

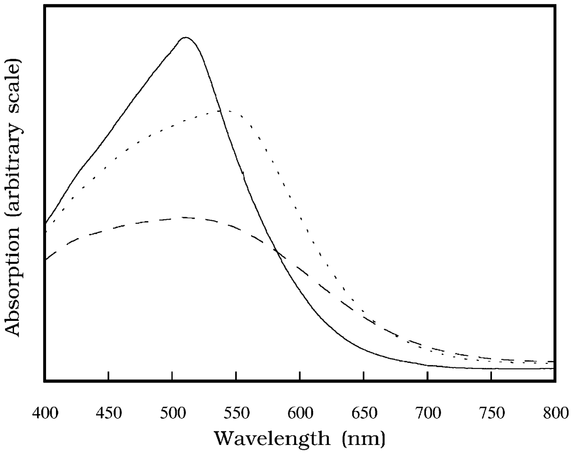


Figure 8. UV/vis spectra of a thin film of $(Et_3S)I_3$ (—), $(Et_3S)I_5$ (- - -), and $(Et_3S)I_7$ (···).

possibility of analyzing the electronic charge distribution among the valence orbitals.[67] This method can therefore be used for testing different bonding theories. The first NQR measurements on polyiodides were reported in 1955, and since then several studies have been performed.[68] Nakamura et al. propose that by examining the coupling constants it is possible to divide triiodides into three groups: symmetric, nearly symmetric, and markedly asymmetric.[69] Iodide exchange studies, obtained by the investigation of line-broadening effects of the iodide signals in triiodide solutions, have also been reported.[70]

It was concluded by several authors that the bonding in trihalides involves p-orbitals with little or no s- and d-orbital contribution.[67-69] This bonding model will be discussed in more detail in section IV.

Mössbauer spectroscopy differs from all other spectroscopic methods used for the characterization of polyiodides, because it utilizes the emission and absorption of γ-rays. The observed transitions are intranuclear and occur between the ground state ($I = 7/2$) and the excited state ($I = 5/2$) for ^{129}I. The advantage of Mössbauer spectroscopy, compared to vibrational spectroscopy, is that it is possible to detect isolated I^- ions and to obtain information about relative site populations.[13a,13b] The former supports the bonding model mentioned above.[19a-b,71] Several investigations have been performed using this technique, and it proved crucial for the characterization of the polyiodide present in the starch−iodine complex. It has also been used with great success in the study of conducting, mixed-valence compounds.[13b] However, even a method this powerful has some disadvantages. The compounds investigated have to be radioactively enriched in ^{129}I. The radioactivity associated with the enrichment process makes it difficult to use this technique. It should be pointed out that ^{127}I also can be used for Mössbauer spectroscopy, but the resolution is considerably lower than for ^{129}I.

Several other methods [e.g., ESCA, ESR, potentiometry, calorimetry, and DTA (differential thermal analysis)][72] have all been applied to the characterization of polyiodides. Space does not permit more detailed discussion of these informative and useful techniques. One new technique worth mentioning, however, is time-resolved and ultrafast laser spectroscopy. Polyiodide systems including the photodissociation of the triiodide ion in ethanol solution has been extensively studied with this technique.[73] Bond cleavage is reported to take place in approximately 300 fs resulting in I_2^- and neutral I (Scheme 5).

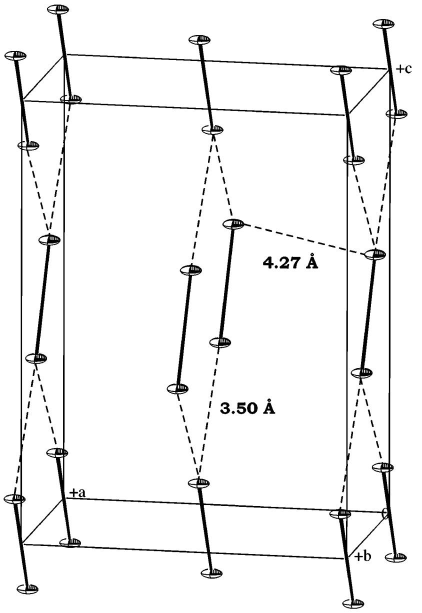


Figure 9. The structure of iodine at 110 K.

It is interesting to note that photodissociation produces a neutral iodine atom, whereas thermal dissociation leads to the iodide ion, which is responsible for the conduction properties of polyiodides.

III. Structure

The classification and description of discrete polyiodides are usually straightforward. However, with increasing iodine content polyiodide network structures emerge, and their description is not always unambiguous. This complication is accentuated by the fact that a wide range of weakly bonded I···I distances, much shorter than the sum of the vdW radii (4.3 Å),[74] are observed. Also, the boundary or limit of what is considered an iodine−iodine bond is not very clear. This will be discussed in section IV.

The polyiodide structures are discussed according to the series $I_{2n+m}{}^{m-}$ ($m > 0$ and $n > 0$). Compounds containing several discrete polyiodide ions resulting in a formal composition according to $I_{2n+m}{}^{m-}$ will be treated together with the smaller ions. The structure of iodine, which is fundamental to the interpretation of polyiodide structures, is also included. The binary metal iodide−iodine and related polyiodide structures are described in separate sections.

III.1 Iodine I_2

The structure of solid iodine can be described as a layered, two-dimensional zigzag-chain network (Figure 9). At 110 K, the intramolecular distances are reported to be 2.715 Å. Several short intermolecular distances are found at 3.496, 3.972 (within the layers), and 4.269 Å (between adjacent layers).[75] The corresponding distances at room temperature are reported to be 2.68, 3.56, 4.04, and 4.40 Å.[76] However, low-temperature bond lengths are usually taken as the reference because room-temperature measurements are less accurate. Iodine undergoes a structural phase transition at elevated pressures being transformed into a metallic phase, in which the intermolecular distances approach the intramolecular ones.[77]

X-ray diffraction studies of liquid iodine have revealed a short-range orientational order with adjacent molecules oriented in a more or less parallel configuration. The intramolecular bond length of I_2(l) is reported as 2.70 Å.[78]

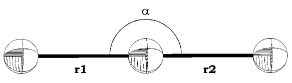
In polyiodides, in addition to intramolecular bonds, which tend to be longer than the normal covalent I−I bond, the intermolecular bonds are much shorter than the vdW distance (4.3 Å). The great range of I−I distances found in polyiodide structures makes it important to define what is considered an ”ordinary” I−I bond. Alcock introduced the term ”secondary bonding” to account for a range of interactions, including charge-transfer bonds.[79] Secondary bonds should, at least theoretically, produce a weakening of the primary bond. For example, the interaction of an I^- with iodine should elongate the intramolecular iodine bond distance. However, to assign secondary bonds, some kind of boundaries have to be established. Coppens suggested that the boundary between intra- and intermolecular distances should be set at 3.3 Å.[13a] His arguments are based on the ”complication” that polymeric chains in some compounds would have to be included, if a higher limit is chosen. This limit, however, makes it difficult to describe many known structures. In general, I···I contacts in the 3.4−3.7 Å range are regarded as secondary bonds and those up to 3.9 Å as weak vdW interactions.[80] As will be seen from the description of the polyiodide structures below, these limits are quite arbitrary, and in the literature different values have been applied to different structures. In this work, we regard polyiodides with I···I interactions longer than 4 Å as discrete. Ab initio quantum chemical studies (see section IV) support this view and is briefly discussed in the sections below.

III.2 Polyiodides within the Series I_{2n+1}^-

III.2.1 Triiodides I_3^-

Structurally, the most studied polyiodide is the triiodide ion. Since approximately 500 triiodides, with very different cations and structural features, have been characterized,[81] it is impossible here to give a comprehensive description of all these structures. Fortunately, however, it is possible to make some generalizations about triiodide structures.

The triiodide ions (**3.1**) are linear (or nearly linear) and can be divided into two types: asymmetric (C_s and C_{iv}) and symmetric (C_{2v} and D_{ih}).



3.1

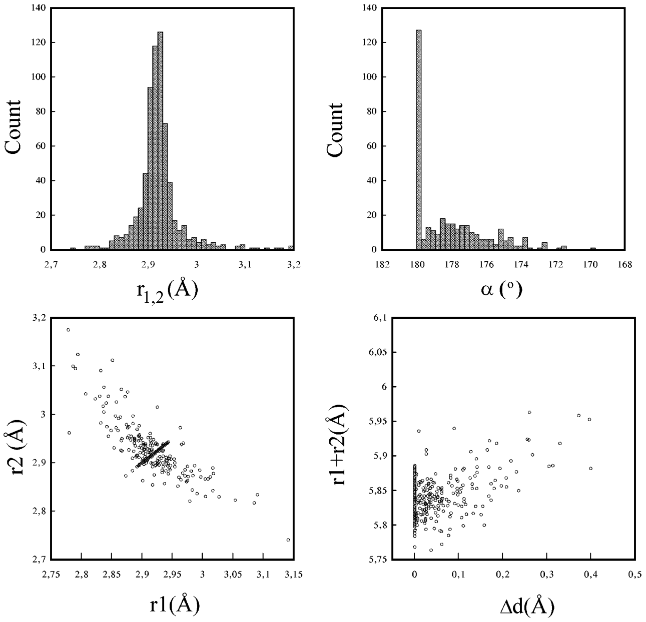


Figure 10. Statistical overview of the triiodide ion structure.

Many triiodide structures are described in the Cambridge Structural Database (CSD),[81] thus providing an excellent tool for demonstrating the structural parameters of triiodide ions. The distances r_1 and r_2 show a wide range of linear flexibility, but the total distance ($r_1 + r_2$) is essentially constant if $\Delta d = |r_1 - r_2|$ is relatively small ($\lesssim$ 0.10 Å; Figure 10). If Δd is large, the total length of the polyiodide increases. The reluctancy of triiodide ions to deviate from linearity is clearly seen in Figure 10.

It is believed that the large linear deformation of the I_3^- ion is a result of the different environments in the solid state. Rusnik et al. characterized the structure of $[(C_6H_5)_4As]I_3$, where because the triiodide ion has no short intermolecular contacts it can be regarded as a ”free” triiodide ion [d(I−I) = 2.90 Å and α = 176.4°].[82] According to the CSD the average d(I−I) for the triiodide ion is 2.92 Å. This is close to the I−I bond length for ”free” triiodide.

Triiodides with a large cation are usually symmetric, whereas asymmetry is induced in those with a small cation. However, the cation size is not the only factor determining the structure/topology of triiodides. For example, in CsI_3, the triiodide ion is asymmetric even though the Cs^+ cation is quite large and in $KI_3 \cdot H_2O$ the triiodide ion is symmetrical even though it is in contact with a small cation.[83] In general, if the effect of cation size is excluded, then the triiodide structures with large Δd are involved in hydrogen bonding or interionic interactions.[23,84] Packing effects and electrostatic interactions may also have to be considered to explain induced asymmetry, such as the observed deviation from ideal symmetry of the triiodide ion in $[(C_6H_5)_4As]I_3$.

The large number of compounds with hydrogen bonding to triiodides (CSD) can be seen in Figure 11, which shows all H···I contacts (shorter than the sum of vdW-radii) for the terminal iodide atom. The distribution is uniform, and the shortest H···I contact is about 2.5 Å. The central iodide atom has a similar distribution.

Table 2. Isolated V/L-Shaped Pentaiodides [d(I···I) > 4 Å]

r_1	r_2	r_3	r_4	α_1	α_2	α_3	compound
2.781	3.088	3.092	2.791	178.4	92.2	178.1	ζ-(BEDT-TTF)$_2$(I$_3$)(I$_5$)[85]
2.760	3.080	3.080	2.760	178.8	83.8	178.8	(valinomycin-K$^+$)$_2$(I$_3^-$)(I$_5^-$)[86]
2.829	2.991	3.259	2.756	173.3	88.6	176.2	[μ-N](I$_5$)[87]
2.801	3.067	3.067	2.801	178.7	102.1	178.0	(DMFc)I$_5$[88]
2.812	2.983	3.115	2.754	177.0	98.2	174.6	[(salen)VOVO(salen)][I$_5$]·MeCN[89]
2.817	3.051	3.187	2.790	177.4	90.2	176.5	[L···H···L]I$_5$[90]
2.820	3.001	3.263	2.743	174.1	84.0	175.4	i-PrTazI$_5$[91]
2.790	3.111	3.111	2.790	177.3	84.6	177.3	[Ag(9)aneS$_3$)$_2$)]I$_5$ [92]

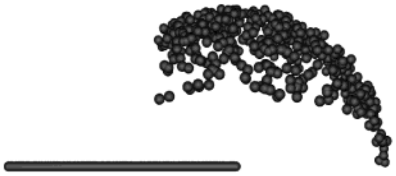
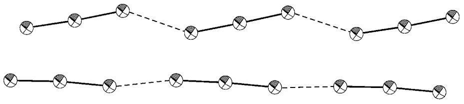


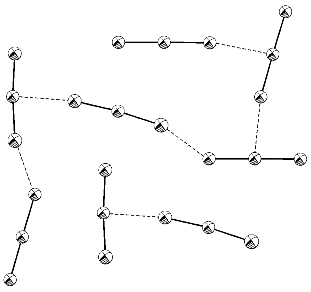
Figure 11. The symmetry reduced distribution of hydrogen around the terminal iodine of the triiodide.

Triiodide ions are usually stacked or layered in T-shape or zigzag patterns. In stacked structures or structures with channels, the triiodides often form infinite linear chains with weak $I_3^-\cdots I_3^-$ interactions (typically at ≥ 3.6 Å, according to CSD).[81]

An example of stacked triiodide ions (C_s symmetry) in infinite chains with weak $I_3^-\cdots I_3$ interactions (4.0–4.2 Å) is found in the structure of (dbcr)I$_3$ (**3.2**).[43] In the structure of (Et$_3$S)I$_3$, the triiodide ions (C_s symmetry) are packed in a characteristic T-shape pattern [d(I···I) = 4.0–4.1 Å] (**3.3**).[42] In addition, linear terminal I···I interactions are present [d(I···I) = 3.9 Å].



3.2



3.3

Figure 12 shows the coordination environment for the triiodide building block in polyiodides. The typical V/L-shaped (see section III.2.2) and T-configurations are clearly observed.[81] However, also a large amount of parallel arrangements can be discerned, especially at 180 degrees. These correspond mainly to the $I_3^-\cdots I_3^-$ interactions mentioned above. Figure 12 also shows that the preferred coordination orientations are 90 and 180° with respect to the terminal iodine atom and 90° with respect to the central iodine atom.

Polyiodide structures are rarely characterized after their ionic packing. However, Knop et al. report that by considering the volume of the formula unit (V$_1$) it is possible to roughly determine the packing type in triiodide structures with compact cations.[23,84] Triiodides with a small V$_1$ correspond to the NaCl type, those with intermediate V$_1$ values to the anti-NiAs type and those with large V$_1$ values to the CsCl type. They considered V$_1$ values of approximately 400 Å as large.

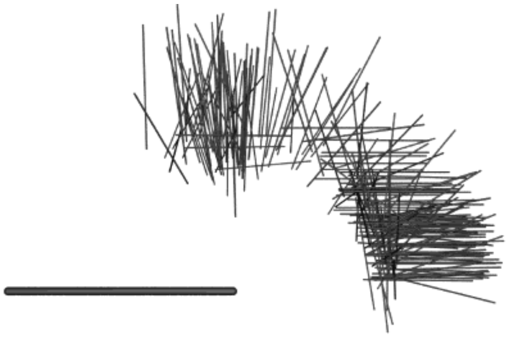


Figure 12. The symmetry reduced distribution of iodine around the terminal iodine of the triiodide.

Bengtsson et al. report LXS results for (Me$_3$S)I$_3$ and (Et$_3$S)I$_3$ melts, which show that these melts consist of discrete, centrosymmetric I_3^- anions and pyramidal R$_3$S$^+$ cations.[46,33d] The intramolecular I–I distances are reported to be 2.908 and 2.915 Å, respectively. The cations are asymmetrically coordinated to the triiodide ions at distances corresponding to the sum of vdW radii of S and I. In the corresponding solid compounds, the triiodides are asymmetric and the bond lengths are 2.915 and 2.946 Å for (Me$_3$S)I$_3$(s) and 2.89–2.95 Å for (Et$_3$S)I$_3$(s). The LXS results for the polyiodide with a formal composition of (Et$_3$S)I$_2$ at 100 °C are essentially analogous to those for (Et$_3$S)I$_3$. The structural features for the triiodide ions are, however, weaker because of the lower formal concentration.[42]

III.2.2 Pentaiodides I_5^-

The structurally characterized pentaiodides have been divided into either V/L-shaped or linear geometries. The V-shaped pentaiodide ions consist of two iodine molecules coordinated to an apical iodide [(I$^-$)·2I$_2$], while the L-shaped one is an iodine molecule coordinated to a triiodide ion [(I_3^-)·I$_2$]. The V- and L-shaped forms are very similar and intermediate structures also exist that may be classified as either form. The linear pentaiodide ion also has an [(I$^-$)·2I$_2$] configuration. Discrete, V/L-shaped pentaiodides have been reported in several cases (Table 2). However, even if there are no strong I···I contacts [d(I···I) < 4 Å] to the discrete I_5^- ions, there are discrepancies between their geometries. This is a result of more or less strong hydrogen bonding, D···I contacts (D = N, S, Se, M, etc.), and packing effects.

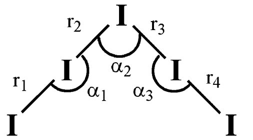


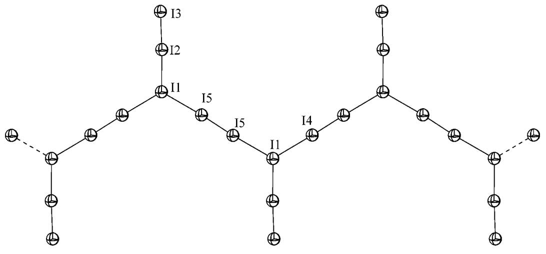
Figure 13. The definition of the I_5^- ion geometry.

The pentaiodides are usually linked to each other by more or less strong intermolecular interactions forming a variety of structures from chains to 3D networks. Bittner reports a comprehensive description of most common types of contact geometries (Figure 14).[80,93] As will be seen later, the V/L-shaped pentaiodides are often encountered as a constituent in the larger polyiodides.

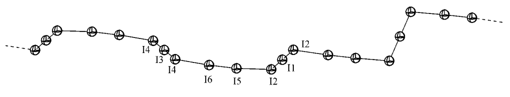
These contact geometries can of course be more or less distorted/twisted and can exist in a cis/trans modification (e.g., Figure 14e,f). The most common extended structural type formed by intermolecular interactions is that of chains of varying composition. We will focus mainly on I_5^- structures having contact geometries different from those described in Figure 14 (for examples of contact geometries of type 14a–i, see refs 81 and 95).

The V-shaped pentaiodides in $[Rb(C_{16}H_{24}O_6)]I_5\cdot H_2O$ are comprised of two structurally similar chains where one of the pentaiodide legs forms the backbone of the chain.[93] The leg stands out without forming a coplanar cis or trans configuration such as that described above. The longest I–I distance in the chain is 3.621 Å, and the unit could also be described as a chain of I_8^{2-} ions (see section III.3.3).

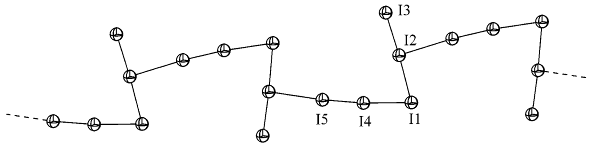
A dimeric pentaiodide configuration with the apical iodide linked with the terminal iodides (3.71 Å) is attributed to the structure of $(UrPr)I_5$.[94] The pentaiodide dimers are connected to form a net (3.80 Å). The I_{10}^{2-} ion (vide infra) is also formed by I_5^- dimers; however, the interaction between the pentaiodides is much stronger than in the case of $(UrPr)I_5$.



3.4



3.5



3.6

The structure of $(BipyH)I_5$ has an unusual trigonal planar configuration, which is formed by an I_3^- connected to two I_2 (**3.4**).[95] The pentaiodide in $(diMeFc)I_5$ (**3.5**) forms a chain that can be described as $^{1}_{\infty}[(I_3^-)_{2/2}\cdot I_2]$, with alternating planar and helical regions. A chain structure which can be regarded as originating from a distorted square network $^{2}_{\infty}[2I_2\cdot I^-]$ is found in the compound $[Ni(NH_3)_6](I_5)_2$ (**3.6**).[88] The terminal iodine atom coordinates to the central atom

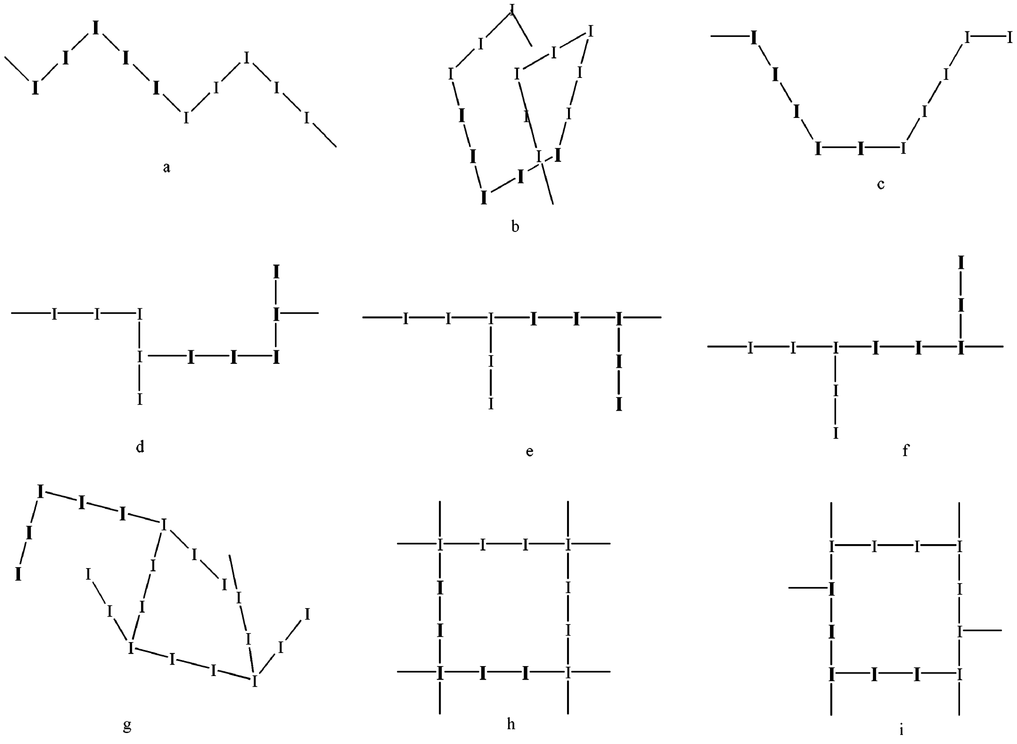


Figure 14. Common contact geometries for pentaiodides (a) zigzag-shaped chain, (b) alternating twinned and zigzag-shaped chain, (c) meander-shaped chain, (d) displaced chain, (e) cis-shaped chain, (f) trans-shaped chain, (g) twinned chain, (h) and (i) square nets.

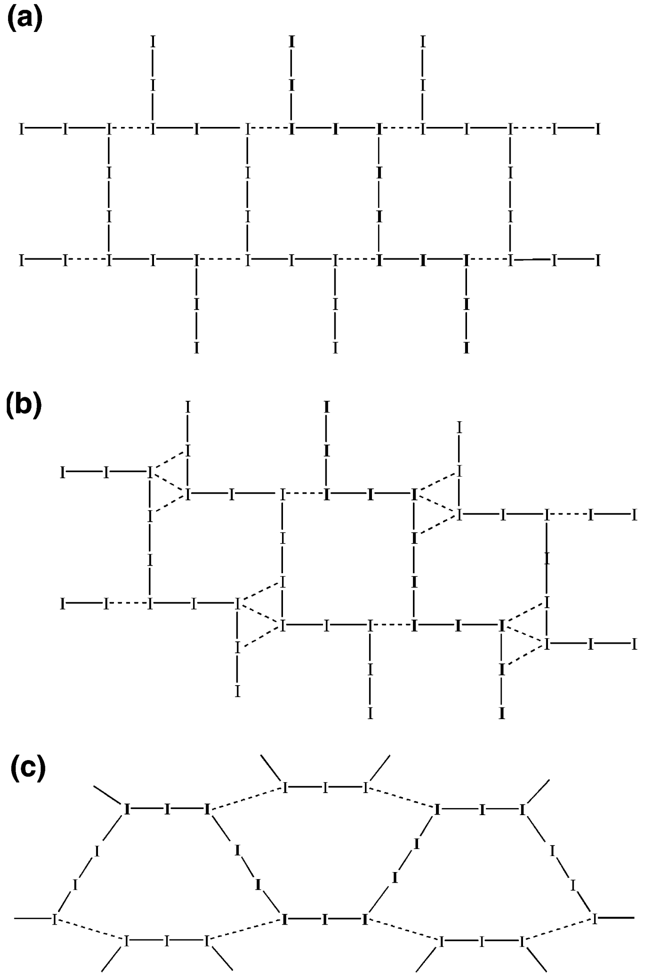


Figure 15. The contact geometries of (a) $(C_6H_4N_2Se{\cdot}C_6H_5N_2Se)I_5$, (b) $Fc_2SeI_5{\cdot}1/2CH_2Cl_2$, (c) $(C_7H_{13}NH)I_5$.

of the preceding I_5^- ion, leading to a dihedral angle of 139.9° with respect to each other in a trans configuration. The anionic structure of $(EDT\text{-}TTF)_2(I_3)_2(I_2)_2$ has a similar configuration to that found in $[Ni(NH_3)_6](I_5)_2$.[96]

The square-planar network $^2_\infty[2I_2{\cdot}I^-]$ exists in several modifications. Figure 15 visualizes the contact geometry in three different square-planar networks. The structure of $(C_6H_4N_2Se{\cdot}C_6H_5N_2Se)I_5$ (Figure 15a) can be regarded as formed by interacting zigzag chains. However, an alternative description is based on I_3^- chains that are interconnected by I_2.[97] A similar geometry is seen in the structure of $(Fc_2Se)I_5{\cdot}1/2CH_2Cl_2$ (Figure 15b). However, because of the displacement of the square nets there are several links between the zigzag chains.[98] The planar network in $(C_7H_{13}NH)I_5$ (Figure 14c)[99] has a distorted square geometry, which is a result of the V-shaped pentaiodide. If the structure is considered as formed by I_3^- chains interconnected by I_2, then the I_3^- ions in this case are connected by both terminal atoms to I_2, and not as in the previous two structures by only one. However, the geometry generates an I_5^- stoichiometry. The square-planar network $^2_\infty[2I_2{\cdot}I^-]$ of $(C_6H_4N_2Se{\cdot}C_6H_5N_2Se)I_5$ (Figure 16) displays a slightly puckered layer, which, as will be seen later, is a common feature of the larger polyiodides.

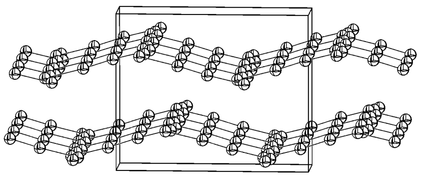
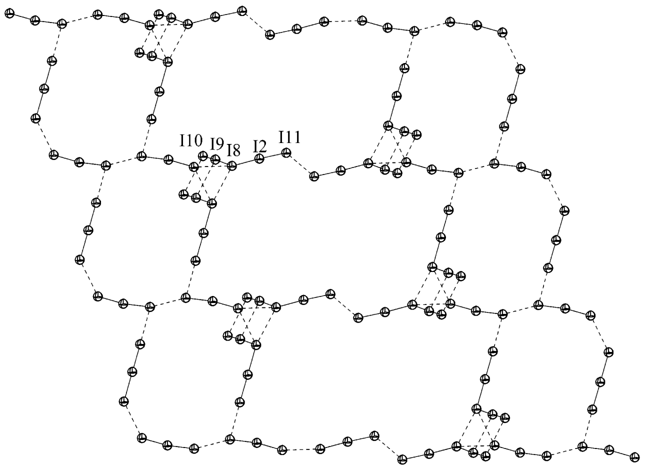


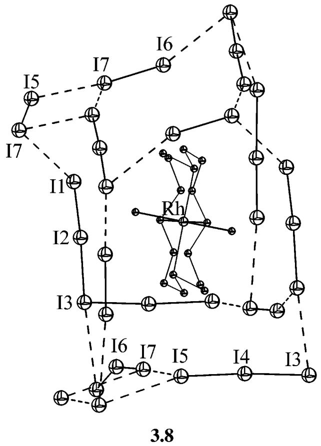
Figure 16. The square planar network $^2_\infty[2I_2{\cdot}I^-]$ of $(C_6H_4N_2Se{\cdot}C_6H_5N_2Se)I_5$.

An unusual, two-dimensional, planar layer has been characterized in the structure of $[Pd_2Cl_2([18]\text{-}ane\text{-}N_2S_4)]_{1.5}I_5(I_3)_2$ (**3.7**).[10b] The network has a topology of fused ribbons of 14- and 24-membered rings, formed by $I_3^-{\cdots}I_3^-$ interactions (3.76−4.22 Å). Two L-shaped pentaiodides, orthogonal to the parallel layers, connect two of these by passing through the centers of the 24-membered rings of a third layer located between them. The connection between two alternating layers is mediated through $I_5^-{\cdots}I_3^-$ interactions (3.57 Å) forming a distorted Z-shaped I_8^{2-} adduct.



3.7

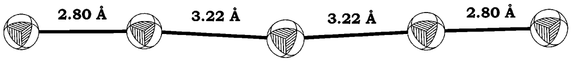
Cage structures, where the cations are situated within the cage cavities formed by the polyiodide interactions, are found in the compounds $[BiI_2(C_6H_{18}N_3OP)_4]I_5$ and $[RhCl_2(C_{12}H_{24}S_4)](I_5){\cdot}I_2$.[100,101] In the former, the cage is formed by a disordered I_5^-, while in the latter it is formed via links between I_2 and I_5^- (**3.8**).



3.8

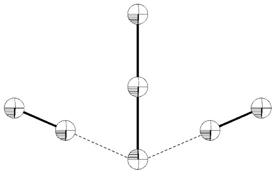
The crystal structures of three compounds containing linear pentaiodide ions have been characterized:

[trimesic acid·$H_2O]_{10}(H^+)(I_5^-)$, [1,1′-(propane-1,3-diyl)-ferrocenium$]_3(I_3)_2(I_5)$ (**3.9**), and (DMT-TTF)$(I_3)(I_5)$.[102−104] They can all be described in terms of two iodine molecules coordinated to a central iodide ion. In the two latter structures, the linear pentaiodide ions are incorporated into infinite chains with I_3^- [$I_3^-\cdots I_5^-\cdots I_3^-$, $d(I\cdots I) > 3.60$ Å]. Linear pentaiodide ions have also been used as models in disordered and/or incommensurate structures.[93,105] Many model compounds (e.g., cyclodextrin) of the blue polyiodide complex with amylose from starch have also been reported to contain linear chains of I_5^- ions, although the small difference in spectral response between the pentaiodide and higher polyiodides suggests the presence of more complicated iodide−iodine fragments.[106]



3.9

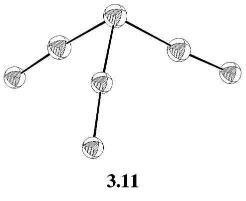
The only X-ray scattering investigation of liquid pentaiodides is the one by Bengtsson et al.[33e] The melts of $(Et_3S)I_x$, $x \geq 4$, can be described as consisting of triiodide ions solvated by the neutral solvent molecules (I_2). This is analogous to the features of solid polyiodides. The coordination geometry projected into two dimensions is shown in **3.10**, where the number of I_2 molecules coordinated to the central I_3^- increases with increasing I_2 concentration. The centrosymmetric triiodide ion and iodine molecules have intramolecular bond lengths of 3.00 and 2.72 Å, respectively.



3.10

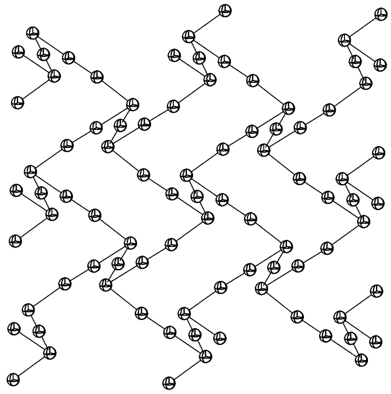
III.2.3 Heptaiodides I_7^-

Heptaiodides have been characterized as $[(I_3^-)\cdot 2I_2]$, $[(I^-)\cdot 3I_2]$, or $[(I_5^-)\cdot I_2]$ with a more or less distorted pyramidal or Z-shape geometry. The crystal structures of $(PPh_4)I_7$ (**3.11**) and [Cu(OETPP)]I_7 have been reported to consist of discrete heptaiodides of the $[(I_3^-)\cdot 2I_2]$ type.[107,108] However, I···I contacts in the 3.6−3.7 Å range exist in both structures (Table 3 and section III.6.2).[20] More commonly, the heptaiodide ions are linked into chains or networks. Although the compounds $(Et_4N)I_7$, (UrPr)I_7, $(EtPh_3P)I_7$, and (TCNQ)I_7 all have an $[(I_3^-)\cdot 2I_2]$ configuration, they display very different structural features.[94,109]



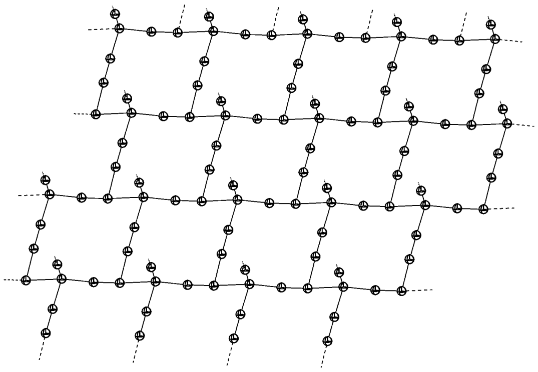
3.11

In $(Et_4N)I_7$, (UrPr)I_7, and $(EtPh_3P)I_7$, the I_7^- ions are linked into two-dimensional networks. $(Et_4N)I_7$ has a zigzag chain (**3.12**) linked into a network, where two iodine molecules interact with each terminal atom of the I_3^- ion, $^{2}_{\infty}[I_3^-(I_2)_{4/2}]$. A similar network is found in $[(Py)_2I]I_7$.[110] The triiodide in $(Et_4N)I_7$ is centrosymmetric (2.92 Å) and is connected with relatively short distances (3.479 and 3.494 Å) to the iodine molecules (2.734 Å).

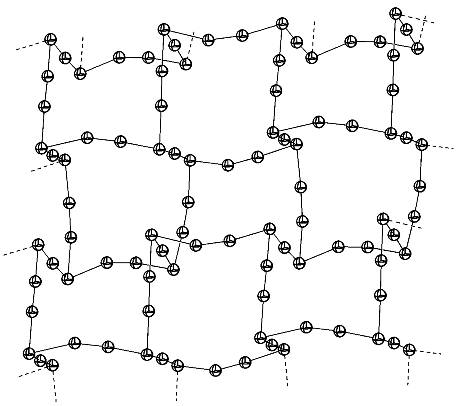


3.12

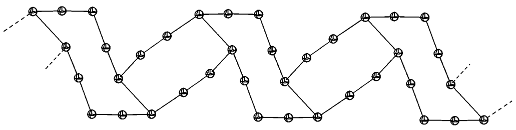
The structures of both (UrPr)I_7 (**3.13**) and $(EtPh_3P)I_7$ (**3.14**) have a layered network. The latter has a puckered layer ($I_7^-\cdots I_7^-$, 3.46 and 3.70 Å), while the former has a “flat” layer ($I_7^-\cdots I_7^-$, 3.62 and 3.70 Å). In (TCNQ)I_7 (**3.15**), an isolated zigzag chain is formed from the interaction between the distorted Z-shaped I_7^- ions. The heptaiodide ions are connected in a cis fashion into parallel chains (3.63 Å), which in turn are interconnected forming a ribbon-like geometry (3.92 Å). The I_7^- ion has one disordered iodide ion (not shown in **3.15**).



3.13

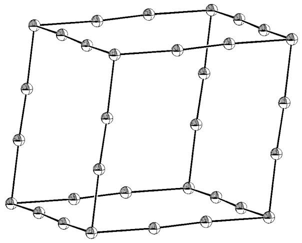


3.14

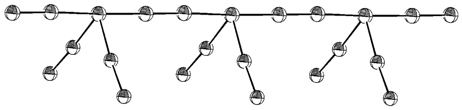


3.15

The crystal structures of [(*N*-methyl-benzothiazole-2(3h)-thione)$_2$I]I_7, [{Ag([18]aneS$_6$)}I_7]$_n$, and [H_3O·18-crown-6]I_7 contain heptaiodide ions with the [(I-)·3I_2] composition.[10a,109d,111] In [(*N*-methyl-benzothiazole-2(3h)-thione)$_2$I]I_7, the I_7^- ions are linked into one-dimensional chains $^1{}_\infty[I_7^-]$. The I_7^- ions in [{Ag([18]aneS$_6$)}I_7]$_n$ form a network of distorted cubes, where the iodide ions occupy the corners and the iodine molecules the edges (**3.16**). Thus, each iodide ion is interacting with six iodine molecules [$d(I-I) = 2.75$ Å and $d(I\cdots I) = 3.36$ Å]. A unique polymeric, $(I_7^-)_n$, sawhorse configuration is found in [H_3O·18-crown-6]I_7 (**3.17**). Since the shortest interaction between the polymeric chains is reported to be 3.81 Å, the ion was regarded as discrete.

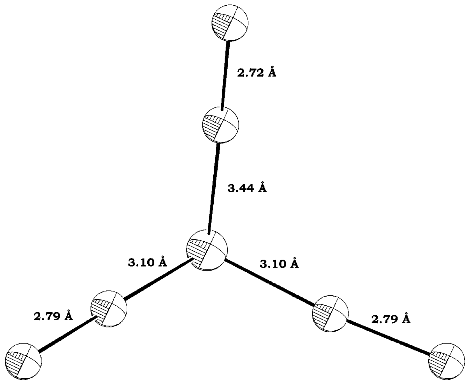


3.16

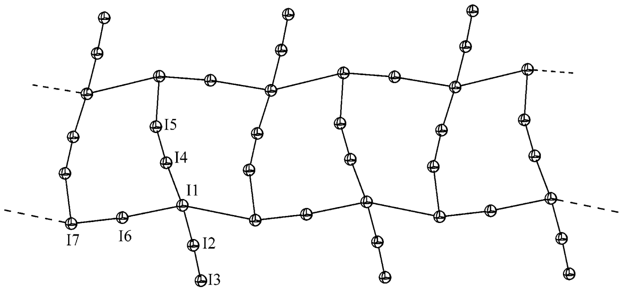


3.17

Tebbe et al. describe the structure of the heptaiodide in (HbiPy)I_7 as a V-shaped pentaiodide coordinated by an I_2 molecule [(I_5^-)·I_2] (**3.18**).[95] These are linked to each other forming infinite chains. The heptaiodides in [HPy]$_2$(I_3)(I_7) and (Fc)I_7 are also best described in terms of an [(I_5^-)·I_2)] configuration.[112,113] In (Fc)I_7, the I_7^- ions are formed by two parallel chains of pentaiodide units connected by iodine molecules to form a rope-like ribbon. Interconnected, parallel sheets of I_7^- are reported for [HPy]$_2$(I_3)(I_7). The I_7^- ion in (TCNQ)I_7 can also be regarded as having an [(I_5^-)·I_2] configuration, but with a quite distorted L-shaped pentaiodide ($I_3^-\cdots I_2$, 3.16 Å). An isolated meandering-like chain of I_7^- is reported in the structure of (i-PrMe$_2$PhN)I_7 (**3.19**).[114] It contains a very asymmetric triiodide ion (2.76 and 3.18 Å) that coordinates to the iodine molecules to form a $^1{}_\infty[(I_2)_2\cdot(I_3^-)]$ configuration. The chains are interconnected to a ribbon-like topology by a quite long contact (3.98 Å).



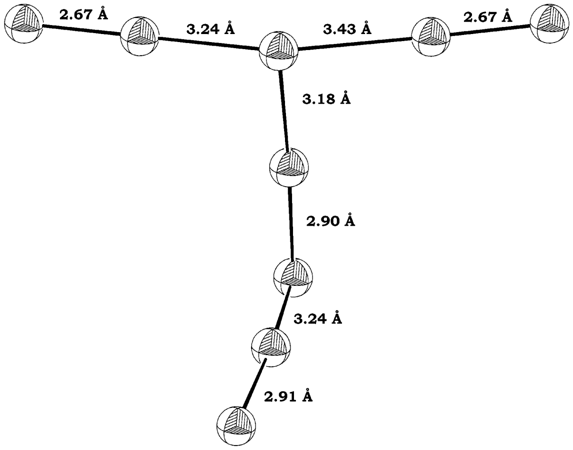
3.18



3.19

III.2.4 Nonaiodides I_9^-

To date, the currently known I_9^- species have been described as having [(I_3^-)·3I_2], [(I_5^-)·2I_2], or [(I_7^-)·I_2] configurations with varying degrees of 2D and 3D architectures. The I_9^- ion in [(CH$_3$)$_4$N]I_9, already characterized by Rundel et al. in 1955, consists of a V-shaped I_5^-, which is coordinated by two iodine atoms (**3.20**). Thus, the composition can be described as [(I_5^-)·2I_2].[115] The pentaiodide ions form a 9.1 Å wide layer. The cations as well as the layer-bridging iodine molecules are positioned between the layers. The nonaiodide in [(Me$_3$Ph)N]I_9 consists of trigonal pyramidal heptaiodides that are chained together by I_2 molecules via the terminal iodine atoms of the heptaiodide.[116]



3.20

A nonaiodide of [(I_3^-)·3I_2] composition is described in the compound [K([15]aneO$_5$)$_2$]I_9.[10b] The three iodine molecules coordinate to a slightly asymmetric I_3^- ion through contacts at 3.40−3.50 Å. The I_9^- ions are linked to each other by weak secondary interactions and vdW contacts, forming puckered cages.

The anionic part of (i-PrMe$_2$PhN)I_9 (**3.21**) consists of an I_9^- ion formed by a V-shaped pentaiodide, containing a very distorted I_3^- ion, coordinated to two

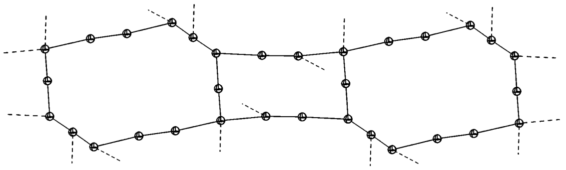
Table 3. Geometric Parameters of the Heptaiodide Ions in [Cu(OETPP)]I_7 and $(PPh_4)I_7$ (Figure 17)

r_1	r_2	r_3	r_4	r_5	r_6	α_1	α_2	α_3	α_4	α_5	α_6	compound
2.717	3.207	3.154	2.764	3.224	2.749	173.0	93.7	177.4	109.7	106.9	173.7	Cu(OETPP)I_7
2.738	3.295	3.281	2.730	3.051	2.814	174.4	85.6	176.8	89.1	97.3	175.3	$(PPh_4)I_7$

Table 4. Isolated I_4^{2-} Ions [d(I···I) > 4 Å] (Figure 18)

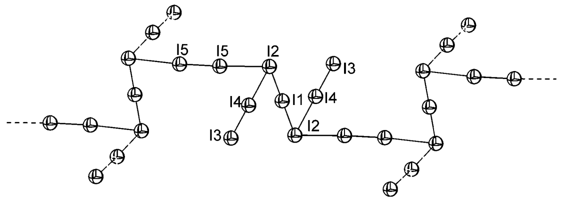
r_1 (Å)	r_2 (Å)	r_3 (Å)	α_1	α_2	compound
3.40	2.82	3.40	178.5	178.8	$(C_5H_7N_2Se\text{-})_2I_3\cdot 1/2I_4$[120]
3.34	2.85	3.34	180	180	$[Ni\{(CH_3)_2SO\}_6]I_4$[121]
3.40	2.78	3.40	180	180	$(\mathrm{phenacetin})_4\cdot H_2I_4\cdot 2H_2O$[122]
3.34	2.85	3.34	180	180	$[Co(DMSO)_6]I_4$[123]
3.20	2.85	3.52	180	180	$[V(MeCN)_6][I_4]$[124]
3.40	2.81	3.40	175	175	$[UO_2(OH)\cdot 3CO(NH_2)_2]_2I_4$[125]
3.22	2.79	3.22	180	180	$Tl_6Au_2I_{10}$[126]
3.2	3.1	3.2	180	180	Tl_6PbI_{10}[127]

I_2 molecules. Alternatively, the structure can also be described as a pyramidal I_7^- ion linked by an iodine molecule.[114] The I_9^- ion is interlinked so that chains with 10- and 14-membered rings are formed $\{^1_\infty[(I_2)\cdot(I_5^-\cdot I_2)]_2\}$. These chains are linked (dotted lines) quite weakly with each other (3.76 and 3.92 Å) to form a complicated network.



3.21

A unique, branched, crank-shaped $^1_\infty(I_9^-)$ chain is found in the structure of $(Rb)I_9$.[117] It can be regarded as being formed from I_2 bridging (3.28 and 3.46 Å) between I_3^- or Z-shaped I_7^- ions (**3.22**). The shortest interchain contact is 4.08 Å.



3.22

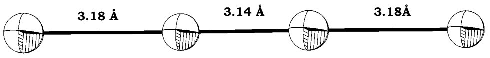
Polyiodides higher than the nonaiodide in the I_{2n+1}^- series have been hypothesized, but so far none have been structurally characterized. The iodine content (9/|−1|) of the nonaiodides is one of the highest of all known polyiodides.

III.3 Polyiodides within the Series I_{2n+2}^{2-}

III.3.1 Tetraiodides I_4^{2-}

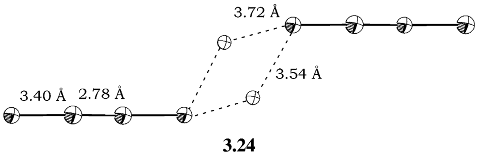
Tetraiodide has been characterized in many different structural environments and is the most frequently encountered polyiodide in the I_{2n+2}^{2-} series. The ion is best described in terms of the coordination of two iodide ions to a central iodine molecule $[(2I^-)\cdot I_2]$. The configuration $[(I^-)\cdot I_3^-]$ has only been found in structures where the ions are isolated and thus only give rise to a formal composition of I_4^{2-}. Discrete (no intermolecular I···I contacts < 4 Å), linear I_4^{2-}, both symmetric and asymmetric forms, have been found in several structures (Table 4). The I_7^{3-} and I_{10}^{4-} ions contain I_4^{2-} ions with the configurations $[(I_3^-)\cdot(I_4^{2-})]$ and $[(2I_3^-)\cdot(I_4^{2-})]$, respectively. In I_7^{3-}, the building blocks are isolated, while they are weakly linked in I_{10}^{4-}. Many formal I_4^{2-} ions have been characterized where the I_3^- is isolated from the I^- ion, thus having the configuration $[(I_3^-)(I^-)]$.[118]

It is notable that the discrete tetraiodide ion reported by Rabenau et al., in Tl_6PbI_{10}, has very similar I−I distances (Table 4, **3.23**) and cannot be directly traced back to any of the fundamental polyiodide building blocks (I^-, I_2, or I_3^-). This is one of very few exceptions from this principle.[119]



3.23

Theoretically, the linear I_4^{2-} ion has been found to be unstable;[128] hence, it is not surprising that many of the characterized tetraiodide ions are coordinated to or stabilized by the surrounding environment. In the amine complexes $[M(NH_3)_4]I_4$ (M = Cu, Cd), investigated by Tebbe et al., the formal tetraiodide ions are coordinated by the metal ion in $M(NH_3)_4^{2+}$.[129] As a consequence, infinite zigzag chains are formed (see section III.6). Similar chains are formed with other metal complexes (e.g., Ir, Pt, Pd, Fe, As, and Sb complexes) and will be discussed in more depth in connection with binary metal iodide−iodine complexes. However, their characterization in terms of tetraiodides is questionable, since the iodide ions should more appropriately be regarded as belonging to the metal ion complex. The tetraiodide ions in the structure $[(\mathrm{phenacetin})_4H_2]I_4\cdot 2H_2O$ are linked into chains through hydrogen bonding (**3.24**).[122]



3.24

III.3.2 Hexaiodides I_6^{2-}

Until now, no isolated I_6^{2-} polyiodide has been structurally characterized. However, the terminal I···I interaction occurring in many triiodide structures can be seen as forming I_6^{2-} units (see section III.2.1). Also, although several structures have the formal composition I_6^{2-} they in fact arise from isolated I_3^- building blocks. Very recently, an I_6^{2-} ion was reported in the structures $[M(Phen)_3]I_7$ (M = Mn, Fe).[23d] These contain a discrete I_3^- ion and, as a consequence of a 50:50 disorder, either I_6^{2-} plus I_2 or zigzag-shaped I_8^{2-} units. The I_6^{2-} ion is comprised of two almost parallel I_3^- ions end-overlapped with

Table 5. Geometrical Parameters of Some Isolated S/Z-Shaped I_8^{2-} Ions (Figure 20)

r_1/r_7	r_2/r_6	r_3/r_5	r_4	α_1/α_6	α_2/α_5	α_3/α_4	compound
2.939/2.872	2.966/3.037	3.637/3.527	2.797	178.5/173.8	107.2/91.0	169.2/174.5	$[Pd(TAAB)]I_8$[132]
2.942/2.878	2.970/3.048	3.65.8/3.532	2.805	178.5/173.8	107.5/90.4	169.2/174.7	$[Pt(TAAB)]I_8$[132]
2.852	2.936	3.398	2.723	175.9	95.7	175.7	$[Cu(phen)_2I]_2I_8$[133]
2.835	3.010	3.394	2.771	174.0	98.9	178.2	$(MePh_3P)_2I_8$[134]
2.830	3.044	3.392	2.773	173.9	131.4	168.2	$(UrMe)_2I_8$[135]
2.864	2.996	3.442	2.749	178.0	97.9	178.3	$[THOE\text{-}DOB]_2(I_3)_2(I_2)\cdot CH_2Cl_2.0.4C_6H_{14}$[136]
2.844	2.983	3.435	2.748	179.3	123.0	172.8	$[(Me_2N)_4naphthalen)]I_8$[137]

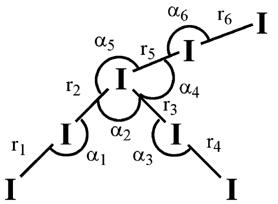


Figure 17. The definition of the I_7^- ion geometry.

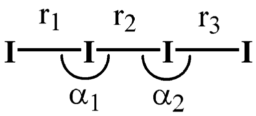


Figure 18. The definition of the I_4^{2-} ion geometry.

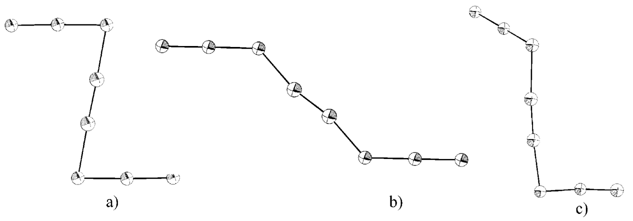


Figure 19. (a) The outstretched, Z-shaped I_8^{2-} ion in $[UrMe]_2I_8$; (b) the Z-shaped I_8^{2-} ion of Cs_2I_8; (c) the deformed I_8^{2-} ion in $[Pd(TAAB)]I_8$.

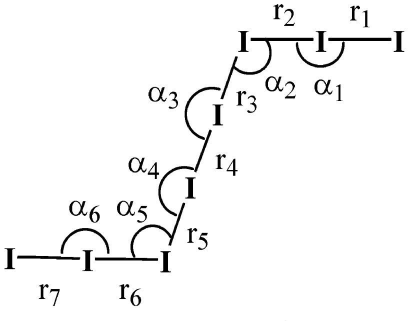


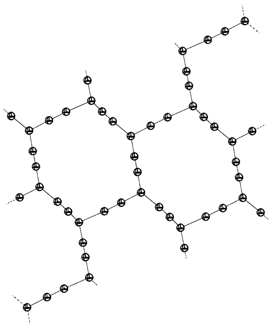
Figure 20. The definition of the I_8^{2-} ion geometry.

the closest I···I intermolecular distance greater than 3.76 Å.

III.3.3 Octaiodides I_8^{2-}

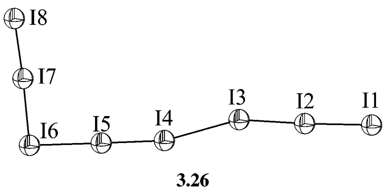
The I_8^{2-} ion usually consists of two I_3^- ions that are connected through the end atoms by an I_2 molecule $[(I_3^-)_2\cdot(I_2)]$. However, $[(I_5^-)\cdot(I_3^-)]$ has also been reported in the literature. Already in 1954, the structure of the first I_8^{2-} ion in Cs_2I_8 was determined by Havinga et al.[130] This ion has a Z-shaped geometry with an $[(I_3^-)_2\cdot(I_2)]$ configuration (Figure 19b). The Z-geometry, out-stretched (S-shaped) or slightly deformed (Figure 20), is the predominating geometry for all structurally characterized octaiodide ions. For example, the Z-shaped I_8^{2-} ion in $[Pd(TAAB)]I_8$ and $[UrMe_3]_2I_8$ is isolated.[131,132] This is a quite common feature for octaiodide ions. The octaiodide in Cs_2I_8 is planar, centrosymmetric with the I_3^- ions in a trans position. The two examples given above are, even though they are isolated, deformed, and twisted from the ideal geometry found in Cs_2I_8.

The octaiodides $\{[(I_3^-)_2\cdot(I_2)]$ configuration$\}$ in the compounds $[Pd(NH_3)_4]I_8$ and $[Mg(H_2O)_6]I_8$ form chains through I···I interactions (3.64 and 3.84 Å, respectively) of the terminal atoms of the triiodide ions.[138] The I_8^{2-} in $[Pd(NH_3)_4]I_8$ is, however, also linked to the Pd atoms (see section III.6.2). In $[Mg(H_2O)_6]I_8$ square nets are formed, while in $[Pd(NH_3)_4]I_8$ broken nets are formed since only one of the triiodide ions is involved in the chain formation.[129a] A similar chain structure is also found in $[C_{16}H_{25}N_2]I_4$, but here the connection is made by only one terminal iodine atom of each triiodide ion.[139] The Z-shaped octaiodides in $[Co(Ur)_6]I_8$ form a ring architecture (**3.25**) through the interaction of both the terminal iodide atoms of the triiodide ions.[140] The contact distances between the ions are 3.45 and 3.93 Å.

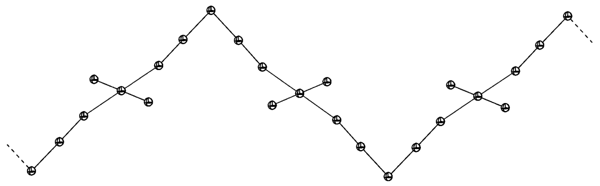


3.25

The unusual $[(I_5^-)\cdot(I_3^-)]$ configuration has been reported in $(UrEt)_2I_8$ (**3.26**) and $[K(benzo\text{-}18\text{-}crown\text{-}6)]_2(I_8)\cdot 1/2EtOH$ (**3.27**).[141] In the latter, the V-shaped pentaiodide coordinates weakly (3.675 Å) to the central iodide atom of the triiodide ion to form an infinite chain, while in the former the pentaiodide coordinates to the terminal iodide (3.627 Å) of the triiodide ion to form an isolated L-shaped octaiodide ion.



3.26



3.27

U-shaped octaiodide ions have been characterized also, but since they form dimers they will be discussed in the hexadecaiodides, I_{16}^{4-}, section. An L-shaped I_8^{2-} ion, with the configuration $[(I_3^-)_2\cdot(I_2)]$, was recently reported in the structure of $(C_{15}H_{12}NS)_2I_8$ (Figure 21a).[142] However, there are several quite short I···I distances (3.50−3.70 Å), which connect the I_8^{2-} [(I1)−(I8)] to the I_3^- and I_5^- ions, also present in the structure forming an extended network (Figure 21b).

An isolated linear $_\infty^1[I_8^{2-}]$ chain has been reported in the disordered structure of $[Mn(bpy)_3](I_3)_{1.5}(I_8)_{0.25}$.[143] The average I−I distance in the chain is 2.92 Å, and only weak interactions between the chain and the triiodide ions are reported. As for many of the other polyiodide ions, the octaiodide ions are connected in several structures by vdW contacts forming chains and layers.

III.3.4 Decaiodides I_{10}^{2-}

The isolated I_{10}^{2-} ion in the structure of $[Cd(12\text{-}crown\text{-}4)_2]I_{10}$ (**3.28**) can be described as a dimer of V-shaped I_5^- ions $[(I^-)\cdot 2I_2]_2$.[144] The intramolecular distances of the iodine molecules are of normal magnitude (2.91 and 2.75 Å), while the I_2−I^- distance is clearly longer than in the isolated pentaiodides (3.44 Å).

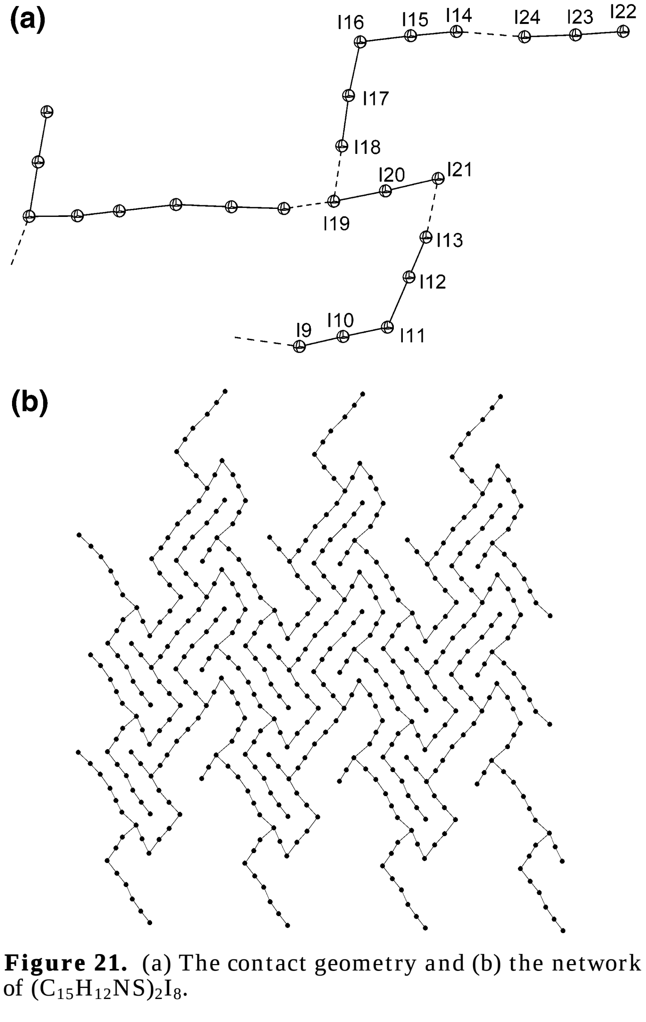
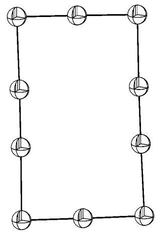


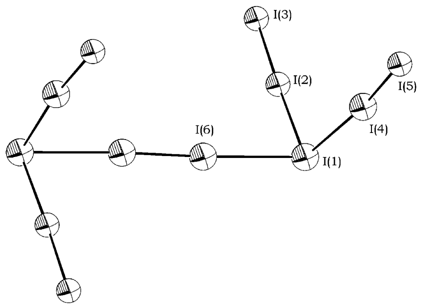
Figure 21. (a) The contact geometry and (b) the network of $(C_{15}H_{12}NS)_2I_8$.



3.28

III.3.5 Dodecaiodides I_{12}^{2-}

The centrosymmetric dodecaiodide ion of $(Me_2Ph_2N)_2I_{12}$ (**3.29**) consists of two antiparallel pentaiodides [I(1)−I(5)] that are linked by an iodine molecule $[(I_5^-)_2\cdot I_2]$ to form a twisted sawhorse geometry.[145] The terminal and apical iodine atoms of the pentaiodides are linked to adjacent pentaiodide ions forming double-chains. Similar $[(I_5^-)_2\cdot I_2]$ configurations are found in $[K(C_{20}H_{24}O_6)]_2I_{12}$, $[K(Crypt\text{-}2.2.2)_2]I_{12}$, and $[Cu(dafone)_3]I_{12}$.[146−148] In the latter, all the iodide atoms are nearly confined to a plane. This is, however, not the case for the other known I_{12}^- ions. In $[K(C_{20}H_{24}O_6)]_2I_{12}$, the terminal iodine atoms are linked to each other forming a zigzag chain, which in turn makes it possible to regard the ion as a long fragment of a triiodide-iodine chain $_\infty^1[(I_3^-)\cdot I_2]$.



3.29

In $\{Ag_2([15]aneS_5)_2\}I_{12}$, a different dodecaiodide configuration is reported by Blake et al.[92] In this case, the I_{12}^{2-} ion is described in terms of an I_4^{2-} unit interacting with two iodine molecules at each end. Hence, the I_{12}^{2-} ion produces a twisted H geometry. The terminal iodide ions of the tetraiodides are attached to the silver atom in the cation $\{Ag_2([15]aneS_5)\}^+$. Finally, a three-dimensional network is formed via S···I contacts from the cation to the terminal iodine atoms. The most recent I_{12}^{2-} ions reported in the literature are those found in structures of polymorphs of $[Fe(phen)_3]I_{12}$(1A and 1B).[23c] In $[Fe(phen)_3]I_{12}$(1A), the dodecaiodide has a network structure, which consists of I_{16} rings in a chair conformation connected by I_2 molecules. The I_{16} rings are comprised of I^- (at the head and foot of the chair), as well as I_2 and I_3^- units. The I−I distances within the network is in the range 2.75−3.55 Å, while the closest I···I interaction is 3.78 Å. The dodecaiodide ion in $[Fe(phen)_3]I_{12}$(1B) can be considered a discrete

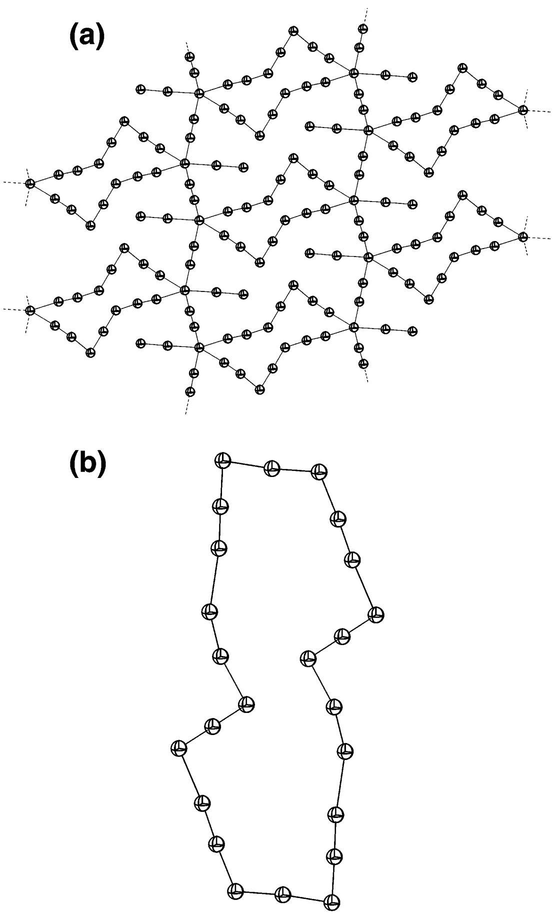


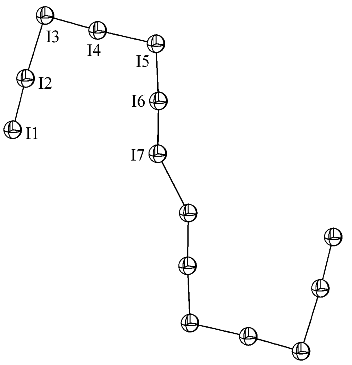
Figure 22. Polymorphs of [Fe(phen)$_3$]I$_{12}$, (a) [Fe(phen)$_3$]-I$_{12}$ (1A), (b) [Fe(phen)$_3$]I$_{12}$ (1B).

I$_{12}$$^{2-}$ ion, which is almost planar with the configuration [I$_5$$^-$···I$_2$···I$_5$$^-$]. The I−I distances range from 2.73 to 3.57 Å. However, there is a contact at 3.71 Å, which, if included, results in a I$_{24}$$^{4-}$ ring. (The shortest distance between the rings is 3.9 Å.) The [Fe(phen)$_3$]I$_{12}$ system is very versatile having a third polymorphic form [Fe(phen)$_3$]I$_{12}$(1C), which has a different polyiodide ion configuration to the 1A and 1B polymorphs (see Figure 22).[23c]

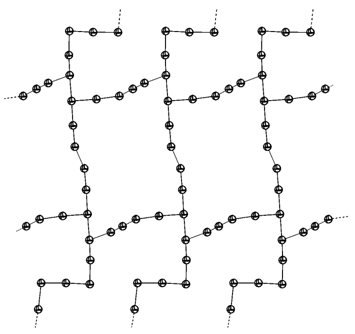
III.3.6 Tetradecaiodides I$_{14}$$^{2-}$

The polymorph [Fe(phen)$_3$]I$_{12}$(1C) contains both a V-shaped I$_5$$^-$ and an (I$_7$$^-$)$_2$ ion.[23c] The (I$_7$$^-$)$_2$ dimeric ion is constructed by two U-shaped I$_7$$^-$ ions (**3.30**), which, in turn, can be regarded as having a [(I$_5$$^-$)·I$_2$] configuration. The I−I distance in the (I$_7$$^-$)$_2$ dimeric ion range from 2.72 to 3.55 Å. The shortest I···I distance between the (I$_7$$^-$)$_2$ and I$_5$$^-$ ions is 3.82 Å. It is notable that no discrete, U-shaped I$_7$$^-$ ion has been reported.

The tetradecaiodide ion found in [Fe(phen)$_3$]I$_{14}$ forms a network structure with formal I$_{22}$ rings (**3.31**).[149] The network I−I contacts are in the range 2.7−3.6 Å, with the next largest I···I distance at 3.93 Å. The structure has been described as being comprised of zigzag I$_7$$^-$ ions and an I$_{14}$$^{2-}$ unit formed by the centrosymmetric dimerization of a V-shaped I$_7$$^-$ ion. However, since I···I distances representing the interaction between the zigzag I$_7$$^-$ ion and the I$_{14}$$^{2-}$ ions are 3.52 and 3.60 Å, respectively, there is some ambiguity as to how best describe the network. Possibly, the structure is better described as a more complicated network formed from the basic building blocks I$^-$, I$_2$, and I$_3$$^-$.



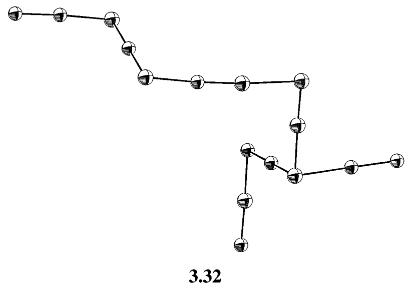
3.30



3.31

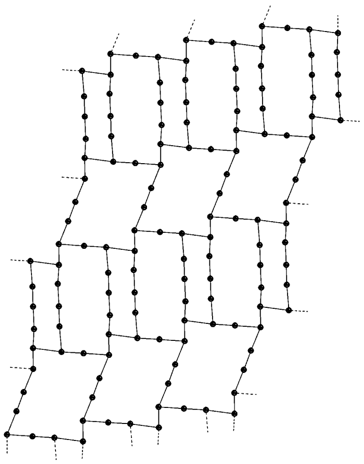
III.3.7 Hexadecaiodides I$_{16}$$^{2-}$

Two Z-shaped heptaiodides [I(1)−I(4) and I(5)−I(8)] linked together and connected to an iodine molecule [I(9)] constitute the hexadecaiodide found in (Me$_2$-Ph$_2$N)$_2$I$_{16}$ (**3.32**).[145] The structure is layered, distances within the layers are ≥ 3.82 Å, and it contain channels where the cations are positioned. A [((I$_5$$^-$)$_2$·I$_2$)·4/2I$_2$] configuration is also found in (Fc)$_2$I$_{16}$.[150] In this case, a 3D network is formed from two V-shaped I$_5$$^-$ ions that are interconnected with iodine through both the terminal and apical iodide atoms of the pentaiodide moiety. The structure (i-PrMe$_2$PhN)I$_8$ (**3.33**) consists of 14-membered rings, which are catenated by iodine molecules and linked in layers with 10- and 14-membered rings to form a mesh.[114] The polyiodide configuration has been described as $_\infty^1$[(I$_7$$^-$)$_2$·I$_2$].



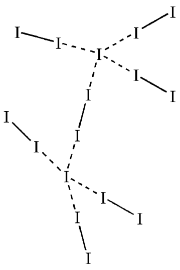
3.32

The spider-shaped I$_{16}$$^{2-}$ ion (**3.34**) found in [(C$_5$-Me$_5$)$_2$Cr$_2$I$_3$]$_2$I$_{16}$ is formed by two approximately planar [I$^-$·(I$_2$)$_3$] units linked to another [I$^-$·(I$_2$)$_3$] unit via an



3.33

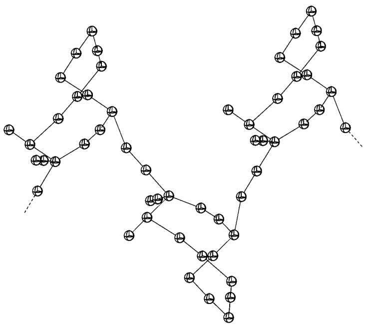
I_2 molecule.[151] There is a large number of I···I contacts in the region 3.6−3.8 Å connecting the I_{16}^{2-} units into layers. The layers are further linked through the central iodine to form a network.



3.34

III.3.8 Octadecaiodides I_{18}^{2-}

The octadecaiodide ion found in $[Fe(phen)_3]I_{18}$ is comprised of a complicated polyiodide network.[149] The network can be regarded as based on the interaction between three I_2 molecules, a V-shaped I_5^- ion and a pyramidal I_7^- entity (I−I cutoff set to 3.30 Å). Many I−I distances are greater than 3.30 Å, which makes it very difficult to provide a clear description of the network. In **3.35** the chain, on which the network is based (I−I ≤ 3.60 Å), is shown. Connecting the chains are four contacts greater than 3.6 Å and below 4 Å.



3.35

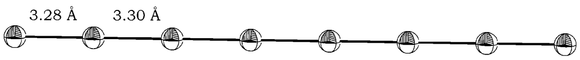
III.4 Polyiodides within the Series I_{2n+3}^{3-}

III.4.1 Heptaiodides I_7^{3-}

The heptaiodide ion has also been claimed as occurring in the compound $[Co(NH_3)_6](I_3)(I_4)$; however, the I_3^- and I_4^{2-} ions are totally isolated from each other.[152]

III.4.2 Octaiodides I_8^{3-}

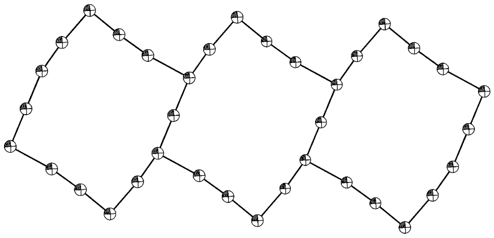
In the structure of $(Me_4Sb)_3I_8$ (**3.36**) an infinite, linear I_8^{3-} ion is present.[153] The I−I distances 3.28 and 3.30 Å alternate along the chain. Every second iodine atom in the chain interacts with the stibonium cation, and the shortest distance between the chains is 5.70 Å. Unusually, this ion cannot be traced back to any of the fundamental building blocks, which is a rare feature shared by the I_4^{2-} ion in Tl_6PbI_{10}.



3.36

III.4.3 Undecaiodides I_{11}^{3-}

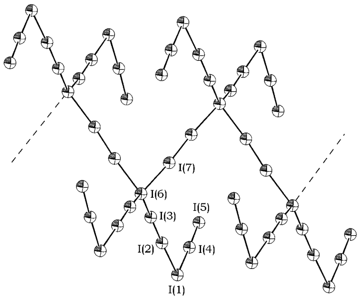
The structure of $[([16]aneS_4)M-I-M([16]aneS_4)]I(I_5)_2$ (M = Pd, Pt) contains a 14-membered polyhalide ring enclosing the M−I−M moiety (**3.37**).[10d] The 14-membered ring, which forms two-dimensional sheets, can formally be regarded as consisting of two V-shaped pentaiodide and one I^- ions.



3.37

III.4.4 Tridecaiodides I_{13}^{3-}

The tridecaiodide in $(Me_2Ph_2N)_2I_{13}$ consists of an infinite zigzag chain {formed by the I^- [I(6)] ions and I_2 [I(7)] molecules} (**3.38**), which is weakly coordinated by two pentaiodides [d(I···I) = 3.60 Å].[154] The polyiodide can be described in terms of the configuration $_\infty^1[\{I^-(I_5^-)_2\}\cdot I_2]$. An S-shaped I_{13}^{3-} ion is reportedly found in the $\{[Pb(phen)_2]_2I(I_{13})\}$ structure.[155] It consists of three triiodide units, where the terminal iodine atom is linked by iodine molecules, $[(I_3^-)_3\cdot 2I_2]$.



3.38

III.4.5 Hexacosaiodides I_{26}^{3-}

The structure of $(Me_3S)_3I_{26}$ can best be described as $[Me_3S]_3(I_7)(I_5)_2\cdot 9/2I_2$, if the I···I contacts longer than 3.36 Å are regarded as intermolecular.[156] Heptaiodides have the $[(I_3^-)\cdot 2I_2]$ configuration, while

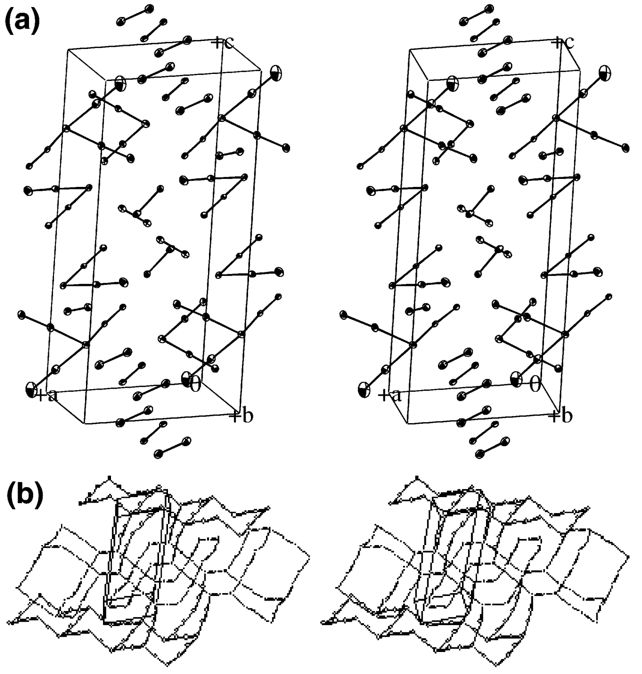
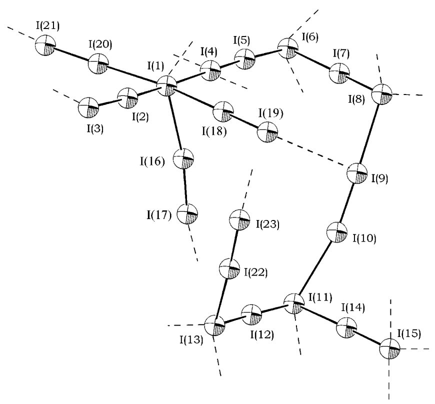


Figure 23. The structure of (a) the building blocks, and (b) the network in $(Me_3S)_3I_{26}$. *Eur. J. Inorg. Chem.* **2000**, 1275. Reprinted with permission of Wiley-VCH. Copyright 2000.

the pentaiodide adopts the V-shaped configuration. If interactions larger than 3.36 Å are included, the I_2 molecules, and the I_5^- and I_7^- ions form a complicated network structure that can be divided into two layers (Figure 23). The longest secondary bond in this network is 3.64 Å.

III.4.6 Nonacosaiodides I_{29}^{3-}

So far, the only I_{29}^{3-} ion described is the one found in the compound $(Fc)_3I_{29}$, (**3.39**).[157] The ion is formed by zigzag chains of I_5^- [I(11)−I(15)] and I_{12}^{2-} [I(1)−I(8), I(18)−I(19), and I(20)−I(21)] ions. These two chains are joined by three different iodine molecules [I(9)−I(10), I(16)−I(17), and I(22)−I(23)], forming a three-dimensional network with an anionic cage structure $[(I_5^-)\cdot(I_{12}^{2-})_{1/2}\cdot 3I_2]$. The ion with the composition I_{12}^{2-} contains a unique, hook-shaped octaiodide [I(1)−I(8)], which is connected to adjacent octaiodides by two iodine molecules. The iodine content in $(Fc)_3I_{29}$ is found to be even higher than in the nonaiodide (29/|−3|).

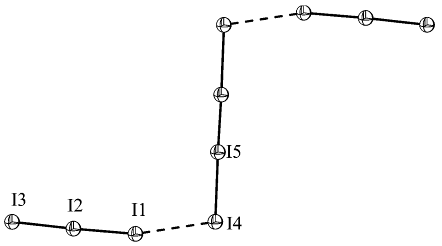


3.39

III.5 Polyiodides within the Series I_{2n+4}^{4-}

III.5.1 Decaiodides I_{10}^{4-}

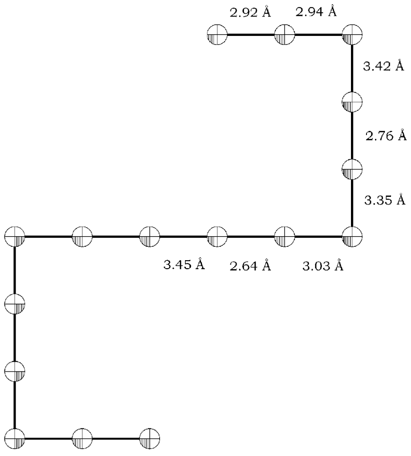
An isolated, Z-shaped I_{10}^{4-} ion with the configuration $[(I_4^{2-})\cdot 2I_3^-]$ (**3.40**), has been postulated as occurring in the structure of $[(C_5H_7N_2Se)_2](I_3)(I_4)_{0.5}$.[158] However, the distance connecting the I_3^- ions with the terminal iodide atoms of the I_4^{2-} anions are greater than 4 Å (4.1 Å), and therefore it is very doubtful if it should be regarded as an I_{10}^{4-} ion.



3.40

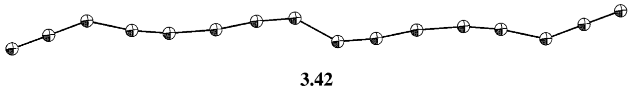
III.5.2 Hexdecaiodides I_{16}^{4-}

Herbstein et al. reported the first hexadecaiodide in $(\text{theobromine})_2\cdot H_2I_8$ (**3.41**).[159] This compound has two I_8^{2-} ions forming an S-shaped I_{16}^{4-} polyiodide ion. This ion is centrosymmetric, almost planar, and best described as $[I_3^-\cdots I_2\cdots I_3^-\cdots I_3^-\cdots I_2\cdots I_3^-]$. The shortest distance between the I_{16}^{4-} ions is reported to be 3.84 Å. Notably, the interacting I_8^{2-} are U-shaped, which is a configuration not found in discrete I_8^{2-} polyiodides. $[Ni(phen)_3](I_{16})_{1/2}\cdot 2CHCl_3$ has a configuration similar to $(\text{theobromine})_2\cdot H_2I_8$ although in this case the I_{16}^{4-} ion is neither centrosymmetric or planar.[135] The Z-shaped I_8^{2-} ions interact very weakly (3.75 Å) and have the two I_3^- ions tilted 97° with respect to each other.



3.41

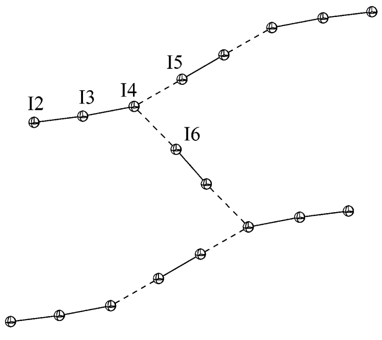
The I_{16}^{4-} ions in $[C_{10}H_{16}N_2O_2S_3]I_{16}$ also have an $[I_3^-\cdots I_2\cdots I_3^-\cdots I_3^-\cdots I_2\cdots I_3^-]$ configuration (**3.42**).[160] However, here it is possible to recognize the outstretched Z-shape configuration found in discrete octaiodides.



3.42

III.5.3 Octadecaiodide I_{18}^{4-}

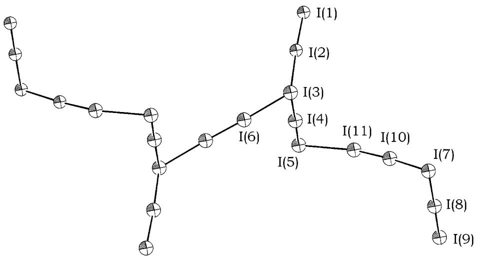
The structure of $[SnI_2(mbit)_2](I_3)_2 \cdot 2/3I_2$ (**3.43**) contains asymmetric triiodide ions as well as disordered iodine molecules that form I_8^{2-} ions with an $[(I_3^-)_2 \cdot (I_2)]$ configuration.[161] The I_8^{2-} ions, that are related through a symmetry center, are linked to each other by a disordered iodine molecule to give the I_{18}^{4-} ion.



3.43

III.5.4 Docosaiodide I_{22}^{4-}

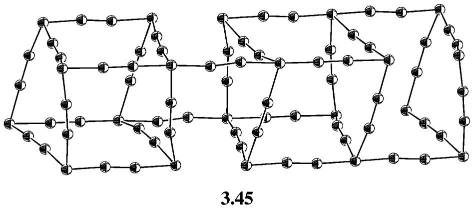
The only reported I_{22}^{4-} ion is found in the structure $(MePh_3P)I_{22}$.[162] It is described as consisting of two pentaiodides [I(9)−I(11)] coordinated to a centrosymmetric I_{12}^{2-} anion [I(9)−I(10)] (**3.44**). The I_{12}^{2-} ion consists of two L-shaped pentaiodide ions, bridged by an iodine molecule. The I_{22}^{4-} ions are interacting through vdW contacts. The ion can therefore be regarded as discrete.



3.44

III.5.5 Hexacosaiodide I_{26}^{4-}

The polyiodide ion in the structure $(DMFc)_4I_{26}$ consists of a three-dimensional network of an iodine-bridged primitive, cubic iodide lattice with every 12th iodine molecule missing (**3.45**).[163] As a consequence, the network has a $[(I^-) \cdot 3I_2]$ configuration with five and six iodide atoms coordinated. The intramolecular I−I distances are in the range 2.73−2.77 Å. The secondary I···I bonds are reported to fall in the 3.23−3.59 Å range. However, no discrete polyiodide ion can be identified in the structure.



3.45

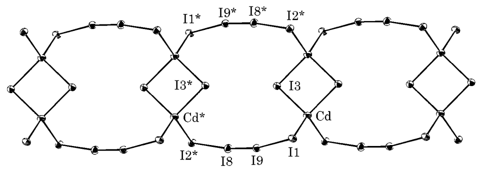
III.6 Metal Iodide-Iodine Structures

This section will focus on metal iodide−iodine structures forming chain and network structures (M−I···I_x contacts shorter than 4.0 Å). The discrete metal iodine−iodide structures (i.e., M−I_X−M and MI_x) and the M−I−Y_x structures (Y = F, Cl, or Br) are not included in this discussion.

A common feature in metal iodide−iodine structures is the existence of bridging tetraiodide units. In most cases, the notation of a tetraiodide ion is only a formal one, since the terminal iodides are weakly bonded compared to the previously described tetraiodides. If the metal iodide−iodine structures are regarded as arising from the interaction between the building blocks M−I and I_2, it can be concluded from CSD that the metal iodides making the strongest interaction with iodine are those corresponding to the late transition metals. This section is divided into two subsections: binary metal iodide−iodine structures and metal iodide−iodine structures with stabilizing ligands (nonbinary metal iodide−iodine structures).

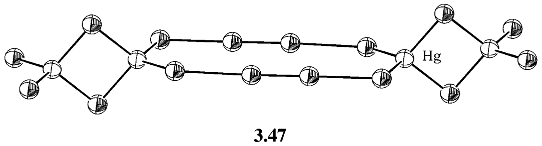
III.6.1 Binary Metal Iodide-Iodine Structures (BMII Structures)

BMII structures with dimeric complex metal iodides are reportedly in $[Et_3S](Hg_2I_6)_{1/2} \cdot 3I_2$, $[Me_3S](Cd_2I_6)_{1/2} \cdot 3I_2$, $[hmtH]_2(Hg_2I_6)_{1/2}(HgI_3) \cdot 1/2I_2$, and $[BEDT\text{-}TTF]_4(Hg_2I_6)(I_8)$.[164−167] The I_2 molecules of the complex $[Me_3S](Cd_2I_6)_{1/2} \cdot 3I_2$, coordinate to the terminal iodides of the $Cd_2I_6^{2-}$ complexes (**3.46**). In this way, a network of infinite zigzag chains of $Cd_2I_6^{2-}$ complexes interspaced by formal I_{10} units is formed. EXAFS data from Cd (K shell) in the 1:10 mixture of CdI_2-$(Et_3S)I_7$ confirms the structural relationship of Cd^{II} both in the liquid reaction medium and the isolated polyiodide compound.



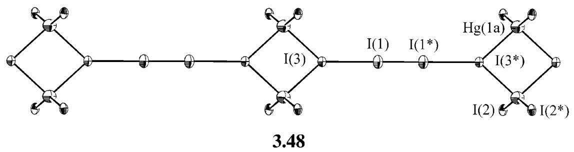
3.46

The mercury compound, $[Et_3S](Hg_2I_6)_{1/2} \cdot 3I_2$, also displays a network structure. However, in this case since the I_2 molecules are coordinated directly to the terminal iodides of $Hg_2I_6^{2-}$ (**3.47**) the network becomes less complicated.



3.47

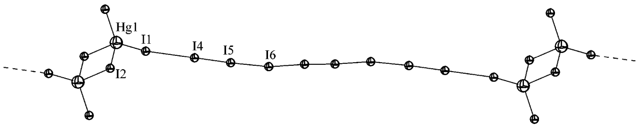
In the $[hmtH]_2(Hg_2I_6)_{1/2}(HgI_3) \cdot 1/2I_2$ complex (**3.48**), the I_2 molecules coordinate to the bridging iodides of the $Hg_2I_6^{2-}$ complexes with an intramolecular I−I distance of 2.7 Å and an intermolecular I···I distance



3.48

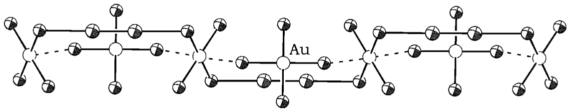
of 3.4 Å. The iodine molecules and $Hg_2I_6^{2-}$ ions form infinite chains.

The $Hg_2I_6^{2-}$ ion in $[BEDT\text{-}TTF]_4(Hg_2I_6)(I_8)$ (**3.49**) is weakly linked (3.7 Å) to a slightly elongated, Z-shaped I_8^{2-} ion to form a zigzag chain. The BEDT-TTF and I_8^{2-} ions are all stacked in the same layer, which is separated from the $Hg_2I_6^{2-}$ ions.



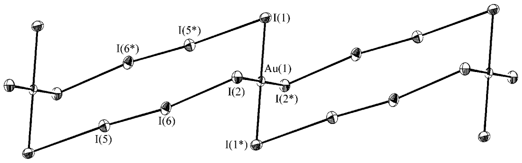
3.49

Square-planar metal iodides linked to iodine are found in $[Et_3S](AuI_4)\cdot 2I_2$ and $[NH_4](AuI_4)\cdot 1/2I_2$.[168,169] The latter consists of almost square-planar AuI_4^- complexes, where every second complex is coordinated by I_2 molecules, thus forming a chain structure (**3.50**). The intra- and intermolecular I−I distances in $[NH_4](AuI_4)\cdot 1/2I_2$ are 2.7 and 3.4 Å, respectively.



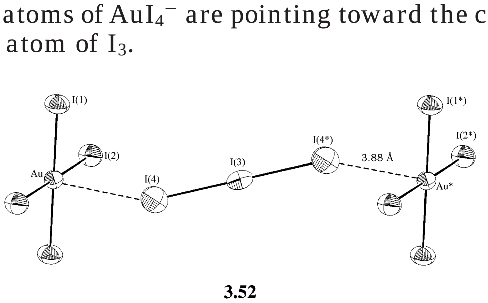
3.50

$[Et_3S](AuI_4)\cdot 2I_2$ also consists of square-planar AuI_4^- complexes perpendicularly linked by iodine. However, here the bridging iodine molecules create infinite double zigzag chains (**3.51**).



3.51

In contrast to the NBMII congeners (vide infra), extended structures with ···IM−I_3−MI··· chains have not been characterized for BMII structures. In the perovskite-like structure $[Me_3S]_2(AuI_4)(I_3)$, the triiodides are oriented to the center of AuI_4^- (**3.52**), but the distance between the gold atom in the square-planar AuI_4^- ion and the terminal iodide of I_3^- is too long to be regarded as bonding.[168] However, the partial negative charge on the terminal iodine atoms in I_3^- and the partial positive charge on the gold atom in AuI_4^- give rise to a fairly strong electrostatic interaction that may explain the orientation of the I_3^- ions in the structure. It is also notable that the iodine atoms of AuI_4^- are pointing toward the central iodine atom of I_3.



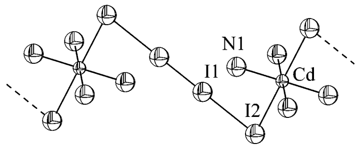
3.52

III.6.2 Nonbinary Metal Iodide–Iodine Structures (NBMII Structures)

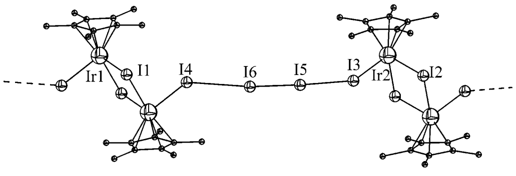
As well as displaying more diverse structural features, the number of NBMII structures is far greater than for BMII. Discrete entities (metal iodide-I_x), which are rare for BMII structures, are commonly found in NBMII structures.

The inorganic compounds $[Cd(NH_3)_4]I_4$ and $[Cu(NH_3)_4]I_4$ (**3.53**) both form infinite, planar, zigzag chains of I_4^{2-} linked to square-planar $[M(NH_3)_4]^{2+}$ (M = Cd or Cu).[129] Thus, the two axial iodine atoms complete a quasi-octahedral coordination around the metal center.

In the structures $[M(C_5Me_5)]_2I_6$ (M = Rh or Ir) (**3.54**), the iodine molecules are linked to the terminal iodides of the "dimeric complex ion", to form a zigzag chain.[170] A similar linkage is found in $\{[Cp^*Cr(I_3)(\mu\text{-}I)]_2\cdot[Cp^*CrI(\mu\text{-}I)]_2\}_n$, whereas only chains are formed in these structures. In the analogous dimeric BMII structures networks are also found.[171]

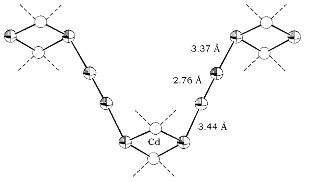


3.53



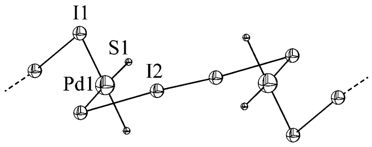
3.54

Pennington et al. report an unusual iodine coordination, similar to **3.48**, as occurring in (4-cnpy)$CdI_2\cdot 2I_2$ (**3.55**).[172] The bridging iodides of CdI_2 are coordinated by iodine, instead of the more common terminal iodides. The intramolecular I−I distance is 2.757(1) Å, while the intermolecular I···I distances are 3.367(1) and 3.436(1) Å.

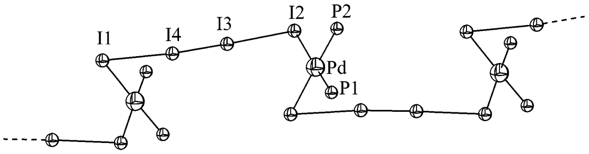


3.55

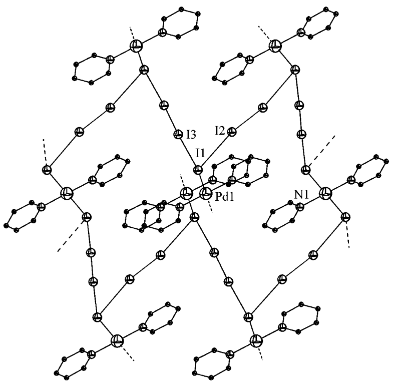
The square-planar Pd complexes $[Pd(C_{18}H_{14}S_2)I_2]$-I_2 (**3.56**) and $[Pd(cis\text{-}Ph_2PCHCHPPh_2)I_4]$ (**3.57**) have a zigzag chain structure similar to the square-planar gold BMII structure (**3.51**). However, only a "single" chain is found in this case.[173,174] In $[Pd(C_{18}H_{14}S_2)I_2]$-I_2, there are also links at 3.7 and 3.9 Å, which if taken into account create a 3D network. A complicated network made from the interaction of 28-membered rings is displayed in the compound (**3.58**) $Pd(py)_4I_6$.[175] Each ring has two Pd atoms included. The copper complex $[Cu(OETPP)]I_7$ has a branched zigzag chain, where every sixth iodide atom coordinated to copper.[176]



3.56

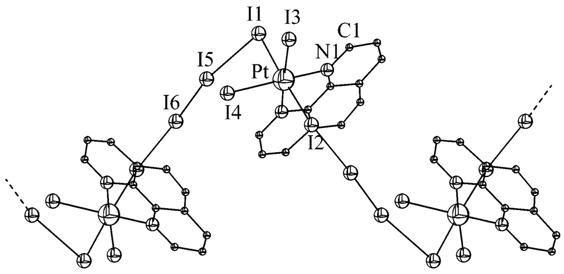


3.57

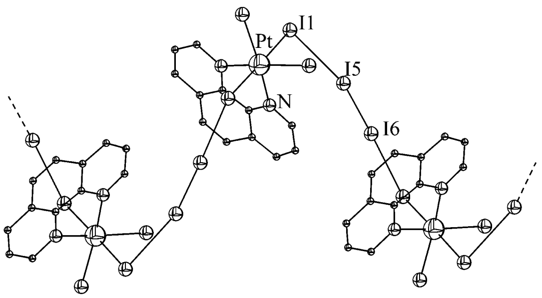


3.58

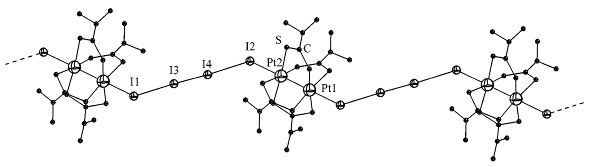
Octahedral metal iodides are the most frequently found among the NBMII structures. The complexes Pt(phen)I_6 and Pt(phen)I_5 (**3.59**, **3.60**) both contain octahedral Pt(phen)I_4 linked by iodine molecules to form zigzag chain structures.[177] In both structures, however, there are several contacts shorter than 4.0 Å. Taking these into account, the structures are converted into networks. The structure of $Pt_2(RCS_2)_4I_2$ (R = PhCH, Me_2CH) (**3.61**) also forms an analogous chain, but in this case there are only two available iodide sites in the dimeric Pt_2 unit for linkage.[178]



3.59

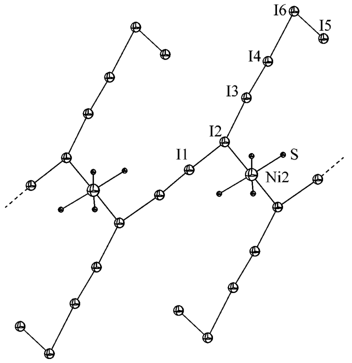


3.60

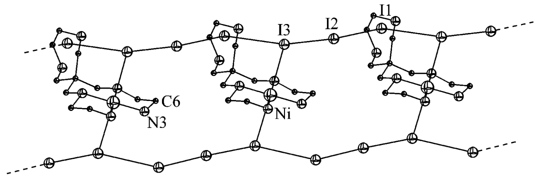


3.61

Iodine linked to octahedrally coordinated nickel is found in the structures [Ni(CH_3LH)$_2$(I_3)$_2$)], [Ni(Pr_2timdt)$_2$][Ni(I)$_2$(Pr_2timdt)$_2$]·5I_2 (**3.62**), and [Ni(HL_1)]I(I_3)$_2$·H_2O (**3.63**).[179−181] All three structures have only two iodide atoms available for linkage. In the two latter compounds chains are formed, while in [Ni(CH_3LH)$_2$(I_3)$_2$)] a layered network consisting of 12-membered rings with two Ni atoms in each ring is observed. The chain in **3.62** is branched and zigzag-shaped, while in **3.63** a chain consisting of strands of 10-membered rings can be discerned.



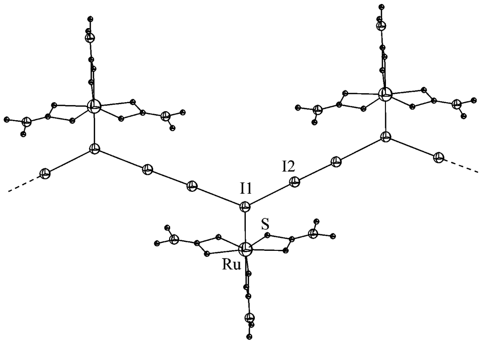
3.62



3.63

In ($N(CH_3)_4$)$_2I_3$(CoI_2(GH)$_2$), a branched chain is formed by the interaction between I_3^- and the L_4CoI_2 unit at 3.9 Å.[182] The I_3^- ions form the common T-shape patterns. A chain structure is also displayed in [{Rh(μ-Pz(I)(CO)(PMe_2Ph)}$_2$(μ-I)]I_5; however, the interaction is quite weak between the metal iodide and the iodine (3.9 Å).[183]

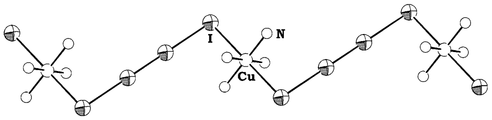
The seven-coordinated ruthenium atom in Ru(Me_2dtc)$_3I_3$ (**3.64**) forms a distorted pentagonal−bipyramidal geometry, where the axial iodide is linked with iodine to form an outstretched zigzag chain.[184]



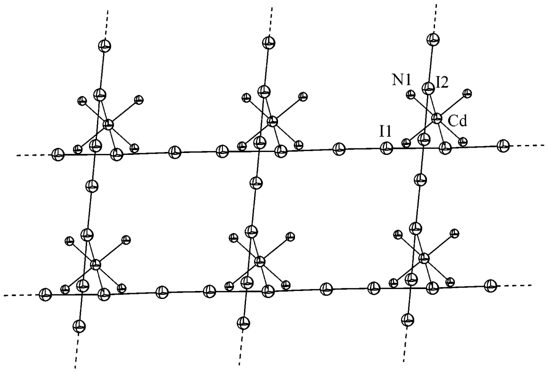
3.64

A few authors have reported that triiodide ions can be incorporated into the coordination sphere of metal ions. The structure of $[Cu(NH_3)_4I_3]I_3$ contains triiodide ions coordinated to the square-planar $Cu(NH_3)_4^{2+}$ cation (**3.65**).[129] Thus, the terminal iodides of the triiodide form a corner in an octahedron in a zigzag chain of the composition $[Cu(NH_3)_4I_3]^{2+}$.

Another triiodide ion intercalated between the chains is merely acting as counterion. In the corresponding cadmium compound, $[Cd(NH_3)_4(I\cdot I_2)_2]$ (**3.66**), the complexes 1,6-$[Cd(NH_3)_4I_2]$ are linked by iodine to form a network of $[Cd(NH_3)_4(I\cdot I_2)_2]$ containing linear chains of ${}^{1}_{\infty}[I_2\cdot I]^-$. Since the $I\cdots I_2$ distance is as long as 3.38 Å, the chain cannot be described in terms of interacting I_3^- ions. The terminal iodide in the I_3^- part of the Z-shaped octaiodide in $[Pd(NH_3)_4]I_8$ coordinates to the square-planar cation $[Pd(NH_3)_4]^{2+}$.[129a]



3.65



3.66

A puckered chain is reported in the structure of $[PtI(C_6H_3\{CHNMe(CH_2)_7MeNCH_2\}_{2.6})(\eta^1\text{-}I_2)]$. The iodine linkage is shifting between the terminal I and the center of the Pt complex.[185]

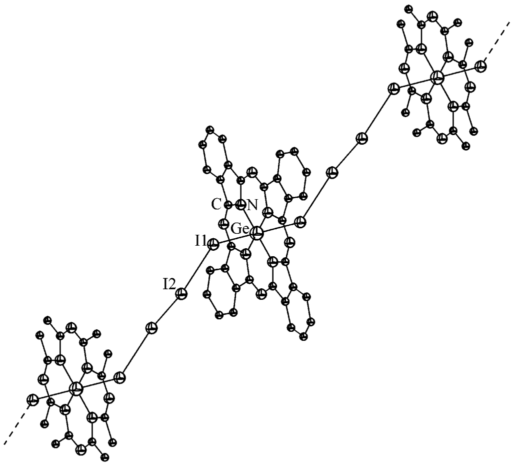
The elements of Group 13 have not been found to form any extended structures with iodine. Lead has been observed as forming iodine complexes. However, due to their thermal instability, it has not been possible to characterize them. Investigations of the $TlI-I_2$ system showed that the redox couple Tl^I/Tl^{III}, like the Au^I/Au^{III} couple, can be exploited in the synthesis of polyiodides with higher iodine content (higher polyiodides).[156]

III.7 Related Structures of Interest

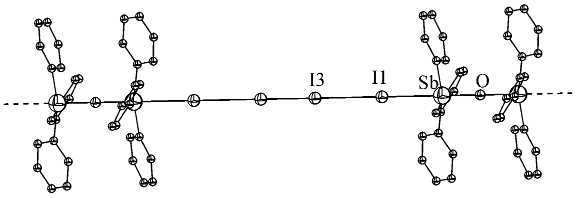
III.7.1 Metalloid Iodide Iodine Structures

The germanium(IV) complex $Ge(Pc)I_2$ (**3.67**) forms a zigzag chain from the linking between the axially coordinated I^- and the bridging I_2 [$d(I\cdots I_2) = 3.49$ Å].[186] An analogous linkage is found in the complex $[Fe(Pc)Cl]_2I_2$.[187]

An ${}^{1}_{\infty}[\cdots I_2-I-As-I-I_2-I-As\cdots]$ chain has been reported in $MeAs(Me_2NNCS_2)I_2$. However, the As–I interactions are quite weak (3.3–3.5 Å).[188] The trigonal–bipyramidally coordinated Sb in $4[(Ph_3SbI)_2O]\cdot I_2$ (**3.68**) has its iodide linked to iodine to form a linear chain. The unusual feature of this structure is that the chain includes an oxygen ${}^{1}_{\infty}[\cdots I_2-I-Sb-O-Sb-I-I_2\cdots]$.[189] The structure $[Sb(S_2CNEt_2)_2I]\cdot(1/2I_2)_{0.56}$ contains a polymeric chain of ${}^{1}_{\infty}[\cdots Sb(S_2CNEt_2)_2-I-Sb(S_2CNEt_2)_2\cdots]$, where adjacent strands are linked with iodine.[190] The analogous compound $[Sb(S_2CNEt_2)_2I]\cdot(1/2I_2)_{0.84}$ has a similar structure, although the increased iodine content results in more compactly bonded strands (stronger I···I interaction) with a concomitant decrease in cell volume.[190]

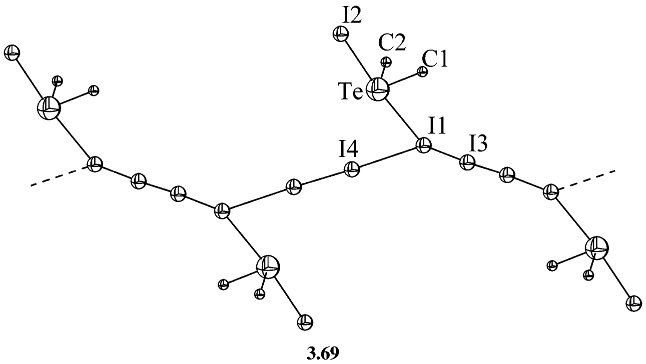


3.67



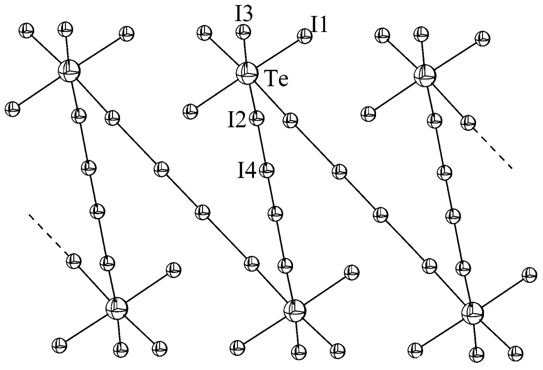
3.68

To our knowledge, the compounds $(CH_3)_2TeI_4$ (**3.69**) and $[(CH_3)_4N]_2TeI_6\cdot I_2$ (**3.70**) are the only structurally characterized tellurium species forming extended iodine structures.[191,192] One of the iodides of $(CH_3)_2TeI_4$ is linked to two iodine molecules to form a outstretched zigzag chain. The coordination around tellurium is completed by two weak Te···I bonds which can be described as distorted octahedral.



3.69

The Te atom in $[(CH_3)_4N]_2TeI_6\cdot I_2$ has a distorted TeI_6 octahedral structure coordinated to iodine to



3.70

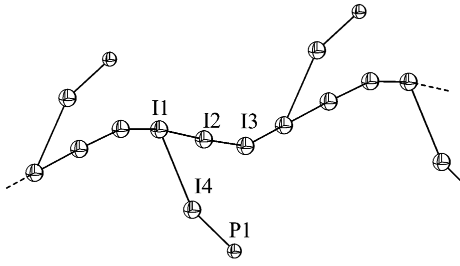
form planar zigzag chains [$d(\mathrm{I{-}I}) = 2.75$ Å and $d(\mathrm{TeI{-}I_2}) = 3.26$ Å].

III.7.2 Charge-Transfer Complexes D–I$_x$, D = N, P, S, or Se

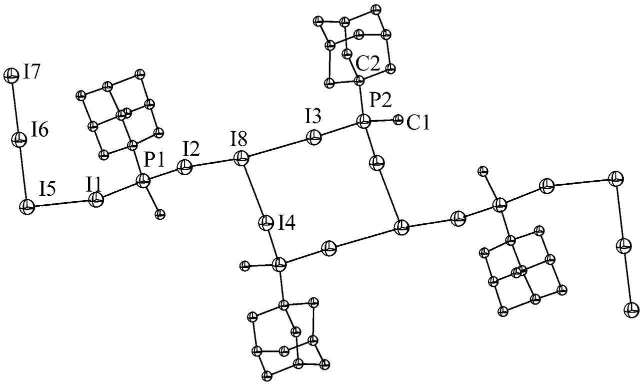
The reaction of organo-Group-15 and -16 donor species with halogens/interhalogens leads to the formation of charge-transfer or adduct complexes. Iodine charge-transfer complexes with donor species such as nitrogen heterocycles, amines, phosphines, thioeters, thioketones, selenoketones, and selenoethers are found. Only compounds in which the interaction D···I$_x$ is intramolecular are considered in this section.

There are many known nitrogen−iodine, charge-transfer compounds, but usually they do not form extended structural features. In the structures $[\mathrm{I(INPPh_3)_2}]\mathrm{I_3}$ and $[\mathrm{I(INPPh_3)_4}]\mathrm{I_3}$, polyiodide−nitrogen rings are formed, although they are not extended. However, a chain structure where the iodides are linked to the strong electrophile 1,4-diiodotetrafluorobenzene and INPPh$_3$ is found in $[\mathrm{I(INPPh_3)_3}][\mathrm{I(C_6F_4I_2)}]$.[193] What is notable is that there are no iodine molecules present in this structure. A chain structure is also found in (CH$_2$-acridine)·I$_2$. Charge-transfer interactions involving “amphoteric” (iodine acting as both Lewis acid and Lewis base) iodine was reported in the structures of (acridine·I$_2$)$_2$·I$_2$, (9-Cl-acridine·I$_2$)$_2$·I$_2$, and (9-Cl-acridine)$_2$·I$_2$.[194] The latter two contain DI$_2$−I$_2$−I$_2$D dimers, while the former contains a D−I$_2$−D dimer (D = acridine/9-Cl-acridine equivalent with electron donor). These are in fact analogues to $\mathrm{I_8}^{2-}$ ($\mathrm{I_3}^-$−I2−I3$^-$, DI$_2$ equivalent with $\mathrm{I_3}^-$) and $\mathrm{I_4}^{2-}$, (I^-−I$_2$−I$^-$, D equivalent with I$^-$), with a new building block replacing I$^-$ as the electron-donor. Thus, the “electron donating I$_2$” corresponds to an $\mathrm{I_3}^-$ analogue.

The first iodophosphonium polyiodide, R$_3$PI$_4$ (R = ferrocenyl), was reported by Gridunova et al.[195] This structure, as well as the structure of $[\mathrm{IP(Ph)_3}]\mathrm{I_3}$ (**3.71**), form distorted chains, where the iodophosphonium cation is coordinated to the polyiodide backbone.[196] The structures Et$_2$PI$_5$ and (i-Pr)$_3$PI$_4$ form a similar chain structure. However, in these cases the chain has a zigzag shape.[197,198] The polyiodide backbone in the compounds $[\mathrm{((i\text{-}Pr)_2PI_2)_2I(I_3)}]$ and (t-Bu)(i-Pr)PI$_4$ are also zigzag shaped but they have longer iodophosphonium cation chains and one further coordinated iodophosphonium cation.[197,199] Both the structures $[\mathrm{(Ad)(Me)PI_2}]_2\mathrm{I(I_3)}$ (**3.72**) and (t-Bu)-(i-Pr)PI$_{4.33}$ have extended structures with eight-membered rings incorporated.[199,200]



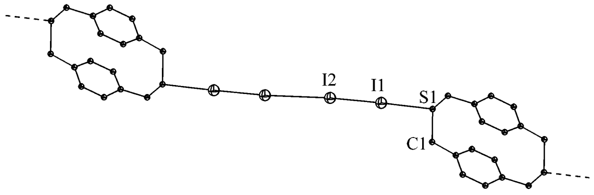
3.71



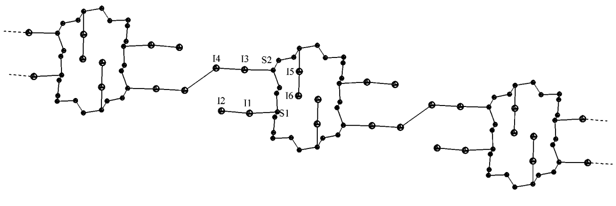
3.72

A large variety of sulfur and iodine charge-transfer compounds have been characterized, in particular many thioether-iodine charge-transfer compounds. These are of particular interest since they are multidentate, acting as multiple donors. The thioether-iodine system has also been shown to exhibit unusual structural features. Here, I$_2$ is acting as a template ordering the macrocyclic metal receptors in the solid state.

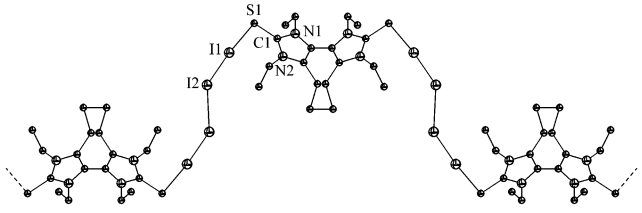
The compounds [CuCl$_2$(dtpcp)(EtOH)], [24]-aneS$_8$·6I$_2$ and (Et)$_4$(todit)·2I$_2$ all have cyclic carbon−sulfur molecules incorporated into the polyiodide backbone.[201−203] The structure shown in **3.73** forms an almost linear chain, while **3.74** and **3.75** show zigzag and U-shaped topologies. The thioether compound (C$_{12}$H$_{24}$O$_4$S$_2$)$_2$·I$_2$ (**3.76**) forms a twisted ladder-like chain with each thioether is doubly linked.[204]



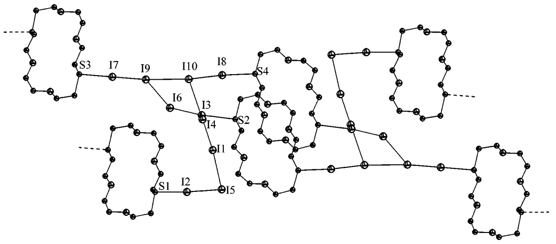
3.73



3.74



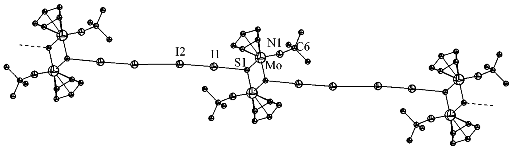
3.75



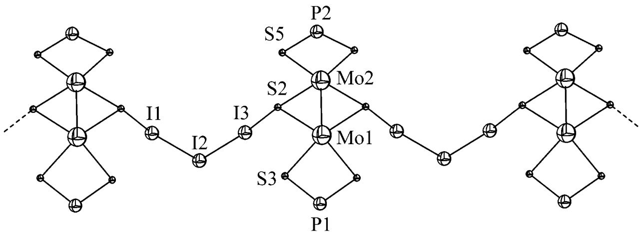
3.76

Chains containing dimeric complexes interacting with iodine, similar to those found for NBMII, have been characterized (**3.77**) [(Cp)Mo(μ-S)N-t-Bu]$_2$ and [Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$S(O$_2$CMe)(SI$_3$)]$_n$ (**3.78**).[205,206]

Network structures, where the thioethers act as 4-fold donors, have been observed in the structures of ([15]-ane-S$_5$)$_2$·7I$_2$ (**3.79**), [14]-ane-S$_4$·4I$_2$ (**3.80**), and [16]-aneS$_4$·4I$_2$ (**3.81**).[202,207] The former two contain 6- and 8-folded polyiodide rings interconnected with the thioethers through S···I or S−I··· interactions. In **3.81**, the thioethers are included in the polyiodide entity forming the corners in a 20-membered ring.

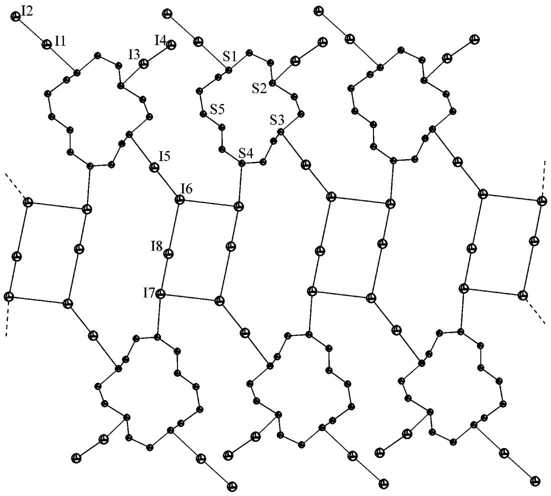


3.77

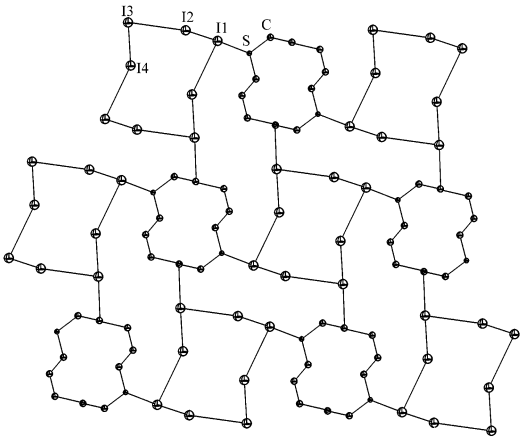


3.78

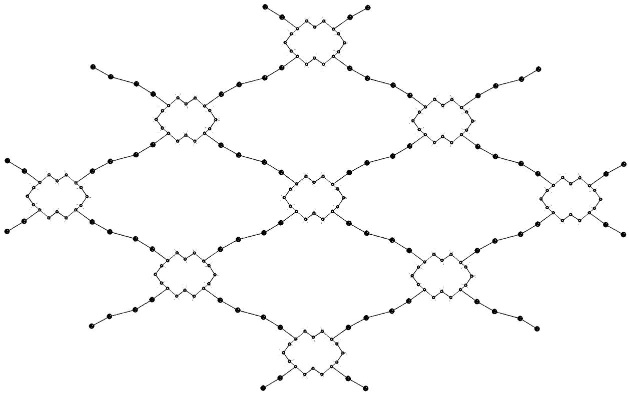
Chain structures similar to those observed in the iodophosphonium polyiodides are also found in the structures of [(Me$_2$N)$_3$PSe]I(I$_3$), [morph$_3$PSe]I(I$_3$)·1/2I$_2$, and (Mebesel)·2I$_2$ (**3.82**).[208,209] (t-Bu)$_3$(I−Pr)PSeI$_7$ has a zigzag chain, but these are interconnected (> 3.4 Å) to form a layer, which in turn is interconnected to a network.[210] The layers consist of connected puckered rings which have V-shaped pentaiodides or V-shaped pentaiodides substituted with Se in the corners. A complicated network is found in (i-Pr)$_4$PSeI$_7$ and can be seen as arising from linked layers that are formed by linked chains of V-shaped pentaiodides and v-shaped pentaiodides substituted with one or two Se atoms. In the case of (t-Bu)$_2$P-(SeI−I)I (**3.83**), the chain structure consisting of linked 10-membered rings also contain phosphorus.[211]



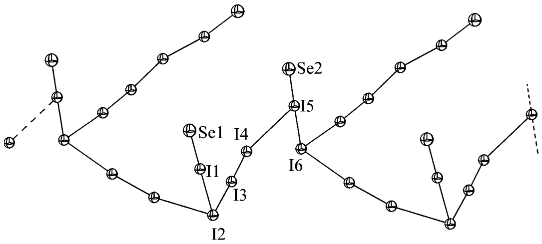
3.79



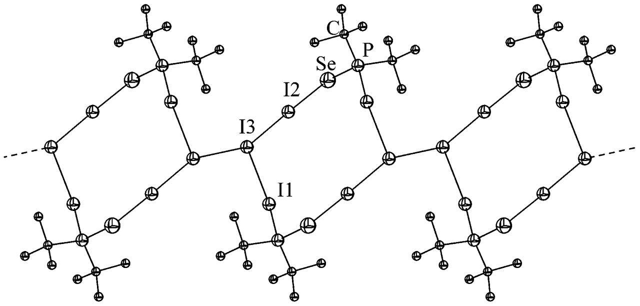
3.80



3.81



3.82



3.83

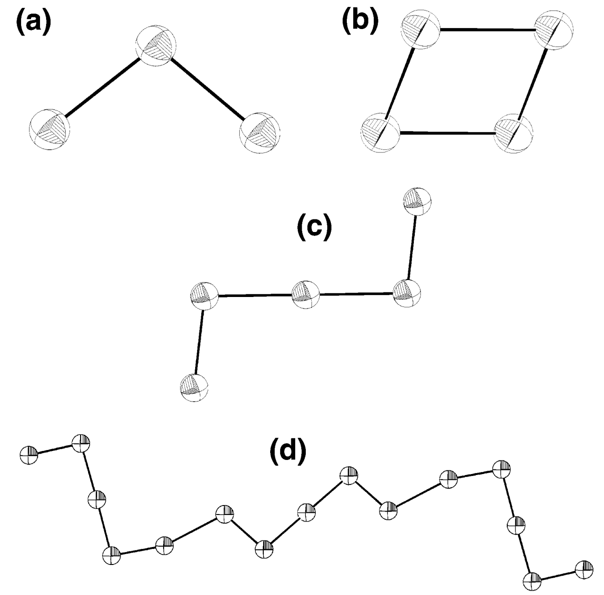


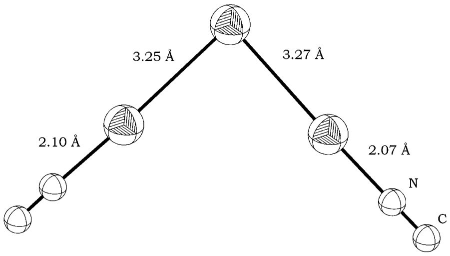
Figure 24. Currently known polyiodonium cations.

III.7.3 Polyiodonium Cations

Iodine can be oxidized with strong oxidizing agents to form polyatomic cations such as I_2^+, I_3^+, I_4^{2+}, I_5^+, and I_{15}^{3+} (Figure 24).[212] As a consequence of the loss of an electron from the π^* orbital, the bond lengths in the cations are shorter than those in neutral iodine (see section 4). The intramolecular bond distance in I_2^+ is reported to be 2.56 Å. The triiodonium ion is V-shaped, while the pentaiodide has a planar Z-shaped structure. Thus, the linear, anionic triiodide ion does not have any structural similarity with its cationic congener. However, in the pentaiodide ions zigzag chains are common and Z-shaped units similar to the geometry of I_5^+ can be identified. The tetraiodonium ion is rectangular and can be regarded arising from two I_2^+ ions interacting through a $\pi^*-\pi^*$ interaction (3.26 Å). The I_{15}^{3+} cation in $I_{15}(SbF_6)_3$ is constructed by three Z-shaped I_5^+ cations weakly connected to each other (3.42 Å). In all of these polyiodonium cations, more or less strong contacts with the anions are reported.

III.7.4 Organic Compounds

Even though the polypseudohalogen ions are unstable under ambient conditions, several have successfully been characterized. Whereas the ions I_2CN^- and $I(CN)_2^-$ are almost linear, $Rb[I(ICN)_2]$ is V-shaped and analogous to the pentaiodides (**3.84**).[213]



3.84

Complexes of halide ions with diiodoacetylene form structures similar to the polyiodides. Analogous to iodine the diiodoacetylene acts as the acceptor and in $P(Ph)_4[I(I{-}C{\equiv}C{-}I)_2]$ the diiodoacetylene molecules are coordinated to the iodide ion forming a distorted tetragonal pyramid.[214] The I···I distances are 3.35 and 3.51 Å.

III.7.5 Other Compounds

Although the vast flora of iodine-containing compounds with exciting structural properties also embrace polyinterhalogen and various intercalation compounds. These are regarded as outside the scope of this review.

IV. Bonding in Polyiodides

The nature of the chemical bond in the hypervalent, octet-rule violating, polyiodides has been of theoretical interest for a long time, and several interpretations have been provided.[128,215] Electrostatic interactions, localized covalent bonds (involving d-orbitals forming ds^np^m-hybrids) or delocalized σ-bonding without significant d-orbital contribution are the models usually proposed.[216] The delocalized σ-bonding model, proposed by Rundel and Pimentel, is the presently accepted one.[217] However, closed-shell interactions have to be introduced to explain many of the interactions displayed in polyiodides.[218]

Using the Rundel-Pimentel model and closed-shell interactions, this section describes the bonding of polyiodides in terms of donor−acceptor interactions. The bonding in gold iodide−iodine systems and metal iodide−iodine systems are discussed in separate sections.

IV.1 Triiodides

A convenient way of visualizing the bonding and electronic structure of the triiodide ion is the utilization of MO energy diagrams. The MO diagrams of the triiodide ion and iodine are shown in Figure 25. The triiodide ion has 22 valence electrons, six of which are distributed in low energy s-orbitals and 12 in orbitals of π-symmetry. The remaining four electrons are delocalized p-electrons, which form the 3-center, 4-electron (3c,4e) bond. The interaction between the $5p_z$-orbital of I^- with the σ_2- and σ_2^*-orbitals of I_2 results in the $2\sigma_u$, $3\sigma_g$, and $3\sigma_u^*$ MOs. The I_2 HOMO is the major contributor to $2\sigma_u$, while the I^- HOMO is the dominating contributor to $3\sigma_g$. This donor−acceptor interaction results in a depopulation of the σ_2-orbital and a subsequent population of the σ_2^*-orbital. This is in agreement with the

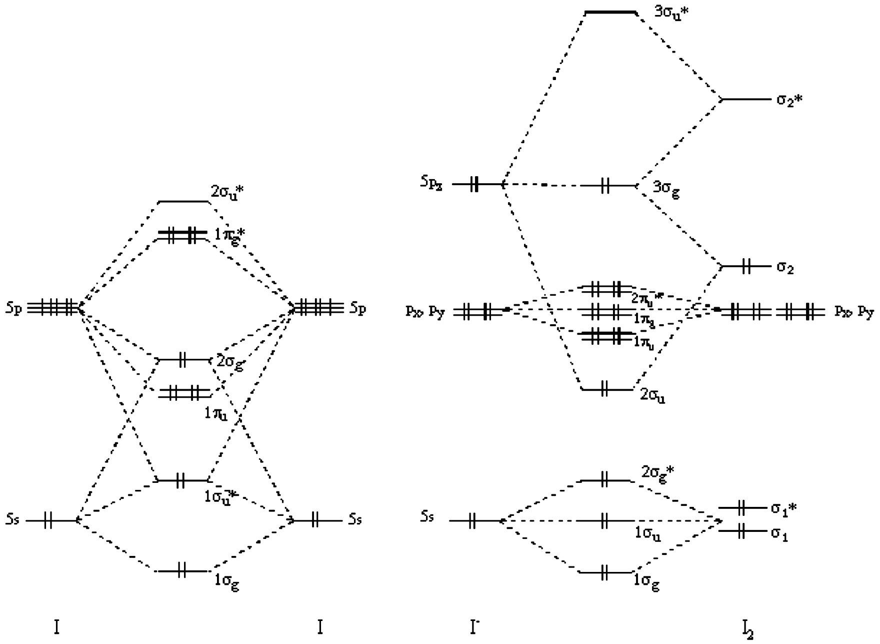
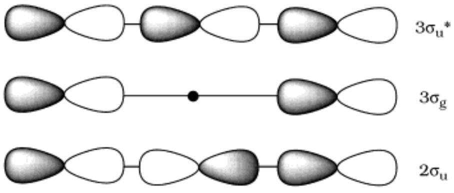


Figure 25. The generalized MO energy diagrams of I_2 and I_3^-.

observed elongation of the I−I bond length when I_2 is interacting with a donor.

An important factor contributing to the triiodide stability is the energy gap between σ_2 and σ_2*. If the gap is small, the stability of the complex increases since the energy match with $5p_z$ is more favorable. Also important for the stability is the contribution of σ_2* to $3\sigma_g$. With a low σ_2* content, $3\sigma_g$ will adopt antibonding character, and, as a consequence, the whole complex is destabilized. As can be seen from the molecular orbitals in **4.1**, the terminal iodides of the triiodide ions are negatively charged.[219] This indicates that an acceptor would be attacked primarily by the terminal iodides. However, Hoffmann and co-workers point out that not only charge control but also orbital control have to be considered. In the case in which the acceptor is I_2, this will not of course make any difference. But if the acceptor is a mixed halogen (e.g., ICl or IBr), orbital control becomes vital.[220] The concentration of electron density on the terminal atoms in the triiodide ion explains the fact that mixed trihalides prefer to have the most electronegative atom in the terminal position. The T-shaped configurations often encountered in triiodides can be similarly explained.



4.1

As was shown in section 3, triiodide ions have a wide range of bond lengths and are nearly linear in almost all structures. The calculated PES of linear deformation is very flat; a result that supports the wide range of bond lengths observed in the crystal structures (Figure 26a).

At room temperature, the thermal energy (≈0.025 eV) would be enough to induce deformations as much as 0.3 Å or even longer (Figure 26b). To bend the triiodide ion, however, much larger energies are required (Figure 26c). By decomposing the interaction energy of a linear and bent triiodide ion, Hoffmann et al. show that the linear geometry is determined by orbital interactions while the most of the bonding energy arises from electrostatic effects.[220]

IV.1.2 Influence of Cation, Hydrogen Bonding, and Solvents

The importance of the cation environment in polyiodide geometry was implied in connection with the description of crystal structures in the preceding sections. Theoretically, the influence of the cation has also been demonstrated. Datta et al. report geometry optimizations of the triiodide in both a flexible (simulating liquids) and a rigid (simulating crystalline environment) counterion cage.[221] The triiodide was shown to be symmetric in the flexible cage but asymmetric in the rigid one. The LXS data for $(R_3S)I_x$ ($x = 2-11$) melts show that the cation is positioned asymmetrically. Hence, the flexible cage model appears not to be applicable in this case (section II). Geometric optimization of a triiodide ion with a point charge (simulating the cation) in the position obtained from the LXS gives rise to an asymmetric triiodide ion. The PES becomes flatter in the r2 direction and steeper in the r1 direction (Figure 27). In other words, as predicted the ability of I_3^- to donate an iodide ion increases in the r2 direction and decreases in the r1 direction. Novoa and co-workers report that side-on position of the cation is preferred over a linear one for the analogous Br_3^- ion.[219]

The influence of hydrogen bonding has also been theoretically confirmed in the model system $H_3C-H\cdots Y-I-Y^-$ (Y = Cl, Br, and I).[222] The H atom makes a short contact with the terminal halogen atom and as expected the interaction increases in the series I

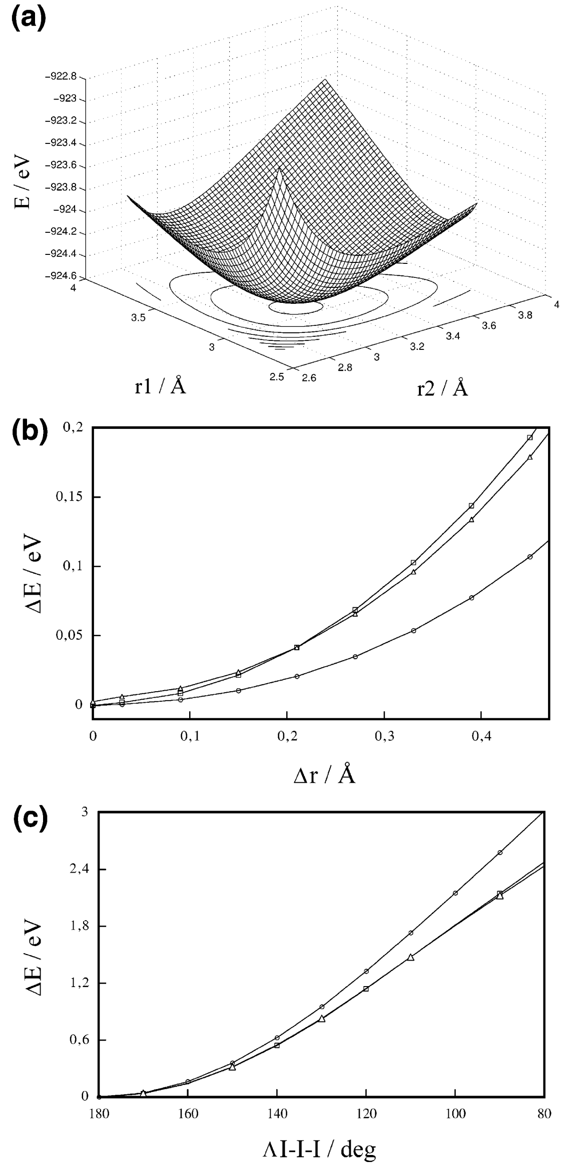


Figure 26. (a) Calculated energy of I_3^- as a function of r1 and r2 (MP2). (b, c) The relative changes in total energy as a function of linear deformation and angular deformation (circles refer to results from HF, squares from MP2 and triangles from CCSD calculations). *J. Chem. Soc., Dalton Trans.* **2000**, 2449, reprinted with permission of the Royal Society of Chemistry. Copyright 2000.

< Br < Cl. The C−H···Y−I−Y^- interaction energy was reported to be 4−8 kJ mol^{-1}. Energies of this magnitude imply significant H-bonding effects in the polyiodide structures. Variation of the angular position of the H-atom was shown not to cause any large energy changes.

Recently, calculations investigating solvent effects have also been performed.[223−225] Sato et al. showed that the electronic structure is strongly influenced by the surrounding solvent molecules.[226] This is particularly evident in aqueous solution where the ground state free energy surface is very flat at the equilibrium position. This indicates an increased occupation of the asymmetric structures. The dissociation energy is smaller in solution, and exchange reactions should proceed more easily as has been confirmed experimentally.

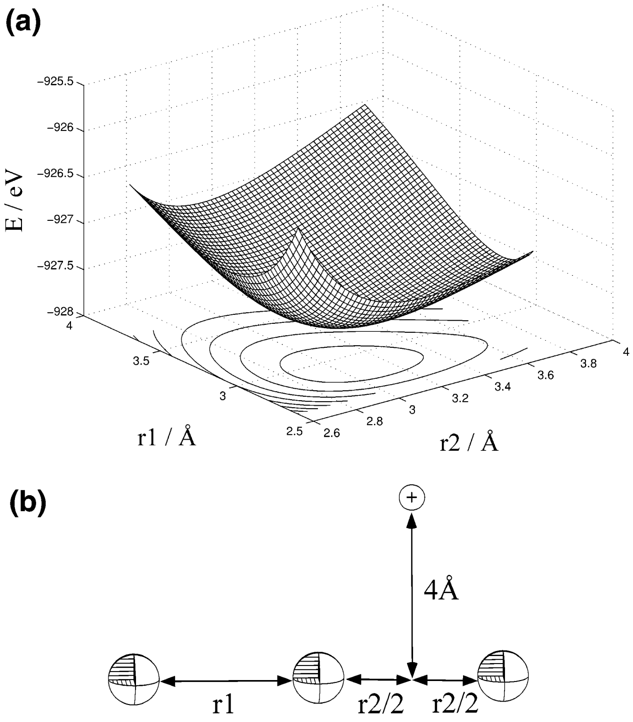


Figure 27. (a) Calculated energy of I_3^- as a function of r1 and r2 (MP2) with the cation modeled by a point charge; (b) the model used for the calculation. *J. Chem. Soc., Dalton Trans.* **2000**, 2449, reprinted with permission of the Royal Society of Chemistry. Copyright 2000.

IV.2 Higher Polyiodides

Geometrical optimization of a linear (D_{ih}) pentaiodide ion results in the $[(I^-)\cdot 2I_2]$ configuration, which also is found in crystal structures. The calculated atomic charges reveal that the central iodine atom is the most negatively charged. Säthre and coworkers have shown that the charge-transfer interaction takes place predominantly through the p-orbitals. Consequently, it is possible to describe the bond in terms of a delocalized (5c,6e) bond in analogy with the Rundle-Pimentel description of the triiodide. Applying a (4c,6e) bond, the linear I_4^{2-} ion can also be described using this model.

Rundle et al. describe the V-shaped pentaiodide ion as a resonance structure of triiodide ions.[217b] Each arm of the V-shaped pentaiodide corresponds to a linear triiodide ion which in turn engages a p-orbital of the apical I^-. Datta et al. report that the linear and V-shaped pentaiodide ions are quite similar with respect to energy and orbital population.[223] Population analysis shows that the bonding is almost completely dominated by the p-orbitals, thus showing that the linear and V-shaped pentaiodide ions can be rationalized using the same general type of bonding scheme.

Lin and co-workers describe the bonding of the V-shaped pentaiodide utilizing the VSEPR model. In this model, the apical iodide has two lone-pairs, and the π-electrons are distributed in three lone-pairs which can be regarded as sp^2-hybridized. They conclude that covalent bonds only exist between atoms having a coordination number of four (ion-pairs included). The bond between the apical iodide ion and the iodine molecules is described as mainly dative.

The zigzag I_8^{2-} ion was also successfully described by Lin et al.[227] The bridging iodine molecules, which cannot interact with the delocalized p-orbitals, instead interact with the sp^2-hybridized π-electrons of the terminal atoms of the triiodide ions. This situation is equivalent to that of the L-shaped pentaiodide, where one triiodide ion is missing from the I_8^{2-} configuration.

The models described above are applicable to other larger polyiodides. However, in several cases problems in the bonding description appear. One example is the I_{16}^{4-} ion, which is comprised of two I_8^{2-} units connected via the terminal iodine atoms of two triiodides (two donors) in each octaiodide. High coordination numbers (≤ 6) and interaction angles deviating considerably from 90 and 180° also contribute to the difficulties in rationalizing the bonding in covalent terms.

The interactions in these cases are more appropriately described as that of vdW or closed-shell type. The transition from covalent bonding to closed-shell interactions is diffuse, a property highlighted by the bond flexibility of the triiodide ion. Indeed, for the higher polyiodides, and even some of the smaller ones, it is not easy to distinguish between a covalent I−I bond and a closed-shell I···I interaction. Thus, even if the interaction can be described using a covalent bonding model it might be better to describe it in terms of closed-shell interactions, depending on the length of the I···I distance.

A statistical analysis of the intra- and intermolecular contacts in polyiodides does not support any specific bonding model.[228] The contacts in triiodide have three preferred regions: 2.7−3.0 Å, 3.4−3.8 Å, and 4.0−4.5 Å (Figure 28a). The latter corresponds to vdW contacts, while the first one corresponds to the intramolecular distances in I_2 and I_3^-. The interpretation of the flat 3.4−3.8 Å region is less obvious, but one hypothesis is that no dramatic qualitative changes in bonding occurs in this region. The contacts in the fragment I−I−I···I are dominated by intermolecular interactions (Figure 28b).

The observed and calculated vibration frequencies for higher polyiodide species, viz. those of I_5^- shown in Table 1, give some insight into the bonding situation. One should be aware, however, of the potential influence of effective reduced masses, solid-state packing, or solvation. More qualitative information is obtained from the vibration modes, as highlighted for the pentaiodide ion studied in ref 50. These results strongly support a bonding model consisting of two iodine molecules coordinated to an apical iodide $[(I^-)\cdot 2I_2]$.

Quantum chemical calculations indicate that the chemical bonding in the secondary-bond region (between 3 and 4 Å) can be very adequately described in terms of weak covalent bonding between I^- and I_2 fragments in polyiodides.[228] The electron density map of the $I_2 \cdots I^-$ interaction shows that there is substantial electron density between the I_2 and I^- fragments at a distance less than 4 Å (Figure 29c). Both the fitted Morse exponential function and the change in electrostatic interaction indicate that covalent interaction, where electron-transfer becomes important, starts at separations of around 4.5 Å. The BSSE-corrected interaction energy at MP2 level for I_3^- as a function of the distance between the centers of mass of the two “fragments” (Figure 30) indicates that the main contributions to the interaction energy, at large distances, are ion-quadrupole, dispersion, and inductive interactions. The dispersion interaction is most apparent at a 4 Å separation of the fragments. This is in rather good agreement with vdW distances found in the literature. At this distance, the BSSE is estimated to account for 2% of the total interaction energy, which from a calculational point of view is fairly acceptable. For separations greater than 5.5 Å, induction and ion-quadrupole interactions dominate. The inclusion of dynamic correlation for the V-shaped pentaiodide results in a substantial shortening of the $I_2{-}I^-$ distances. However, the total electron density map (Figure 29d) and NLMO/NPA bond orders indicate charge-transfer or covalent interactions in the range of ”secondary bonding”. Also, the difference electron density map (Figure 30) shows a charge-transfer from two independent 5p-orbitals of the I^- fragment to the 5p−5p-orbital based LUMOs of the two I_2 fragments, thus mimicking the bonding situation in I_3^-. Thus, the term ”secondary bonding” should be regarded as a purely pragmatic invention to facilitate structural rationalization in polyiodides.

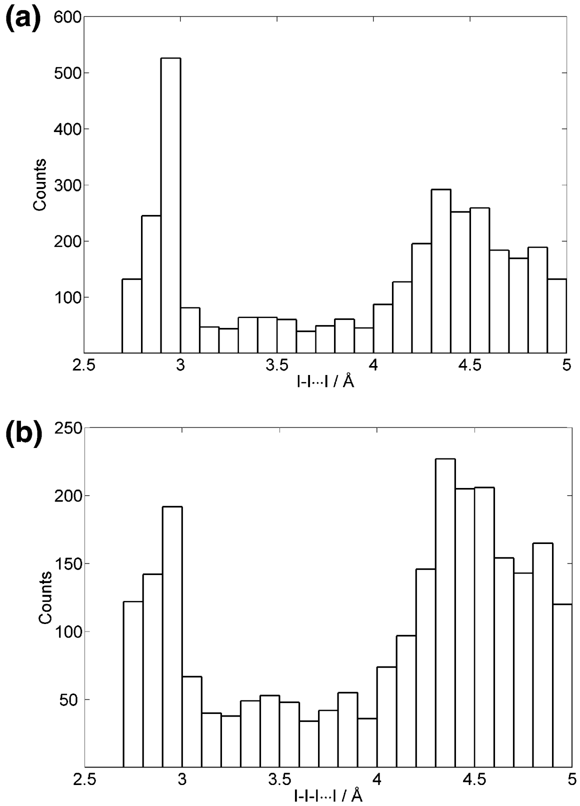


Figure 28. Histogram of I−I distances from an (a) I_2 and (b) I_3 fragment. *Eur. J. Inorg. Chem.* **2002**, 1203, reprinted with permission of Wiley-VCH. Copyright 2002.

IV.3 Metal Iodide−Iodine Systems

The I···I interactions in the binary gold, cadmium, and mercury iodide−iodine structures are most ap-

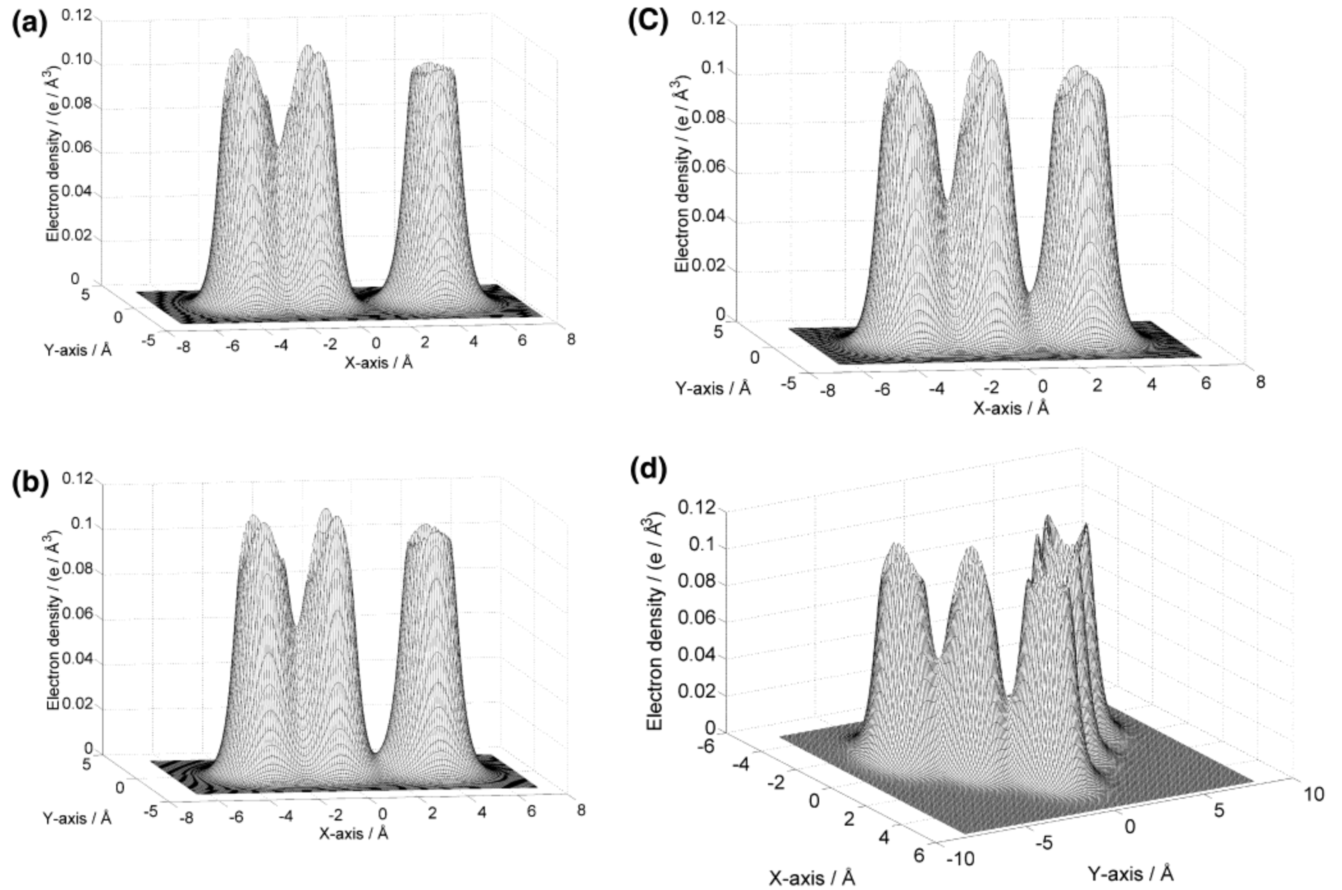


Figure 29. The total electron density of the $I_2 \cdots I^-$ interaction in I_3^- at (a) 5.0 Å, (b) 4.0 Å, and (c) 3.5 Å; (d) the total electron density of the pentaiodide ion. In panels a–c, the iodide is on the right-hand side and the increase in total electron density between the I^- and the I_2 fragments going from 5.0 to 3.5 Å can clearly be seen, approach almost 1/3 of the one between the iodine atoms in the I_2 fragment at 3.5 Å. *Eur. J. Inorg. Chem.* **2002**, 1203, reprinted with permission of Wiley-VCH. Copyright 2002.

propriately described as being analogous to the bonding in polyiodides. Notably, the interaction between the donor and acceptor generally is weaker than in the pure polyiodides [at least if based on $d(I \cdots I)$ values]. Thus, the complex metal iodides are less strong donors than I^- and I_3^-. In nonbinary metal iodide–iodine systems, the $I \cdots I$ interaction in general is stronger than in the binary systems.

IV.3.1 Gold ≈ Iodine?

Both neutral iodine and gold have an n-1 valence electron configuration ([Kr]$4d^{10}5s^25p^5$ and [Xe]$4f^{14}5d^{10}6s^1$, respectively). Consequently, both the ions I^- (s^2p^6) and Au^- ($d^{10}s^2$) have closed valence shells. An interesting feature of gold is that it is the most electronegative of all metals. Actually, the electronegativity is very close to that of iodine (gold 2.4 and iodine 2.5).[229a] In addition, gold is considered as having halogen-like behavior in several complexes.[229] This implies that gold iodides should show similarities to the polyiodides. A comparison between some gold halides and polyhalides is shown in Table 6. The AuI_2^- ion is linear and thus geometrically analogous to the I_3^- ion. Both the $AuCl_4^-$ and ICl_4^- ions are square-planar. However, no example of a square-planar polyiodide has been characterized. As shown in section III, only linear and V/L-shaped pentaiodides are known.

Table 6. Comparison of Gold and Iodine Ions

ox state	gold halide	polyhalide	geometry
-I	Au^-	I^-	∼
+I	AuI_2^-	II_2^-	linear
+I	$AuCl_2^-$	ICl_2^-	linear
+III	$AuCl_4^-$	ICl_4^-	square planar
	AuI_4^-	I_5^-	square planar; linear or V/L-shaped

When comparing the energies for AuI_4^- and I_5^-, it becomes clear that the square-planar geometry not is the most stable one in either case. For both ions, the L-shaped geometry is lower in energy, 58.6 and 75.8 kJ mol^{-1} (MP2) lower than for the square-planar geometry of AuI_4^- and I_5^-, respectively.[168] In the case of I_5^-, an even lower total energy can be obtained by allowing the ion to relax into the V-shaped geometry discussed above. However, this conformation is only favored by 3.9 kJ mol^{-1} (MP2) compared to the L-shaped one.

The difference in energy between different geometries is small in both systems being of the same order of magnitude as moderately strong hydrogen bonds (10–65 kJ mol^{-1}). Despite all this, it is interesting to note that the angles in the two L-shaped ions AuI_4^- and I_5^- are almost identical, and that the only significant difference is the length of the linear component (terminal $I \cdots I$ distance in AuI_2^- 5.312 Å and in I_3^- 5.940 Å).[168]

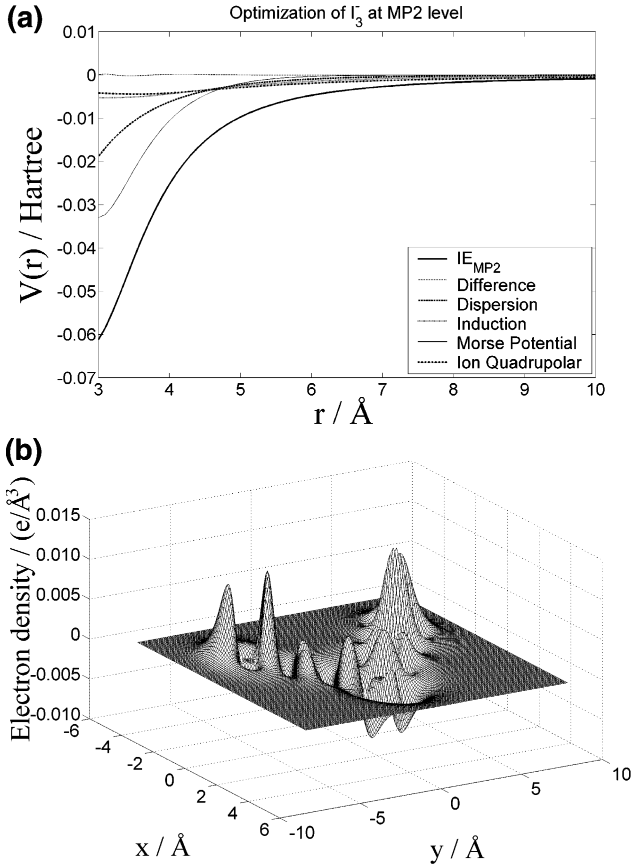


Figure 30. (a) The interaction energy at MP2 level and models as function of the shortest distance between the fragments plotted; (b) the difference electron density of the $I^-\cdots I_2$ interaction in I_5^-. *Eur. J. Inorg. Chem.* **2002**, 1203, reprinted with permission of Wiley-VCH. Copyright 2002.

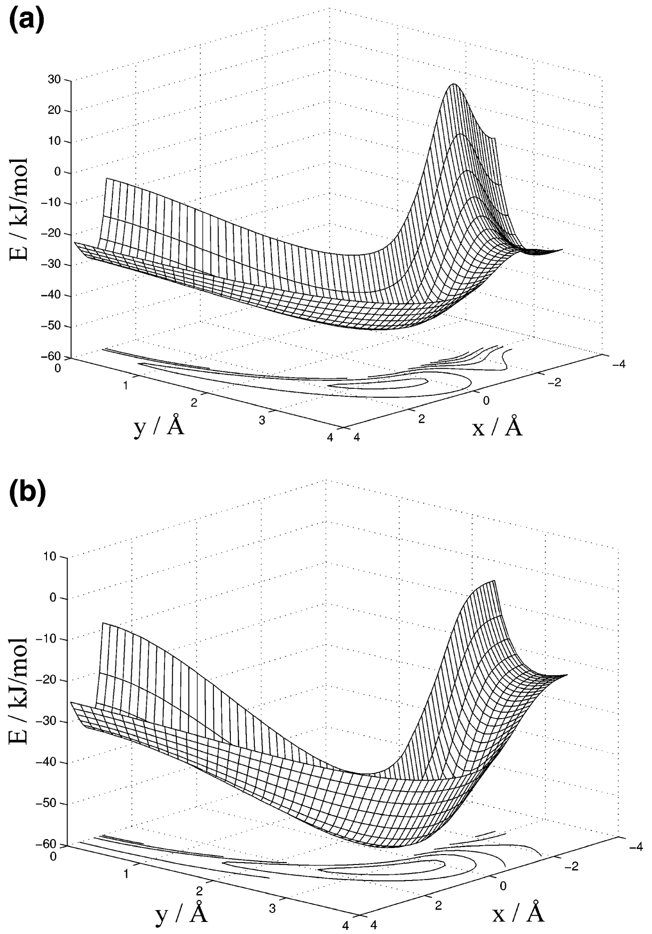


Figure 31. The counterpoise corrected PES of (a) $I_3^-\cdots I_2$ and (b) $AuI_2^-\cdots I_2$. *Chem. Eur. J.* **1999**, 305, reprinted with permission of Wiley-VCH. Copyright 1999.

The similarity between the L-shaped AuI_4^- and I_5^- implies that AuI_2^- is an appropriate guest molecule in polyiodide structures, and that AuI_2^- and I_3^- could be expected to be exchangeable. The PES's of $I_3^-\cdots I_2$ and $AuI_2^-\cdots I_2$ interaction support this assumption.

The PES of I_3^- and I_2 (Figure 31a) display two minima, one corresponding to the L-shaped geometry described above and one T-shaped. This is surprising since to date no discrete, T-shaped polyiodide structures have been reported. However, BSSE (basis set superposition error) contributes significantly to the interaction energy in the investigated range. The largest contribution, and hence the largest error, is found for the T-shaped structure. The energy difference between the L-shaped and the T-shaped geometry is significant, and even larger when corrected for BSSE. The relative difference in energy might explain why only L-shaped I_5^- ions are observed experimentally. However, in solid triiodide compounds the triiodide ions often form T-shaped aggregates and networks.

The corresponding PES of AuI_2^- and I_2 (Figure 31b) displays only one minimum, the one corresponding to the bent L-shape. This indicates that it should be possible to use AuI_2^- to replace I_3^- in polyiodides, or vice versa in gold(I) compounds containing AuX_2^-.

A comparison between the two PES shows that the interaction between AuI_2^- and I_2 is significantly stronger than the one between I_3^- and I_2, $I_3^-\cdots I_2$ having a flatter potential surface than $AuI_2^-\cdots I_2$. Therefore, the potential energy surface for the pure polyiodide is more strongly affected by BSSE. After counterpoise correction the interaction energy is decreased by 20% at the L-shaped minimum compared with a modest change of 7% for the PES of $AuI_2^-\cdots I_2$.

Thus, calculations show that AuI_2^- and I_3^-, and AuI_4^- and I_5^- are closely related and that both complex AuI_2^- and AuI_4^- ions are suitable candidates as guest molecules in polyiodide networks. This hypothesis is also verified, at least partly, by the experimental isolation of such exchange compounds (section III.6.1).

V. Concluding Remarks

Polyiodide compounds exhibit a vast diversity of structures, preferentially of low-dimensional character, with conducting properties ranging from insulators to metals. The present review is the first comprehensive overview of polyiodide chemistry since the 1970s, during which time the results of a large number of investigations have been published. These studies on both their structures and physical properties, of pure and substituted, solid as well as liquid polyiodides, have shown that their macroscopic properties can be understood through the level of interaction between three fundamental, simple building blocks: I^-, I_2, and I_3^-.

In this review, increasing structural complexity is attributed to the increase in I_2 content of the compounds and through the interaction between the fundamental building blocks. The literature data have been systematized and relations to the corresponding charge-transfer as well as metal-iodide substituted compounds have been made. The structural and physical properties have also been related to the bonding properties in terms of weak covalent bonding extending to rather long I–I separations.

The fundamental knowledge of polyiodide materials is now such that the application of polyiodide systems into interesting directions involving electronic and magnetic materials, host–guest compounds and as electrolytes for use in electrochemical devices, such as batteries and solar cells, is unprecedented.

VI. Acknowledgments

The Swedish Research Science Council is acknowledged for their financial support. Jan Rosdahl is thanked for his help in preparing this review. Also, the Royal Society of Chemistry and Wiley-VCH are acknowledged for permission to reprint the in-text figures 3.10, 3.46, and 3.51 in addition to the figures explicitly noted in the figure legends.

VII. Abbreviations

Ad	adamantyl
BEDT-TTF	bis(ethylenedithio)tetrahydrofulvalene
BOS	bond order surface
BSSE	basis set superposition error
CCSD	coupled cluster singles and doubles
4-cnpy	4-cyanopyridine
Cp	cyclopentadienyl
CSD	Cambridge Structural Database
dafone	4,5-diazafluoren-9-one
dbcr	dibenzo-18-crown-6
DMET	2-(4,5-dimethyldidelenol-2-ylidene)-5,6dihydrodithiolo [4,5-b]dithiin
DMFc	decamethylferrocene
DMSO	dimethyl sulfoxide
DMT-TTF	bis(dimethylthio)tetrahydrofulvalene
Dod	dodecyl
Dtpcp2,11-dithia[3.3]	paracyclophane
$(Et)_4$todit	4,5,6,7-tetrathiocino[1,2-b:3,4-b′]diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione
EXAFS	extended X-ray absorption fine structure
Fc	ferrocene
$(GH)_2$	glyoxime
HF	Hartree–Fock
hmt	hexamethylenetetramine
HOMO	highest occupied molecular orbital
L	$(C_5H_5)Fe(C_5H_4)C(O)CH_2Fe(C_5H_5)(CO)_2$
LUMO	lowest unoccupied molecular orbital
LXS	liquid X-ray scattering
mbit	1,1′-bis(3-methyl-4-imidazoline-2-thione)-methane
mebesel	*N*-methylbenzo-thiazole-2(3H)-selone
MP2	Møller–Plesset perturbation, 2nd order
μ-N	(μ-nitrido)((tetraphenylporphyrinato)iron)-((phthalocyaninato)iron)
NLMO	natural localized molecular orbitals
NPA	natural population analysis
Oc	*n*-octyl
OETPP	octaethyltetraphenylporphyrin
Pc	phthalocyaninate(2-)
PES	potential energy surface
Phen	1,10-phenanthroline
i-PrTaz	1,3,5-triisopropyl-tetrahydro-1,3,5-triazinium
Py	pyridine
Pz	pyrazolato
RDF	radial distribution function
R_2timdt	1,3-dialkylmidazolidine
Salen	*N*,*N*′-ethylenebis(salicylideneiminate) dianion
TAAB	tetrakis-(anhydroaminobenzaldehyde)
TCNQ	tetra-cyanoquinodinlethanide
TTT	tetrathiatetracene
Ur	urotropin, hexamethylenetetramine (cf. hmt)
vdW	van der Waals

VIII. References

(1) Weeks, M. E. In *Discovery of the Elements*; Journal of Chemical Education: Easton, PA, 1945. Curtouis, B. *Ann. Chim.* **1813**, *91*, 304.
(2) Gay Lussac, J. L. *Ann. Chim.* **1814**, *91*, 5.
(3) Pelletier, P.; Caventou, J. B. *Ann. Chim.* **1819**, *10*, 164.
(4) Jörgensen, S. M. *J. F. Prakt. Chem.* **1870**, *2*, 347.
(5) Teitelbaum, R. C.; Ruby, S. L.; Marks, J. *J. Am. Chem. Soc.* **1980**, *102*, 3522.
(6) Colin, J. J.; de Claubry, H. G. *Ann. Chim.* **1814**, 90, 87. Greenwood, N. N.; Earnshaw, A. In *Chemistry of the Elements*; Pergamon Press: 1990, Chapter 17.
(7) Jörgensen., S. M. *J. F. Prakt. Chem.* **1870**, *2*, 433.
(8) Coindet, J. F. *Ann. Chim.* **1820**, *15*, 49.
(9) Mooney, R. C. L. *Z. Kristallogr.* **1935**, *90*, 143.
(10) (a) Blake, A. J.; Gould, R. O.; Parsons, S.; Radek, C.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 237. (b) Blake, A. J.; Gould, R. O.; Li, W. S., Lippolis, V.; Parsons, S., Radek, C.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 293. (c) Blake, A. J.; Devilliano, F. A.; Gould, R. O.; Li W.-S.; Lippolis, V., Parsons, S.; Radek, C.; Schröder, M. *Chem. Soc. Rev.* **1998**, *27*, 195. (d) Blake, A. J.; Lippolis, V.; Parsons, S.; Schröder, M. *Chem. Comm.* **1996**, 2207. (e) Bailey, R. D.; Hook, L. L.; Pennington, W. T. *Chem. Comm.* **1998**, 1181. (f) Rietman, E. A. *Mater. Res. Bull.* **1990**, *25*, 649.
(11) Stegemann, H.; Tebbe, K.-F.; Bengtsson L. A. *Z. Anorg. Allg. Chem.* **1995**, *621*, 165. Lang, E. S.; Strähle, J. *Z. Anorg. Allg. Chem.* **1996**, *622*, 981.
(12) Landrum, G. A.; Goldberg, N.; Hoffman, R. *J. Chem. Soc., Dalton* **1997**, 3605 (and references therein).
(13) (a) Coppens, P. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 1, p 333. (b) Marks, T. J.; Kalina, D. W. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 1, p 197.
(14) Muller, H.; Madsen, D.; Wanka, S.; Wosnitza *J. Synth. Met.* **2001**, *120*, 737. McDonald, R.; Brom, H.; Laukhina, E.; Singleton, *J. Synth. Met.* **2001**, *120*, 865.
(15) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J., *J. Chem. Soc. Chem. Commun.* **1977**, 579. Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem.* **1974**, *12*, 11. Chiang, C. K.; Fischer, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098. Chiang, C. K.; Druy, M. A.; Gau, S. C.; Heeger, A. J.; Louis, E. J.; MacDiarmid, A. G.; Park, Y. W.; Shirakawa, H. *J. Am. Chem. Soc.* **1978**, *10*, 1013. Heeger, A. J. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2591.
(16) Stegemann, H.; Reiche, A.; Schnittke, A.; Füllbier, H.; *Electrochim. Acta* **1992**, 183, 379. Stegemann, H., Thesis, University of Greiwswald, 1989.
(17) de Grotthus, C. J. D. *Ann. Chim.* **1806**, *58*, 54.
(18) Owens, B. B.; Pate, B.; Skarstad, P. M.; Worburton, D. L. *Solid State Ionics* **1983**, *9/10*, 1241. Falques, E.; Molinre, P.; Berdahl, P.; Nguyen, T. P.; Mansot, J.; *Phys. C.* **1994**, *219*, 297. Salaneck, W. R.; Thomas, H. R.; Bigelow, R. W.; Duke, C. B.; Plummer, E. W.; Heeger, A. J.; Macdiarmid, A. G.; *J. Chem. Phys.* **1980**, *73*, 4746. Licht, S. *Sol. Energy Mater. Sol. Cells* **1995**, *38*, 305. Rajpure, K. Y.; Bhosale, C. H. *Mater. Chem. Phys. 2000, 64*, 14. Grätzel, M. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 314. Rajpure K. Y.; Bhosale C. H. *Mater. Chem. Phys.* **2000**, *63*, 263. Licht, S.; Khaselev, O.; Ramakrishnan, P. A.; Faiman, D.; Katz, E. A.; Shames, A.; *Sol. Energy Sol. Mater. Cells* **1998**, *C51*, 9. Owens B. B.; Bottleberghe J. R. *Solid State Ionics* **1993**, *62*, 243. Rajpure K. Y.; Bhosale, C. H. *Chem. Mater. Chem. Phys.* **2000**, *64*, 70.

(19) Tebbe, K.-F. In *Homoatomic Rings, Chains, Macro-moleules of Main-Group Elements*; Rheingold, A. L, Ed.; Elsevier: Amsterdam 1977; p 551. Tebbe, K.-F., Thesis, University of Köln, 1975. Stepin, B. D.; Stepina, S. B. *Russ. Chem. Rev.* **1986**, *55*, 812. Popov, A. I. In *Polyhalogen Complex Ions in Halogen Chemistry*; Gutman, Ed.; Academic Press: London, 1967; p 225. Popov, A. I., *Int. Rev. Sci., Inorg. Chem. Ser. II*, Butterworth: London, 1975, *3*, 53. Popov, A. I.; Surles, T., Interhalogen Compounds; Polyhalide Anions, *Int. Rev. Sci., Inorg. Chem. Ser. II*, Butterworth: London, 1975, *3*, 177. Wiebenga, E. H.; Havinga, E. E.; Boswijk, K. H. *Adv. Inorg. Chem. Radiochem.* **1961**, *3*, 133.

(20) Tebbe, K.-F. *Z. Kristallogr. Suppl.* **1996**, *11*, 52.

(21) Fornier de Violet, P. *Chem. Phys. Lett.* **1976**, *37*, 478.

(22) Davies, C. G.; Gillespie, J. R.; Irel, P. R.; Sowa, J. M. *Can. J. Chem.* **1974**, *52*, 2048. Faggiani, R.; Gillespie, R. J.; Kapoor, R.; Lock, C. J. L.; Vekris, J. E. *Inorg. Chem.* **1988**, *27*, 4350. Passmore, J.; Sutherl, G.; White, P. S. *Inorg. Chem.* **1981**, 2169. Apblett, A.; Grein, F.; Johnson, J. P.; Passmore, J.; White, P. S. *Inorg. Chem.* **1986**, *25*, 422. Passmore, J.; Taylor, P.; Whidden, T.; White, P. S. *Can. J. Chem.* **1979**, *57*, 968. Bigoli, F.; Pellingheli, M. A.; Crisponi, G.; Deplano, P.; Trogu, E. F. *J. Chem. Soc., Dalton Trans.* **1985**, 1349.

(23) (a) Robertson, K. N.; Cameron, T. S.; Knop, O. *Can. J. Chem.* **1996**, *74*, 1572. (b) Bakshi, P. K.; James, M. A.; Cameron T. S.; Knop O. *Can. J. Chem.* **1996**, *74*, 559. (c) Horn, C.; Scudder, M.; Dance, I. *CrystEngComm* **2000,** *9*, 1. (d) Horn, C.; Scudder, M.; Dance, I. *CrystEngComm* **2001**, *1*, 1. f) Horn, C.; Scudder, M.; Dance, I. *CrystEngComm* **2000**, *36*, 1. (e) Horn, C.; Scudder, M.; Dance, I. *CrystEngComm* **2001**, *2*, 1.

(24) Palmer, D. A.; Ramette; R. W.; Mesmer, R. E. *J. Solution Chem.* **1984**, *9*, 673. Ramette, R. W.; Ford, Jr, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 5001. Genser, E. E.; Connick, R. E. *J. Chem. Phys.* **1973**, 58, *3*, 990.

(25) Bailar, J. C.; Eméleus, H. J.; Nyholm, R.; Trotman-Dickenson, A. F. *Comprehensive Inorg. Chem.* **1973**, *2*, 1539.

(26) Calabrese, V. T.; Khan, A. *J. Phys. Chem. A.* **2000**, *104*, 1287.

(27) Blake, A. J.; Gould, R. O.; Li, Wan-Sheung; Lippolis, V.; Parsons, S.; Schröder, M. *Cryst. Eng.* **1999**, *2*, 153.

(28) Menon, S.; Rajasekharan, M. V. *Inorg. Chem.* **1997**, *36*, 4983.

(29) Stegemann, H.; Reiche, A.; Schnittke, A; Füllbier, H. *Electrochim. Acta* **1992**, *183*, 379. Stegemann, H. Thesis, University of Greiwswald, 1989.

(30) Andersson, A.; Sun, T. S. *Chem. Phys. Lett.* **1970**, *6*, 611. Stojakovic, D. R. Ph.D. Thesis, Northwestern University, Evanston, Illinois, **1977**.

(31) Magana, R. J.; Jannin, J. S., *Phys. Rev.* **1985**, *32b*, 3819.

(32) Shanabrook, B. V.; Lannin, J. S. *Solid State Com.* **1981**, *38*, 49.

(33) (a) Milne, J. *Spectrochim. Acta* **1992**, *48a*, 553. (b) Deplano, P., Devillanova, F. A.; Ferraro. J. A, Isaia, F., Lippolis, V.; Mercuri, M. L., *Appl. Spectrosc.* **1992**, *46*, 1625. (c) Zambounis, J. S.; Kamitsos, E. I.; Patsis, A. P.; Papavassiliou, G. C. *J. Raman Spectrosc.* **1992**, *23*, 81. (d) Bengtsson L.; Füllbier H.; Holmberg B.; Stegemann, H. *Mol. Phys.* **1991**, *73*, 283.

(34) (a) Besnard, M.; Del Campo, N. *J. Mol. Liq.* **1991**, *48*, 183. (b) Shen, Y. R.; Rosen, H.; Stenman, F., *Chem. Phys. Lett.* **1968**, 1, 671. (c) Klaboe, P. *J. Am. Chem. Soc.* **1967**, *89*, 3667.

(35) Kochi, J. K. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1227.

(36) Nakashima, S.; Norimoto, M.; Harima, H.; Hamanaka, Y.; Grigoryan, L. S.; Tokumoto, M. *Chem. Phys. Lett.* **1997**, *268*, 359.

(37) Faulques, E.; Molinie, P.; Berdahl, P.; Nguyen, T. P.; Mansot, J.-L. *Physica* **1994**, *C219*, 297. Kishio, K.; Pooke, D.; Trodahl, H. J.; Subramaniam, C. K.; Kotaka, Y.; Kitao, S.; Maeda, Y. *J. Supercond.* **1994**, *7*, 117.

(38) Howard, Jr., W. F.; Andrews, L. *J. Am. Chem. Soc.* **1975**, *97*, 2956.

(39) Boyle, P. D.; Christie, J.; Dyer, T.; Godfrey, S. M.; Howson, I. R.; McArthur, C.; Omar, B.; Pritchard, R. G.; Williams, G. R. *J. Chem. Soc., Dalton* **2000**, *18*, 3106.

(40) Deplano, P.; Ferraro, J. R.; Mercuri, M. L.; Trogu, E. F. *Coord. Chem. Rev.* **1999**, *188*, 71. Bigoli, F.; Deplano, P.; Ienco, A.; Mealli, C.; Mercuri, M. L.; Pellinghelli, M. A.; Pintus, G.; Saba G.; Trogu, E. F. *Inorg. Chem.* **1999**, *38*, 4626.

(41) Deplano, P.; Devillano, F. A.; Ferrara, J. R.; Mecuri, M. L.; Lippolis, V.; Trogu, E. F. *Appl. Spectrosc.* **1994**, *48*, 1236.

(42) Svensson P. H.; Kloo, L. *J. Chem. Soc., Dalton Trans.* **2000**, 2449.

(43) Kloo, L.; Svensson, P. H.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* **2000**, 1061.

(44) Gabes, W.; Gerding, H. *J. Mol. Struct.* **1972**, *14*, 267.

(45) (a) Maki, A. G.; Foneris, R. *Spectrochim. Acta* **1967**, 23a, 867. (b) Kaya, W.; Mikami, N.; Udgawa, Y.; Ito, M. *Chem. Phys. Lett.* **1972**, *16*, 151. (c) Heyde, M. E.; Rimai, L.; Kilponen, R. G.; Gill, D. *J. Am. Chem. Soc.* **1972**, *94*, 5222. Gabes, W.; Gerding, H. *J. Mol. Struct.* **1972**, *14*, 267.

(46) Bengtsson, L. A.; Oskarsson Å; Stegemann, H.; Redeker, A. *Inorg. Chim. Acta* **1994**, 215, 33.

(47) Mittag, H.; Stegemann, H.; Füllbier, H.; Irmer, G. *J. Raman. Spectrosc.***1989**, *20*, 251.

(48) Parrett, F. W.; Taylor, N. J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2461.

(49) Nour, E. M.; Chen, L. H.; Laane, J. *J. Phys. Chem.* 1986, *90*, 2841.

(50) Sharp, S. B.; Gellene, G. I. *J. Phys. Chem.* **1997**, *101*, 2192.

(51) (a) Ferraro, J. R.; Martin, K.; Furlani, A.; Russo, M. V. *Appl. Spectrosc.* **1984**, *38*, 267. (b) Deplano, P.; Devillano, F. A.; Ferraro, J. R.; Mecuri, M. L.; Lippolis, V.; Trogu, E. F. *Appl. Spectrosc.* **1994**, *48*, 1236. (c) Teitelbaum, R. C.; Ruby, S. L.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 3322.

(52) Ayad, M. M. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2369. Nour, E. M.; Chen, L. H.; Laane, J. *J. Raman Spectrosc.* **1986**, *17*, 467. Nour, E. M.; Chen, L. H.; Laane, J. *J. Phys. Chem.* **1986**, *90*, 2841. Nour, E. M.; Shahada, L. A.; Sadeek, S. A.; Teleb, S. M. *Spectrochim. Acta 1995*, 471. Nour, E. M.; Shahada, L. A.; Alkaabi, S. S. *Bull. Chim. Fr.* **1989**, 727. Nour, E. M.; Shahada, L. *Spectrochim. Acta* **1989**, *45A*, 1033. Nour, E. M. *Spectrochim. Acta* **1999**, *167*, 1033.

(53) (a) Bandrauk, A. D.; Truong, K. D.; Carlone, C.; Hanson, A. W. *J. Phys. Chem.* **1987**, *91*, 2063. (b) Spiro T. G. *Acc. Chem. Res.* **1974**, *7*, 339. (c) Zambounis, J. S.; Kamitsos, E. I., Terzis, A.; Papavassiliou, G. C. *J. Mol. Struct.* **1988**, *174*, 1989.

(54) (a) Kiefer, W.; Bernstein, H. J. *Chem. Phys. Lett.* **1972**, *16*, 5. (b) Loos, K. R.; Jones, A. C. *J. Phys. Chem.* **1974**, *22*, 2306. (c) Mohammed, M. R.; Sherman, W. F. *J. Mol. Struct.* **1984**, *115*, 27. (d) Zambounis, J. S.; Kamitsos, E. I.; Patsis, A. P.; Papavassiliou, G. C. *J. Raman Spectrosc.* **1992**, *23*, 81.

(55) Lewis. G. N.; Wheeler, P. *Z. Physik. Chem.* **1906**, *56*, 179.

(56) Audrieth, L. F.; Birr, E. J. *J. Am. Chem. Soc.* **1933**, *55*, 668.

(57) (a) Zingaro, R.; Ver-Werf, C. A.; Kleinberg, J. *J. Am. Chem. Soc.* **1951**, *73, 88*. (b) Kortum, G.; Wiliski, H. *Z. Phys. Chem.* **1953**, *202*, 35.

(58) Reid, C.; Mulliken, R. S. *J. Am. Chem. Soc.* **1954**, *76*, 3869.

(59) Tassaing, T.; Besnard, M. *J. Phys. Chem.* **1997**, *101*, 2803.

(60) (a) Akamuta, H.; Inokuchi, H.; Matsunaga, Y. *Bull Chem. Soc. Jpn.* 1956, *29*, 213. (b) Uschida, T.; Akamatu, H. *Bull Chem. Soc. Jpn.* **1962**, *35*, 6. (c) Kommandeur, J.; Hall, F. R. *J. Phys. Chem.* **1961**, *34*, 129.

(61) Emge, T. J. *J. Am. Chem. Soc.* **1986**, 695.

(62) Kusabayashi, S.; Mikawa, H.; Kawai, S.; Uchida, M.; Kiriyama, R. *Bull Chem. Soc. Jpn.* **1964**, *37*, 811.

(63) (a) Gabes, W.; Stufkens, D. J.; Gerding, H. *J. Mol. Struct.* **1973**, *17*, 329. (b) Gabes, W.; Stufkens, D. J. *Spectrosc. Chim. Acta* **1974**, *30A*, 1835.

(64) Kim, H. *Biopolymers* **1982**, *21*, 2083.

(65) (a) Noltemeyer, M.;. Saenger, W. *Nature* **1976**, *259*, 26. (b) Saenger, W. A. *Naturwissenschraften* **1984**, *71*, 31.

(66) Mizuno, M.; Tanaka, J.; Harada, I. *J. Phys. Chem.* **1981**, *85*, 1789.

(67) (a) Gabes, W.; Stufkens, D. J.; Gerding, H. *J. Mol. Struct.* **1974**, *20*, 343. (b) Bowmaker, G. A.; Hacobian, S. *Aust. J. Chem.* **1968**, *21*, 551. (c) Harada, H., Nakamura, D.; Kubo, M. *J. Magn. Reson.* **1974**, *13*, 56. (d) Lucken, E. A. C. *Z. Anal. Chem.* **1975**, *273*, 337.

(68) Kojima, S.; Shimauch, A.; Hagiwara, S.; Abe, Y. *J. Phys. Soc. Jpn.* **1955**, *23*, 1963.

(69) Nakamura, D.; Kubo M. *Adv. Nucl. Quadrupole Reson.* **1975**, *2*, 117.

(70) Genser, E. E.; Connick, R. E. *J. Chem. Phys.* **1973**, *58*, 990.

(71) (a) Ehrlich, B. S.; Kaplan, M. *J. Chem. Phys.* **1969**, *351*, 603. (b) Teitelbaum, R. C.; Ruby, S. T.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3215. (c) Teitelbaum, R. C.; Ruby, S. T.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 3522.

(72) (a) Arban, M.; Holmberg, S.; Lundholm, M.; Siegbahn, H.; Gropen, O.; Wahlgren, U. *Chem. Phys.* **1983**, 113. (b) Morss, L. R. J. *Chem. Therm.* **1975**, *7*, 709. (c) Buchem, R. *Präperative und röntgenographische Untersuchungen an Polyiodiden von Ferrocen, decamethylferrocen und 1,1′-Dimethylferrocen*, Thesis, Köln, 1996. (d) Emge, T. J. *Inorg. Chem.* **1985**, *12*, 1736. (e) Dong, T.-Y.; Lin, H.-M.; Hwang M.-Y.; Lee T.-Y.; Tseng, L.-H.; Peng, S.; Lee, G. *J. Organomet. Chem.* **1991**, *414*, 227.

(73) (a) Banin, U.; Ruhman, S. *J. Phys. Chem.* **1993**, *98*, 4391. (b) Johnson, A. E.; Myers, A. B. *J. Phys. Chem.* **1996**, *100*, 2497.

(74) vdW radii of iodine are given in a number of references with a slight variation from 3.9 to 4.3 Å.

(75) van Boljhuis, F.; Koster, P. B.; Migchelsen, T. *Acta Cryst* **1967**, *23*, 90.

(76) (a) Kitaigorodskii, A. I.; Khotsyanova, T. L.; Struchkov, Y. T. *Zh. Fiz. Khim.* **1953**, *27*, 780. (b) Kitaigorodskii, A. I.; Khotsyanova, T. L.; Struchkov, Y.T. *Chem. Abstr.* **1955**, *49*, 2143.

(77) (a) Fujii, Y.; Hase, K.; Ohishi, Y.; Onodera, A.; Shimomura, O.; Takemura, K. *Phys. Rev. Lett.* **1987**, *58*, 796. (b) Takemura, K.; Minomura, S.; Shimomura, O.; Fujii, Y. *Phys. Rev. Lett.* **1980**, *45*, 1881.

(78) Marel, C. V. D.; Bras, W.; van der Lugt, W. *Mol. Phys.* **1988**, *64*, 445.

(79) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

(80) Bittner, M. *Präperative und röntgenographische Untersuchungen an Polyiodiden von 2,2′-Bipyridin*, Ph.D. Thesis, 1994, Köln.

(81) Cambridge Structural Database System, Database V. 5.14, 1997.

(82) Rusnik, J.; Swen-Walstra, S.; Migchelsen, T. *Acta Crystallogr.* **1972**, *B28*, 1331.
(83) Thomas, R.; More, F. H. *Acta Crystallogr.* **1980**, *B36*, 2869.
(84) Robertson, K. N.; Bakshi, P. K.; Cameron, T. S.; Knop, O. *Z. Anorg. Allg. Chem.* **1997**, *623*, 104.
(85) Beno, M. A.; Geiser, U.; Kostka, K. L.; Wang, H. H.; Webb, K. S.; Firestone, M. A.; Carlson, K. D.; Nunez, L.; Whangbo, M. H.; Williams, J. M. *Inorg. Chem.* **1987**, *26*, 1912.
(86) Neupert-Laves; K.; Dobler; M. *Helv. Chim. Acta* **1975**, *51*, 432.
(87) Ercolani, C.; Jubb, J.; Pennesi, G.; Russo, U.; Trigiante, G. *Inorg. Chem.* **1995**, *34*, 2535.
(88) Tebbe, K.-F.; Buchem, R. *Z. Anorg. Allg. Chem.* **1998**, *624*, 671.
(89) Hills, A.; Hughes, D. L.; Leigh, G. J.; Sers, J. R. *J. Chem. Soc., Dalton* **1991**, *1*, 61.
(90) Furmanova, N. G.; Struchkov, Yu. K. *Koord. Khim.* **1980**, *6*, 1275.
(91) Stegemann, H.; Oprea, A.; Nagel, K.; Tebbe, K.-F.*Z. Anorg. Allg. Chem.* **1997**, *623*, 89.
(92) Blake, A. J.; Gould, R. O.; Li, Wan-Sheung; Lippolis, V.; Parsons, S.; Radek, C.; Schröder, M. *Inorg. Chem.* **1998**, *37*, 5070.
(93) Pantenburg, I.; Tebbe K.-F. *Z. Naturforsch.* **2001**, *B56*, 271.
(94) Tebbe K.-F.; Nagel, K. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1323.
(95) Tebbe, K.-F.; Bittner, M. *Z. Anorg. Allg. Chem.* **1995**, *621*, 218.
(96) Shibaeva, R. P.; Lobkovskaya, R. M.; Yagubskii, E. B.; Kosttyucenko, E. E. *Sov. Phys. Crystallogr.* **1986**, 31, 657.
(97) Gieren, A.; Hubner, T.; Lamm, V.; Neidlein, R.; Droste, D. *Z. Anorg. Allg. Chem.* **1985**, *523*, 33.
(98) Kramer, J. A.; Herbstein, F. H.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1980**, *102*, 2293.
(99) Jander, J.; Pritzkow, H.; Trommsdorff, K.-U. *Z. Naturforsch.* **1975,** *B30*, 720.
(100) Farrugia, L. J.; Norman, N. C.; Pickett, N. L. *Acta Crystallogr.* **1998**, *C54*, 476.
(101) Blake, A. J.; Li, W. S.; Lippolis, V.; Schröder, M. *Acta Crystallogr.* **1998**, *C54*, 1410.
(102) Herbstein, F. H.; Kapon, M. *Acta Cryst.* **1972**, *A28*, 574.
(103) Dong, T.-Y.; Lin, H.-M.; Hwang, M.-Y.; Lee, T.-Y.; Tseng, L.-H., Peng, S.; Lee, G. *J. Organomet. Chem.* **1991**, *414*, 227.
(104) Akutagawa, T.; Abe, Y.; Nezu, Y.-I.; Nakamura, T.; Kataoka, M., Yamanaka, A.; Inoue, K.; Inabe, T.; Christensen, C. A.; Becher, J. *Inorg. Chem.* **1998**, *37*, 2330.
(105) Luss, H. R.; Smoth, D. L. *Acta Crystallogr.* **1980**, *B36*, 1580.
(106) (a) Cramer, F.; Bergmann, U.; Manor, P. C.; Noltemeyer, M. *Ann. der Chem.* **1976**, *7/8*, 76. (b) Noltemeyer, M.; Saenger, W. *J. Am. Chem. Soc.* **1980**, *102*, 2710. (c) Cramer, F.; Bergmann, U.; Manor, P. C.; Noltemeyer, M.; Saenger, W. *Liebigs Ann. Chem.* **1976**, 1169. (d) Herbstein, F. H.; Kaftory, M.; Kapon, M.; Saenger, W. *Z. Kristallog.* **1981**, *154*, 11. (e) Hinrichs, W.; Buttner, G.; Steifa, M.; Betzel, C. H.-; Zabel, V.; Fannemuller, B. P.; Saenger, W. *Science* **1987**, *238*, 205. (f) Someno, T.; Hoshizakit; Kozawa, K.; Uchid, A. T.; Hayashi, H.; Sugano T.; Kinoshita, M. B. *Chem. Soc. Jpn.* **1991**, *64*, 921. (g) Calabrese, V. T.; Khan, A. *J. Polymer Sci., Sect. A* **1999**, *37*, 2711. (h) Cesaro, A.; Edvino, J.; Silvano, S. *Biopolymers* **1980**, *19*, 1491. (i) Cesaro, A.; Benegas, J. C.; Ripoll, D. R. *J. Phys. Chem.* **1986**, *90*, 2787. (j) Ziegast, G.; Pfannemüller, B. *Int. J. Biol. Macromol.* **1982**, *4*, 419.
(107) Poli, R.; Gordon, J. C.; Khanna, R. K.; Fanwick, P. E. *Inorg. Chem.* **1992**, *31*, 3165.
(108) Renner, M. W.; Barkigia, K. M.; Zhang, Y.; Medforth, C. J.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1994**, *116*, 8582.
(109) (a) Tebbe, K.-F.; Gilles, T. *Acta Cryst.* **1993**, *C49*, 2042. (b) Junk, P. C.; MacGillivray, L. R.; May, M. T.; Robinson, K. D.; Atwood, J. L. *Inorg. Chem.* **1995**, *34*, 539. (c) Tebbe, K.-.F, Farida, T. *Z. Naturforsch.* **1995**, *b50*, 1685. **(**d) Bryce, M. R.; Lay, A. K.; Chesney, A.; Batsanov, A. S.; Howard, J. A. K.; Buser, U.; Gerson, F.; Merstetter, P. *J. Chem Soc., Perk. Trans.* **1999**, *2*, 755.
(110) Hassel, O.; Hope, H. *Acta Chem. Scand.* **1961**, *15*, 407.
(111) Demartin, F.; Deplano, P.; Devillanova, F. A.; Isaia, F.; Lippolis, V.; Verani, G. *Inorg. Chem.* **1993**, *32*, 3694.
(112) Hendrixson, T. L.; Horst, M. A.; Jacobson, R. A. *Acta Crystallogr.* **1991**, *C47*, 2141.
(113) Tebbe, K.-F.; Buchem, R. *Z. Kristallogr.* **1995**, *210*, 438.
(114) Tebbe K.-F.; Loukili R. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1175.
(115) James, W. J.; Hach, R. J.; French, D.; Rundle, R. E. *Acta Crystallogr.* **1955**, *8*, 814.
(116) Bell, P. *Darstellung und Struktur der Polyiodide des Trimethylphenylammoiniums*, Diplomarbeit, Köln, 1986.
(117) Kameya, M.; Naito, T.; Inabe, T. B. *Chem. Soc. Jpn.* **2000**, *73*, 61.
(118) Lazarini, F. *Acta Crystallogr. B.* **1977**, *33*, 1957. Cingi, M. B.; Lanfredi, A. M. M.; Tiripiccio, A.; Boli, G.; Clemente, D. A. *Inorg. Chim. Acta* **1981**, *52*, 237. Toman, K.; Honzl, J.; Jecny, J. *Acta Cryst. C* **1965**, *18*, 673. Reetz, M. T.; Arion, V. B.; Goddard, R.; Simonov, Y. A.; Kratsov, V.; Lipkowskij, C. *Inorg Chim Acta* **1995**, *238*, 23.Bossek, U.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg Chim Acta* **1989**,*165*, 123. Florke, U.; Haupt, H. J.; Karpenstein, I.; Chaudhuri, P. *Acta Crystallogr.* **1993,** *C49*, 1625. Young, C. G.; Kocaba, T. O.; Yan, X. F.; Tiekink, E. R. T.; Wei, L. W.; Murray, H. H.; Coyle, C. L.; Stiefel, E. I. *Inorg. Chem.* **1994**, *33*, 6252. Bryan, C. D.; Cordes, A. W.; George, N. A.; Haddon, R. C.; MacKinnon, C. D.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S. *Chem. Mater.* **1996**, *8*, 762. Canty, A. J.; Honeyman, R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *424*, 381. Fesnhchenko, G.; Miroshnichenko, V. V.; Chernega, A. N.; Yurchenko, R. I. *Zh. Obs. Khim.* **1994**, *64*, 225. Adcock, J. L.; Gakh, A. A.; Pollitte, J. L.; Woods, C. *J. Chem. Soc.* **1992**, *114*, 3980. Runschke, C.; Meyer *Z. Anorg. Allg. Chem.* **1997**, *623*, 1493.
(119) Stoeger, V. W.; Schultz, H.; Rabenau, A. *Z. Anorg. Allg. Chem.* **1977**, 432, 5.
(120) Bigoli, F.; Demartin, F.; Deplano, P.; Devillanova, F. A.; Isaia, F.; Lippolis, V.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F. *Inorg. Chem.* **1996**, *35*, 3194.
(121) Long, D.-L-; Hu, H.-M.; Chen, J.-T.; Huang, J.-S. *Acta Crystallogr. C.* **1999**, *55*, 339.
(122) Herbstein, F. H.; Kapon, M.; Schwotzer, W. *Helv. Chim. Acta.* **1983,** *66*, 35.
(123) Tkachev V. V.; Lavrenteva E. A.; Roshchupkina O. S.; Lavrentev I. P.; Atovmyan L. Y. *Koord. Khim.* **1994**, *20*, 674.
(124) Hitchcock P. B.; Hughes D. L.; Leigh G. J.; Saers J. R.; Desouza J.; Mcgarry C. J.; Larkworthy L. F. *J. Chem. Soc., Dalton Trans.* **1994**, *24*, 3683.
(125) Mikhailov Y. N.; Kuznetzov V. G.; Kovaleva, E. S. *Zh. Strukt. Khim.* **1968**, *9*, 710.
(126) Stoeger, W.; Rabenau, A. *Z. Naturforsch.* **1979**, *B34*, 685.
(127) Rabenau, A.; Schulz, H.; Stoeger, W. *Naturwissenschaften* **1976**, *63*, 245.
(128) Sæthre, L. J.; Gropen, O.; Sletten, J. *Acta Chem. Scan.* **1988**, *A42*, 16.
(129) (a) Tebbe, K.-F.; Freckmann, B. *Z. Naturforsch.* **1982**, *37b*, 542. (b) Tebbe, K.-F.; Plewa, M. *Z. Anorg. Allg. Chem.* **1982**, *489*, 111.
(130) Havinga, E. E.; Boswijk, K. H.; Wiebenga, E. H. *Acta Crystallogr.* **1954**, *7*, 487.
(131) Hon, P. K.; Mak, T. C.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 2916.
(132) Jircitano, A. J.; Colton, M. C.; Mertes, K. B. *Inorg. Chem.* **1981**, *20*, 890.
(133) Freckman, B.; Tebbe, K.-F. *Acta Cryst.* **1981**, *A37*, C228. Freckman, B.; Tebbe, K.-F. *Z. Kristallog.* **1981**, *134*, 274.
(134) Tebbe, K.-F.; Elessawi, M.; Elkhalik, S. A. *Z. Naturforsch.* **1995**, *B50*, 1429.
(135) Grafe-Kavoosian, A.; Nafepour, S.; Nagel, K.; Tebbe, K.-F. *Z. Naturforsch.* **1998**, *B53*, 641.
(136) Balch, A. L.; Koerner, R.; Olmstead, M. M.; Mazzanti, M.; Safari N.; Stclaire, T. *J. Chem. Soc. Chem. Commun.* **1995**, 6, 643.
(137) Kirsch, A.; Krieger, C.; Staab, H. A.; Neugebauer, F. A. *Tetrahedron Lett.* **1994**, *35*, 8365.
(138) Morey, T. R. *Acta Cryst.* **1982**, *B24*, 1968.
(139) Kuhn, N.; Kotowski, H.; Steimann M.; Speiser, B.; Wurde, M.; Henkel, G. *J. Chem. Soc Perkin Trans.* **2000**, *2*, 353.
(140) Kuzmina, N. E.; Palkina, K. K.; Savinkina, E. V.; Kozlova, I. A.; Kuznetsov, N. T. *Zh. Neorg. Khim.* **2000**, *45*, 10.
(141) Tebbe, K.-F.; Dombrowski I. *Z. Anorg. Allg. Chem.* **1999**, *625*, 167.
(142) Richter, R.; Seidelmann, O.; Beyer, L. *Z. Anorg. Allg. Chem.* **1999**, *625*, 511.
(143) Ramalakshmi, D.; Reddy, K. R.; Padmavathy, D.; Rajasekharan, M. V.; Arulsamy, N.; Hodgson, D. J. *Inorg. Chim. Acta* **1999**, *284*, 158.
(144) Wieczorrek, C. *Acta Cryst.* **2000**, *C56*, 1082.
(145) Tebbe, K.-F.; Gilles, T. *Z. Anorg. Allg. Chem.* **1996**, *622*, 138.
(146) Tebbe, K.-F.; El Essawi, M. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1046.
(147) Tebbe, K.-F.; El; Kavoosian, A. *Z. Naturforsch. B.* **1993**, *48*, 438.
(148) Menon, S.; Rajasekharan, M. V. *Inorg. Chem.* **1997**, *36*, 4983.
(149) Horn C.; Scudder M.; Dance, I. *CrystEngComm* **2001**, 2, 1. I14/I18.
(150) Tebbe, K.-F.; Buchem, R. *Z. Kristallogr.* **1996**, *211*, 689.
(151) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1990**, *112*, 1860.
(152) Tebbe K.-F. *Acta Cryst. C39*, 154.
(153) Behrens, U.; Breunig, H. J.; Denker, M.; Ebert, K. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 987.
(154) Tebbe K.-F., Gilles, T *Z. Anorg. Allg. Chem.* **1996**, *622*, 138.
(155) Crump, W. *Präperative und röntgenographische Untersuchungen Polyiodid-verbindungen des bleis*, Ph.D. Thesis, Köln, 1995.
(156) Svensson, P. H.; Raud, G.; Kloo, L. *Eur J. Inorg. Chem.* **2000**, *6*, 1275.
(157) Tebbe, K.-F.; Buchem, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1345.
(158) Bigoli, F.; Demartin, F.; Deplano, P.; Devillanova, F. A.; Isaia, F.; Lippolis, V.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F. *Inorg. Chem.* **1996**, *35*, 3194.
(159) Herbstein, F. H.; Kapon, M. *J. Chem. Soc., Chem. Commun.* **1975**, 677.
(160) Bigoli, F.; Pellingheli, M. A.; Crisponi, G.; Deplano, P.; Trogu, E. F. *J. Chem. Soc., Dalton Trans.* **1985**, 1349.

(161) Bigoli, F.; Deplano, P.; Devillanova, F. A.; Lippolis, V.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F. *Inorg. Chim. Acta* **1988**, *1*, 3.
(162) Tebbe, K.-F.; Farida, T., *Z. Naturforsch*. **1995**, *50b*, 1440.
(163) Tebbe, K.-F.; Buchem, R. *Z. Anorg. Allg. Chem*, **1998**, *624*, 671.
(164) Stegemann, H.; Tebbe, K.-F.; Bengtsson, L. A. *Z. Anorg. Allg. Chem*. **1995**, *621*, 165.
(165) Svensson, P. H.; Bengtsson-Kloo, L. *J. Chem. Soc., Dalton Trans.* **1998**, 1425.
(166) Svensson, P. H.; Kloo, L. *Inorg. Chem*. **1999**, *38*, 3390.
(167) Bu, X. H.; Coppens, P. *Acta Cryst*. **1992**, *C48*, 1565.
(168) Svensson, P. H.; Rosdahl, J.; Kloo, L. *Chem. Eur. J.* **1999**, *5*, 305.
(169) Lang, E. S.; Strähle, J. *Z. Anorg. Allg. Chem*. **1996**, *622*, 981.
(170) Millan, A.; P Bailey, M.; Maitlis, P. M. *J. Chem. Soc. Dalton Trans.* **1982**, 73.
(171) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1990**, *112*, 1860.
(172) Bailey, R. D.; Hook, L. L.; Pennington, W. T., *J. Chem. Soc., Chem. Commun.* **1998**, 1181.
(173) Gray, L. R.; Gulliver, D. J.; Levason, W.; Webster, M. *Acta Crystallogr.* **1983,** *C39*, 877.
(174) Gray, L. R.; Gulliver, D. J.; Levason, W.; Webster, M. *Inorg. Chem*. **1983**, *22*, 2362.
(175) Tebbe, K.-F.; Grafe-Kavoosian, A.; Freckmann, B.; Teil B, *Z. Naturforsch*. **1996**, *51*, 999.
(176) Renner, M. W.; Barkigia, K. M.; Zhang Y.; Medforth, C. J.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1994**, *116*, 8582.
(177) Buse, K. D.; Keller, H. J.; Pritzkow, H. *Inorg. Chem*. **1977**, *16*, 1072.
(178) Bellitto, C.; Bonamico, M.; Dessy, G.; Fares, V.; Flamini, A. *J. Chem. Soc., Dalton Trans*. **1986**, 595.
(179) Revenko, M. D.; Vyrtosu, N. I.; Gerbeleu, N. V.; Simonov, Yu. A.; Bourosh, P. N.; Sobolev, A. N. *Zh. Neorg. Khim*. **1988**, *33*, 2353.
(180) Bigoli, F.; Deplano, P. F. ; Devillanova, A.; Ferraro, J. R.; Lippolis, V.; Lukes, P. J.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F.; Williams, J. M. *Inorg. Chem*. **1997**, *36*, 1218**.**
(181) McAuley, A.; Subramanian, S. *Inorg. Chem*. **1991**, *30*, 371.
(182) Megnamisi-Belombe, M.; Nuber, B. *Z. Naturforsch*. **1991**, *46b*, 635.
(183) Tejel, C.; Bordonaba, M.; Ciriano, M. A.; Edwards, A. J.; Clegg, W.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem*. **1999**, *38*, 1108.
(184) Mattson, B. M.; Pignolet, L. H. *Inorg. Chem*. **1977**, *16*, 488.
(185) van Beek, J. A. M.; van Koten, G.; Dekker: G. P. C. N.; Wissing, E.; Zoutberg, M. C.; Stam, C. H. *J. Organomet. Chem*. **1990**, *394*, 659.
(186) Janczak, J.; Razik, M.; Kubiak, R. *Acta Crystallogr.* **1999**, *C55*, 359.
(187) Palmer, S. M.; Stanton, J. L.; Jaggi, N. K.; Hoffman, B. M.; Ibers, J. A. *Inorg. Chem*. **1985**, *24*, 2040.
(188) Beurskens, G.; Noordik, J. H.; Cras, J. A. Recueil, J. *R. Neth. Chem. Soc.*, **1979**, *98*, 416.
(189) Almond, M. J.; Drew, M. G. B.; Rice, D. A.; Salisbury, G.; Taylor, M. J. *J. Organomet. Chem*. **1996**, *522*, 265.
(190) Mckie, G.; Raston, C. L.; Rowbottom, G. L.; White, A. H. *J. Chem. Soc., Dalton Trans*. **1981**, 1361.
(191) Pritzkow, H. *Inorg. Chem*. **1979**, *18*, 311.
(192) Kiriyama, H.; Nishizaki *Bull. Chem. Soc. Jpn*. **1986**, *59*, 2415.
(193) Grebe, J.; Geiseler, G.; Harms, K.; Neumüller, B.; Dehnicke, K. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 222.
(194) Rimmer, E. L.; Bailey, R. D.; Hanks , T.W.; Pennington, W. T. *Chem. Eur. J.* **2000**, 6, 4071.
(195) Gridunova, G. V.; Shklover, V. E.; Struchkov, Yu. T.; Vilchevskaya, V. D.; Podobedova, N. L.; Krylova, A. *J. Organomet. Chem*. **1982**, *238*, 297.
(196) Cotton, F. A.; Kibala, P. A. *J. Am. Chem. Soc.* **1987**, *109*, 3308.
(197) Stenzel, V.; Jeske, J.; du Mont, W.-W.; Jones, P. G. *Inorg. Chem*. **1995**, *34*, 5166.
(198) Cross, W. I.; Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G.; Sheffield, J. M.; Thompson, G. M. *J. Chem. Soc., Dalton Trans.* **1999**, *16*, 2795.
(199) Stenzel, V.; Jeske, J.; du Mont, W.-W.; Jones, P. G. *Inorg. Chem*. **1997**, *36*, 443.
(200) Feshchenko, N. G.; Miroshnichenko, V. V.; Chernega, A. N.; Yurchenko, R. *Zh. Obshch. Khim*. **1994**, 64, 225.
(201) Yamamoto, M.; Wu, L. P.; KurodaSowa, T.; Maekawa, M.; Suenaga, Y.; Munakata, M. *Inorg. Chim. Acta* **1997**, 258, 87.
(202) Blake, A. J.; Devillanova F. A.; Garau A.; Gilby L. M.; Gould R. O.; Isaia F.; Lippolis V.; Parsons S.; Radek C.; Schröder M. *J. Chem. Soc., Dalton Trans.* **1998**, 2037.
(203) Atzei, D.; Deplano, P.; Trogu, E. F.; Bigoli, F.; Pellinghelli, M. A.; Sabatini, A.; Vacca, A. *Can. J. Chem*. **1989**, *67*, 1416.
(204) Tipton, A. L.; Lonergan, M. C.; Stern, C. L.; Shriver, D. F. *Inorg. Chim. Acta* **1992**, *201*, 23.
(205) Allshouse, J.; Haltiwanger, R. C.; Allured, V.; Dubois, M. R. *Inorg. Chem*. **1994**, 33, 2505.
(206) Lee, J. Q.; Sampson, M. L.; Richardson, J. F.; Noble, M. E. *Inorg. Chem*. **1995**, 34, 5055.
(207) Blake, A. J.; Cristiani, F.; Devillanova, F. A.; Garau, A.; Gilby, L. M.; Gould, R. O.; Isaia, F.; Lippolis, V.; Parsons, S.; Radek, C.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1997**, *8*, 1337.
(208) Rudd, M. D.; Lindeman, S. V.; Husebye, S. *Acta Chem. Scand.* **1997**, *51*, 689.
(209) Cristiani, F.; Demartin, F.; Devillanova, F. A.; Isaia, F.; Lippolis, V.; Verani, G. *Inorg. Chem*. **1994**, *33*, 6315.
(210) Seppala, E.; Ruthe, F.; Jeske, J.; Du Mont, W. W.; Jones, P. G. *J. Chem. Soc., Chem Commun*. **1999**, 1471.
(211) Jeske, J.; Du Mont, W. W.; Jones, P. G. *Chem. Eur. J.* **1999**, *5*, 385.
(212) (a) Davies, C. G.; Gillespie, J. R.; Irel, P. R.; Sowa, J. M. *Can. J. Chem*. **1974**, *52*, 2048. (b) Faggiani, R.; Gillespie, R. J.; Kapoor, R.; Lock, C. J. L.; Vekris, J. E. *Inorg. Chem*. **1988**, *27*, 4350. (c) Passmore, J.; Sutherl, G.; White, P. S. *Inorg. Chem*. **1981**, 2169. (d) Apblett, A.; Grein, F.; Johnson, J. P.; Passmore, J.; White, P. S. *Inorg. Chem*., **1986**, *25*, 422. (e) Passmore, J.; Taylor, P.; Whidden, T.; White, P. S. *Can. J. Chem*., **1979**, *57*, 968.
(213) (a) Fröhlich, R.; Tebbe, K.-F. *Acta Cryst*. **1982**, *B38*, 1225. (b) Fröhlich, R.; Tebbe, K.-F. *Z. Kristallogr.* **1981**, *156*, 39.
(214) Ghassenzadeh, M.; Harms, K.; Dehnicke, K. *Chem. Ber.* **1996**, *129*, 259.
(215) (a) Arban, M.; Holmberg, S.; Lundholm, M.; Siegbahn, H.; Gropen, O.; Wahlgren, U. *Chem. Phys.* **1983**, 113. (b) Bowmaker., G. A.; Boyd., P. D. W.; Sorrenson, R. J. *J. Chem. Soc., Faraday Trans.* **1984**, *80*, 1125. (c) Gutsev, G. L. *Zh. Strukt. Khim*, **1989**, 3041. (d) Gutsev, G. L. *Zh. Fiz. Khim*. **1992**, *66*, 2998. (e) Kertesz, M.; Vonderviszt, F. *J. Am. Chem. Soc.* **1982**, *104*, 5889. (f) Havinga, E. E.; Wiebenga, E. H. *Rec. Trav. Chim. Pays-Bas* **1959**, *78*, 724. (g) Wiebenga, E. H.; Krach, D. *Inorg. Chem*. **1969**, *8*, 738. (h) Gabes, W.; Nijman-Meester, M. A. M. *Inorg. Chem*. **1973**, *12*, 589. (i) Hollingworth, R. W.; Hacobian, S. *Aust. J. Chem*. **1974**, *27*, 1381. (j) Scharfenberg, P. *Chem. Phys. Lett.* **1979**, *65*, 304. (k) Mizuno, M.; Tanaka, J.; Harada, I. *J. Phys. Chem*., **1981**, *85*, 1789. (l) Tasker, P. W. *Mol. Phys*. **1977**, *33*, 511. (m) Wright, T. G.; Lee, E. P. F. *Mol. Phys.* **1993**, *79*, 995.
(216) (a) Arkel, A. E. V.; de Boer, J. H. *Rec. Trav. Chim*. **1928**, *47*, 593. (b) Pauling, L. In *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, New York, 1940.
(217) (a) Pimentel, G. C. *J. Chem. Phys.* **1951**, *19*, 446. (b) Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4321.
(218) Pykkö, P. *Chem. Rev*. **1997**, *97*, 597.
(219) Novoa, J.; Mota, F.; Alvarez, S. *J. Phys. Chem*. **1988**, *92*, 6561.
(220) Rum, G. A. L.; Goldberg, N.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1997**, 3605.
(221) Datta, S. N.; Ewig, C. S.; Wazer, J. R. V. *J. Mol. Struct.* **1978**, *48*, 407.
(222) Novoa, J. J.; Mota, F.; Whangbo, M.-H.; Williams, J. M. *Inorg. Chem*. **1991**, *30*, 4.
(223) Ogawa, Y.; Oghi, T.; Kikuchi, O. *J. Mol. Struct.* **1998**, *429*, 187.
(224) Margulis, C. J.; Coker, D. F.; Lyndel-Bell, R. M. *Chem. Phys. Lett.* **2001**, *341*, 557.
(225) Koslowski, T.; Vöhringer, P. *Chem. Phys. Lett.* **2001**, *342*, 141.
(226) Sato, H.; Hirata, F.; Myers, A. B. *J. Phys. Chem*. **1998**, *102*, 2065.
(227) Lin, Z.; Hall, M. B. *Polyhedron* **1993**, *121*, 499.
(228) Kloo, L.; Rosdahl, J.; Svensson, P. H. *Eur. J. Inorg. Chem*. **2002**, 1203.
(229) (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1990, Chapter 28. (b) Holleman, A. F. V.; Wiberg, E. V. In *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter: Berlin New York, Vol. 101, 1995. (c) Jones, P. G. *Gold Bull.* 1981, *14*, 102. (d) Olsson, L.-F. , 1998, personal communication.

CR0204101