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Polyiodo-iodates Containing Five or More Iodine Atoms

B.D.Stepin and S.B.Stepina

The results of theoretical and experimental studies of the chemistry of polyiodo-iodates—complexes of iodine containing five or more iodine atoms in the anion—have been reviewed. The molecules of heterocyclic compounds with a planar configuration, chelates of *d* elements with macrocyclic planar ligands, and organic and inorganic polymers containing cavities and channels, on oxidation with iodine, tend to form compounds with polymeric anions in the form of quasi-one-dimensional chains. New ideas on iodine as a complex-forming species have been examined.
The bibliography contains 222 references.

CONTENTS

I. Introduction 812
II. Penta-iodides 812
III. Hepta-iodides 813
IV. Octa-iodides 814
V. Nona-iodides 816
VI. Undeca-iodides 816
VII. Polyiodo-iodates with chain anions 817
VIII. Summary 820

I. INTRODUCTION

Polyiodo-iodates containing five or more iodine atoms not only may be discrete, $[I_5]^-$, $[I_7]^-$, $[I_9]^-$, and $[I_8]^-$ but also may form chains containing as units the anions $[I_3]^-$ and $[I_5]^-$.[1-7] The study of the correlation between the interatomic distances and valence angles in polyiodo-iodate anions, and the analysis of vibrational and rotational spectroscopic data, indicate that there is a genetic relationship between the structures of these anions and the structure of the $[I_3]^-$ anion.[4,6] Aqueous and non-aqueous solutions contain chiefly anions with composition $[I_3]^-$, whose formation constants have been determined fairly accurately. The formation of $[I_5]^-$ anions in non-aqueous solutions has been assumed. The existence in solution of hepta-iodide and nona-iodide anions and anions with a chain structure has not been reliably established, however. These anions are apparently formed in the layer next to the surface in a crystallising substance during the establishment of the most stable structures, involving repeated transfer of the cations and anions from lattice sites to the solution and back again. The stability of the anions decreases from $[I_5]^-$ to $[I_9]^-$, the external conditions remaining constant.[8] Polyiodo-iodate anions readily undergo changes in structure and composition under the influence of even slight changes in the environment.

Subsequent sections examine present-day ideas on the nature of polyiodo-iodate anions.

II. PENTA-IODIDES

Penta-iodides contain the $[I_5]^-$ anion.[1] An anion with this composition has been detected in tetra-alkylammonium[9-15] and quinuclidine[16] compounds, in the iron complexes $[Fe(Et_2S_2.CN)_3][I_5]$,[17] $\{[Fe(C_5H_5)(C_5H_4)]_2Se\}[I_5]$,[18] and $[Fe(C_{10}H_9)].[I_5]$,[19] and in various ammines[20-22] and ethylenediamine complexes,[23] although in the last two groups of compound the composition of the anion was established only by chemical analysis, and not always qualitatively.[20-23]

A study[3] of the reaction of dithizone with molecular iodine showed that the crystal structure of the polyiodo-iodate formed contains dimers with the composition $[(\text{dithizone})I]^+-[I_5]^--I_2-[I_5]^-[(\text{dithizone})I]^+$ with an angular (85.5°) $[I_5]^-$ anion.

In all the systems, studied up to the present, of the type $MI-I_2$ and $MI-I_2$–solvent at 0–25 °C (M = K, Rb, or Cs), an $M[I_5]$ phase was not detected.[24-31] A very small region corresponding to the crystallisation of the incongruently melting (+9.8 °C) $(NH_4)[I_5]$ was detected only in the $NH_4I-I_2-H_2O$ system at 0 °C.[32] In the systems $(NR_4)I-I_2-C_6H_6$ (or $C_6H_6CH_3$) at 6 °C and 25 °C, the phase $(NMe_4)[I_5]$ is formed.[33] This compound also crystallises in the $(NMe_4)I-I_2$ system.[34]

The evidence[35] for the possible formation of the incongruently melting compounds with the composition $[M(NH_3)_4][I_5]_2$ (M = Zn or Cd) in $[M(NH_3)_4]I_2-I_2$ system is not unambiguous.[4] The logarithms of the formation constants (lg β) of the $[I_5]^-$ anion in the reaction:

$$[I_3]^- + I_2 \rightleftarrows [I_5]^-$$

for different solvents at 25 °C and activity coefficients of the components of the system close to 1 were: H_2O 0.95,[36] C_2H_5OH 1.8,[37,38] CH_3NO_2 1.51, $C_6H_5NO_2$ 2.3–2.8,[8,39] propylene carbonate 1.9.[40] The temperature dependence (t in °C) $\lg \beta = 0.954 + 0.0308(t - 25)$ for aqueous solutions gives for this reaction the values $\Delta G^0_T = -5.4$ kJ mole^{-1} and $\Delta H^0_T = 50.1$ kJ mole^{-1}.[36] The thermodynamic characteristics of the reaction

$$(NMe_4)[I_3]\,(\text{crystalline}) + I_2(\text{crystalline}) = (NMe_4)[I_5]$$

are: $\Delta G^0_{298} = -13.4 \pm 0.03$ kJ mole^{-1}, $\Delta H^0_{298} = -9.2 \pm 0.4$ kJ mole^{-1}, $\Delta S^0_{298} = 13.4 \pm 1.7$ kJ mole^{-1} K^{-1}.[41]

The structure of the bis(di-iodine)iodate(−1) anion $[I_5]^-$ is given in Fig.1. The anion has an almost planar (±0.12 Å) *V*-shaped configuration with an angle of 88.2–96.5°. The complex-forming species in the anion is the I^- ion, and the ligands are polarised iodine molecules with an interatomic distance of 2.75–2.93 Å. The I^--I_2 bond is weak, and its length is 3.01–3.31 Å.[3,16,17,42-46] The force constant of the

vibrations of the complex-forming species is low (0.15×10^5 dyne cm^{-1}), and the ion is readily deformed in an unsymmetrical crystal field, forming chain and cyclic structures (Fig. 2).[3,16,18,44,45,47]

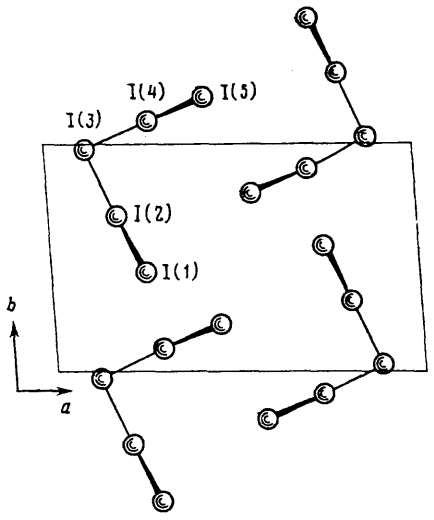


Figure 1. Projection of the $[I_5]^-$ anions of the compound $[Fe(Et_2S_2CN)_3][I_5]$ on the *ab* plane:[17] angles: I(1)–I(2)–I(3) = 176.2°; I(2)–I(3)–I(4) = 88.2°; interatomic distances (Å): I(1)–I(2) = 2.799; I(2)–I(3) = 3.148; I(3)–I(4) = 3.015; I(4)–I(5) = 2.837.

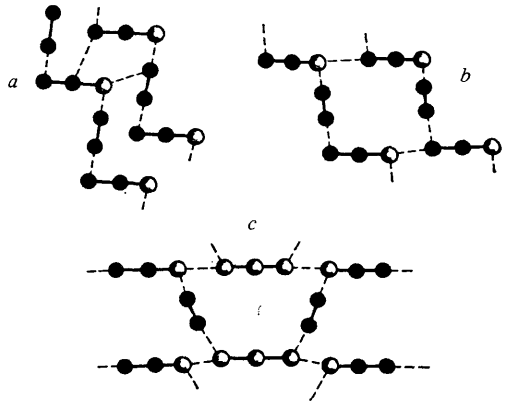


Figure 2. Schematic representation of the polyiodo-iodates in various bis(di-iodine)iodates:[18,44] *a*) [(phenacetin)$_2$H][I_5]; *b*) [bis(ferrocenyl)selenium][I_5].0.5CH_2Cl_2; *c*) [(quinuclidine)H][I_5]; the black circles denote the iodine atoms of the coordinated iodine molecules.

A calculation[48] of the energies of formation of the $[I_5]^-$ anion in the reaction

$$I^- + 2I_2 = [I_5]^-$$

confirmed its *V*-shaped configuration. The energy for this structure is lower than the energies of formation of the linear, square-planar, and *T*-shaped configurations.

The chemical shifts in the $[I_5]^-$ anion have been examined in terms of six-electron MO, of which the three MO of lowest energy (two bonding and one non-bonding) are completely occupied by electrons. The complex-forming species has an effective charge of −0.5e, and the terminal atoms of the ligands from −0.13e to −0.26e. The iodine atoms directly attached to the complex-forming atom, however, carry positive charges of from 0.08e to 0.11e (from different calculations).[49]

The existence of the $[I_5]^-$ anion as a structural unit is confirmed by data obtained by vibrational spectroscopy,[14] analysis of the nuclear quadrupole resonance spectra,[50] Mössbauer spectroscopy,[51] and X-ray spectroscopy.[52]

The electronic spectra of solutions of compounds containing $[I_5]^-$ anions in acetonitrile and 1,2-dichloroethane (λ_{max} = 295 nm, lg ε = 4.65–4.68 and λ_{max} = 365 nm, lg ε = 4.40 to 4.42 respectively[10,15]) are identical to those of polyiodo-iodates containing the anions $[I_3]^-$, $[I_7]^-$, and $[I_9]^-$.

The existence of $[I_6]^{2-}$ anions in aqueous solutions[36] and of $[I_6]^-$ anions in the crystalline phase[19] is unlikely.

III. HEPTA-IODIDES

Hepta-iodides contain the $[I_7]^-$ anion.[1] This anion has been detected in tetra-alkylammonium polyiodo-iodates[14,15,53,54] and various ammines,[20–22] and in dilute solutions containing iodine and lanthanide iodides in molar ratios close to $I^- : 3I_2$.[55,56] Unfortunately, in almost all the works cited the compositions of the bis(di-iodine)tri-iodates obtained by preparative methods were established only from an incomplete chemical analysis, and the formation of the $[I_7]^-$ anion in solution was established using the spectrophotometric version of the Ostromyslenskii–Job method, not applicable in this case.

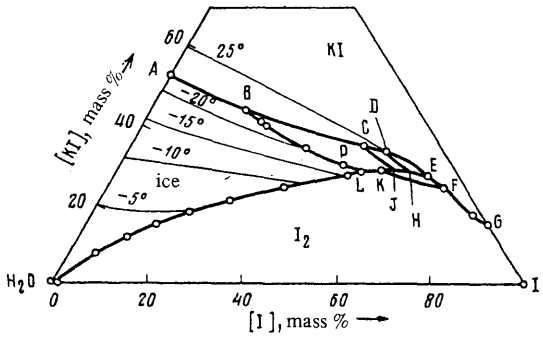


Figure 3. Triangular projection of the polythermal equilibrium diagram of the KI–I_2–H_2O system;[25] crystallisation fields: K[I_3].H_2O—DEHD; K[I_7].H_2O—KJHEFK; α-K[I_3].2H_2O—BCJKLPB; β-K[I_3].2H_2O—CDHJC.

The results obtained in a study of a number of systems in which the formation of bis(di-iodine)tri-iodates has been detected are contradictory. Thus in the purely eutectic KI–I_2 system, the formation of K[I_7] was established erroneously[29] (because of poor experimental technique, part of

the solidus line was taken as an extremely flat liquidus curve). A number of papers describe the study of $KI-I_2-H_2O$ systems,[24,25,27,29–31,57] but the only apparently reliable data are those in Refs.25, 31, and 57 on the existence of $K[I_7].H_2O$ (Fig.3), although in this case also the individuality of the new phases was not confirmed by chemical methods of analysis.

Studies of $MI-I_2-C_6H_6$ systems (6 °C and 25 °C, M = K or Rb) have shown that phases containing the $[I_7]^-$ anion always crystallise as the following solvates, which decompose readily in air: $K[I_7].2C_6H_6$,[29,57] $Rb[I_7].4C_6H_6$, and $Rb[I_7].2C_6H_6$ (Fig.4). This apparently explains the contradictory conclusions regarding the existence of the solvate $K[I_7].2C_6H_6$.[26,28,29,33,57] Compounds containing the $[I_7]^-$ anion were not detected in the systems containing CsI.[28,58] The reasons for the non-existence of regions corresponding to the crystallisation of the phases $M[I_5].xC_6H_6$ (M = Rb or Cs) in the above systems, and the appearance of the non-solvated phase $Cs_2[I_8]$ when RbI is replaced by CsI, have not yet been established.

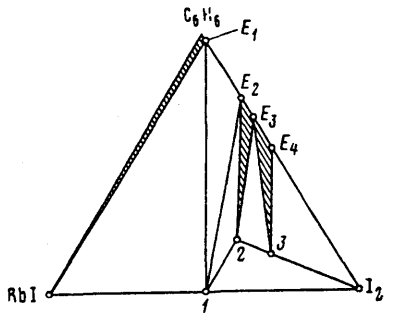


Figure 4. Equilibrium diagram of the $RbI-I_2-C_6H_6$ system, 25 °C:[28] *1*) $Rb[I_3]$; *2*) $Rb[I_7].2C_6H_6$; *3*) $Rb[I_9].2C_6H_6$; compositions of the eutonic points (I_2, M): $E_1 = 0.01325$; $E_2 = 0.3425$; $E_3 = 0.393$; $E_4 = 0.545$.

The structure of the $[I_7]^-$ anion is given in Fig.5.[53] The $[I_7]^-$ anion can be represented as the bis(di-iodine)tri-iodate ion $[(I_3)(I_2)_2]^-$, in which the unusual complex-forming species is the symmetrical $[I_3]^-$ anion, to which are coordinated two iodine molecules, which are situated at equal distances (3.43 Å) from the terminal atoms of the central ion and which are weakly bonded to it.[59] The $[I_3]^- - I_2$ distance is slightly less than I_2-I_2 distance in crystalline iodine (3.56 Å). The structure of polymeric polyiodo-iodate anions is beginning to form in this anion. The thermodynamic characteristics of the reaction

$$(NEt_4)[I_3]\,(\text{crystalline}) + 2I_2 = (NEt_4)[I_7]\,(\text{crystalline})$$

are $\Delta G^0_{298} = -22.0 \pm 0.6$ kJ mole^{-1}, $\Delta H^0_{298} = -23 \pm 1.2$ kJ mole^{-1}, and $\Delta S^0_{298} = -3.8 \pm 3$ J mole^{-1} K^{-1}.[41]

IV. OCTA-IODIDES

Octa-iodides are polyiodo-iodates containing the doubly-charged $[I_8]^{2-}$ anion. The following compounds containing this anion have been synthesised: $Cs_2[I_8]$,[28,33,58,60–62] $[(DMX)_2H_2][I_8]$,† [44] $[M(TACD)][I_8]$ # (M = Ni, Pd, Pt),[63–65] $[Co(en)_2X_2][I_8]$ § (X = Cl^-, I^-, NO_2^-, and NCS),[66] and $[Ni(en)_3][I_8]$, crystallised from methanol.[67]

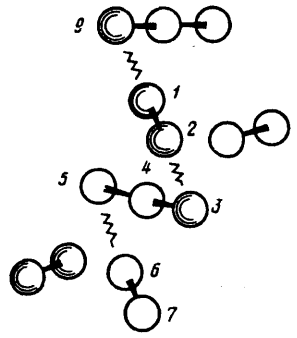


Figure 5. Fragment of the structure of the $[I_7]^-$ anion of the polyiodo-iodate $(NEt_4)[I_7]$ at −175 °C;[53] the hatched iodine atoms are in the same plane; *1*–*7*) iodine atoms in the anion; interatomic distances (Å): I(1)–I(2) = 2.73; I(2)–I(3) = 3.43; I(3)–I(4) = 2.90; I(4)–(I(5) = 2.90; I(5)–I(6) = 3.43; I(6)–I(7) = 2.73.

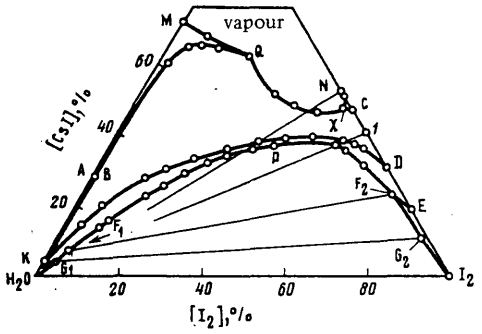


Figure 6. Polythermal equilibrium diagram of the $CsI-I_2-H_2O$ system[62] (pressure 740–750 mmHg, temperature from −5 °C to +305 °C); crystallisation fields: CsI—MQBAM; I_2—EF_2G_2; $Cs[I_3]$—CXQBKDC; $Cs_2[I_8]$—KDEFPF$_1$K; point N—$Cs[I_3]$; *1*—$Cs_2[I_8]$.

In the $CsI-I_2-H_2O$ system in the temperature range from −5 °C to +305 °C, only two new phases are formed: $Cs[I_3]$ and $Cs_2[I_8]$ (Fig.6). With increase in temperature, the range of crystallisation of the incongruently soluble $Cs_2[I_8]$ decreases, and at 80 °C, a range of separation into layers in the liquid phase appears. The temperature range of the congruent solution of $Cs_2[I_8]$ is very narrow, from 79.5 °C (curve PF_2) to 89.0 °C (curve KD). In the range from

† DMX = 3,7-dimethylxanthine.

TACD = 1,3,5,13-tetra-azocyclohexadecine.

§ en = ethylenediamine.

51.5 °C (isotherm F_1F_2) to 79.5 °C (isotherm PF_2), $Cs_3[I_8]$ dissolves to give two liquid phases. The field F_1PF_2 is the range of the phase equilibrium between $Cs_2[I_8]$ crystals and two liquid phases. According to Ref.68, caesium octa-iodide (but not $Cs[I_5]$) is also formed in the $CsI-I_2$ system (Fig.7), crystallising from the melt below 136 °C. In the $CsI-I_2-C_6H_6(C_6H_5CH_3)$ systems, the largest crystallisation range corresponds to $Cs_2[I_8]$.[28,33,58]

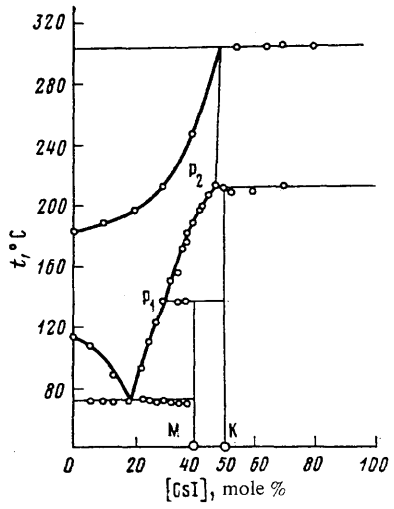


Figure 7. $CsI-I_2$ system (pressure 745 mmHg);[60] coordinates of the point P_1: 136 °C (or 141.2 °C [82]) and 30 mole % CsI; M—$Cs_2[I_8]$; K—$Cs[I_3]$.

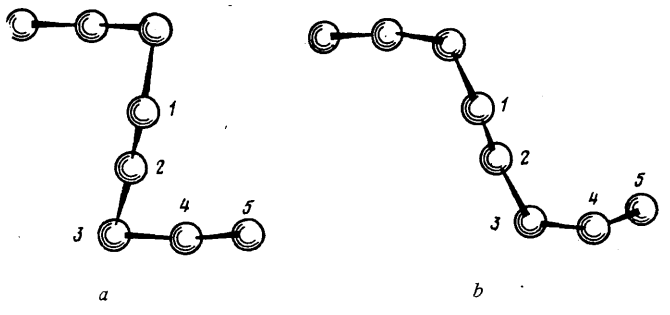


Figure 8. Structure of the $[I_8]^{2-}$ anion;[70,71] *a*) $Cs_2[I_8]$, *b*) $[(CH_2)_6N_4(CH_3)]_2[I_8]$; interatomic distances (Å): *a*) 1–2 = 2.83; 2–3 = 3.42; 3–4 = 3.00; 4–5 = 2.84; *b*) 1–2 = 2.773; 2–3 = 3.386; 3–4 = 3.038; 4–5 = 2.830.

The structure of the $[I_8]^{2-}$ anion is shown in Fig.8. In all polyiodo-iodates studied, the $[I_8]^{2-}$ anion does not have a centre of symmetry and is not planar.[69–71] The complex-forming species in the anion is the strongly polarised iodine molecule, and the ligands are $[I_3]^-$ anions. The $[I_8]^{2-}$ anion is apparently bis(tri-iodido)di-iodate $[(I_2)(I_3)_2]^{2-}$. The representation of the structure of these anions and the separation of their functional parts depend to a large extent on the interpretation of the data on interatomic distances and symmetry. The $[I_8]^{2-}$ anions, when combined with heterocyclic arene cations, can form $[I_{16}]^{4-}$ dimers (Fig.9).[44,63,71] Data on the configurations of polyiodo-iodate anions have been reviewed.[4,72]

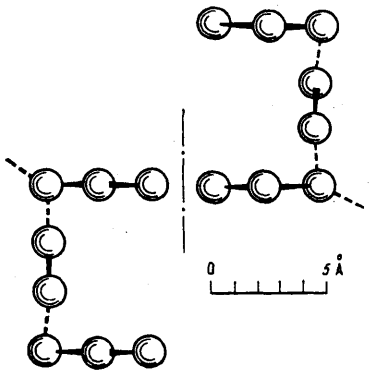


Figure 9. Structure of the $[I_8]^{2-}$ anion in the compound $[(DMX)_2H_2][I_8]$.[44]

The effective charges are +0.08e on the central atoms of the ligands of the $[I_8]^{2-}$ anion, −0.38e on the atoms directly joined to the central iodine molecule, and −0.71e on the terminal atoms.[73,74] Each atom of the central iodine molecule carries a charge of −0.06e.

Studies[75,76] of the thermal stability of $Cs_2[I_8]$ confirmed the results of the structural studies. At 137 °C (or 139° to 140 °C [69]), caesium octa-iodide undergoes incongruent fusion:

$$Cs_2[I_8] \rightarrow \text{melt}\P + Cs[I_3]\,(\text{crystalline}) + I_2(\text{gas})$$

Further heating leads to an increase in the solubility of $Cs[I_3]$ in the melt and hence to a change in the slope of the $\lg p = f(1/T)$ curves, where p is the dissociation pressure, and to the appearance of an inflection at 170 °C. At about 205 °C in the melt, $Cs[I_5]$ decomposes to CsI(crystalline) and iodine. The system after 205 °C is in the same state as in the incongruent fusion of $Cs[I_3]$ (Fig.10), and this explains why the enthalpy changes for the volatilisation of iodine from the two melts practically coincide (46.9 kJ $mole^{-1}$).[75]

The thermal analysis curves for $Cs_2[I_8]$ indicate that the complex decomposes in two stages when heated in air under conditions allowing the free removal of the dissociation products:

$$Cs_2[I_8]\,(\text{crystalline}) = 2Cs[I_3]\,(\text{crystalline}) + I_2(\text{gas})$$

(the start of the inflection on the DTG curve corresponds to 42 °C, and the maximum to 96 °C) and

$$Cs[I_3]\,(\text{crystalline}) = CsI(\text{crystalline}) + I_2(\text{gas})$$

(start of the inflection 107 °C, maximum 158 °C).

¶ The melt presumably contains CsI and I_2 in the ratio corresponding to the composition $Cs[I_5]$.

Thus the rupture of the chemical bonds in the $[(I_3)-I_2-(I_3)]^{2-}$ anion can take place in two ways: the two bonds may break simultaneously, or only one of them may break to give the ions $[I_5]^-$(liquid) + $[I_3]^-$(crystalline).

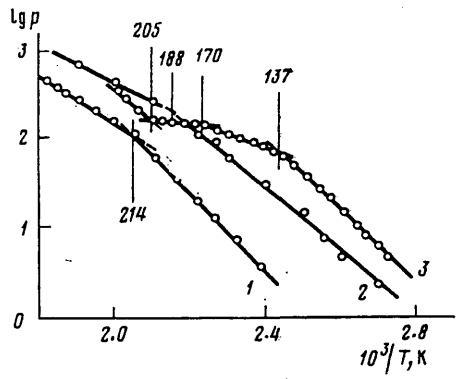


Figure 10. Temperature dependence of the dissociation pressure of polyiodo-iodates:[75,76] *1*) $Cs[I_3]$; *2*) $Rb[I_3]$; *3*) $Cs_2[I_8]$; the temperatures of the phase transformations are given in °C.

The kinetics of the first stage of the thermal dissociation of $Cs_2[I_8]$ in air, described by the equations $dm/d\sigma = km^n$ and $k = Z_0 \exp(-E/RT)$, where m is the mass of the specimen, τ the time, k the reaction rate constant, n the order of the reaction, E the apparent activation energy, and Z_0 the pre-exponential term, are characterised by the quantities $E = 79.1 \pm 1.2$ kJ mole^{-1}, $Z_0 = (1.3 \pm 0.4) \times 10^{11}$ min^{-1}, $\lg k = 11.114 - 4130/T$ (for $n = 1$).[77,78] Thus the rate of the thermal dissociation is determined by the rate of the diffusion of iodine through the interface. Increase in the decomposition temperature displaces the process into the kinetic range ($n \geq 1$). The dependence of the frequency factor Z on the order of the reaction is given by the equation $Z = Z_0 m_0^{1-n}$, where Z_0 is the frequency factor for $n = 1$, and m_0 the original number of moles of $Cs_2[I_8]$.

The thermodynamic characteristics of the reaction

$$Cs_2[I_8]\,(\text{crystalline}) = 2Cs[I_3]\,(\text{crystalline}) + I_2(\text{crystalline})$$

are: $\Delta G^0_{298} = 2.6$ kJ mole^{-1}, $\Delta H^0_{298} = 3.3$ kJ mole^{-1}, and $\Delta S^0_{298} = 2.5$ kJ mole^{-1} K^{-1}.[79]

V. NONA-IODIDES

Nona-iodides are polyiodo-iodates containing the $[I_9]^-$ anion. The appearance of phases with this anion has been established only in the study of non-aqueous systems: $(NMe_4)I-I_2-C_6H_6(C_6H_5CH_3)$ at 6 °C and 25 °C [33] and $MI-I_2-C_6H_6$, where M = K, Rb, or Cs at 25 °C [26,28,29] (the phases $K[I_9].3C_6H_6$, $Rb[I_9].2C_6H_6$, and $2Cs(I_9].3C_6H_6$). In the opinion of Popov and co-workers,[15] in certain organic solvents, for example acetonitrile, the formation of $[I_9]^-$ anions is impossible, because of their complete electrolytic dissociation.

In the $(NMe_4)I-I_2$ [34] and $[Ni(NH_3)_6]I_2-I_2$ [80] systems, the formation of phases with the compositions $(NMe_4)[I_9]$ and $[Ni(NH_3)_6][I_9]_2$ has been established. The conclusion[28,81] that the phase $Rb[I_9]$ may be formed in the $RbI-I_2$ system appears doubtful.[82,83] A large number of syntheses of tetra-alkylammonium nona-iodates has been carried out.[10,11,14,54,84] The data given in Refs. 54 and 84 on the compositions of the complexes appear doubtful, however, because of the unsatisfactory methods of chemical analysis.

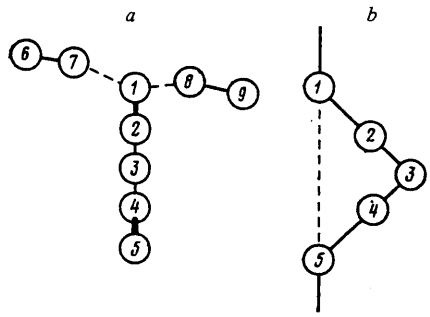


Figure 11. Structure of the $[I_9]^-$ anion in the complex $(NMe_4)[I_9]$;[85] *a*) view from above; *b*) view from the side; interatomic distances (Å): 1–2 = 3.18; 2–3 = 2.90; 3–4 = 3.24; 4–5 = 2.91; 6–7 = 2.67; 8–9 = 2.67; 7–1 = 3.43; 8–1 = 3.24; angle 2–3–4 = 86.5°.

Up to the present, only the structure of $(NMe_4)[I_9]$ (Fig. 11) has been studied in detail.[85] The anion contains as complex-forming species the $[I_3]^-$ ion, which coordinates three iodine molecules, two of which lie in the same plane and have interatomic distances which are almost the same as in crystalline iodine. The third iodine molecule is strongly polarised. The unusual arrangement of the ligands is also apparently responsible for the asymmetry and bending of the complex-forming species. This anion can be provisionally regarded as the tris(di-iodine)tri-iodate anion $[(I_3)(I_2)_3]^-$. The thermodynamic characteristics of the reaction

$$(NMe_4)[I_5]\,(\text{crystalline}) + 2I_2(\text{crystalline}) = (NMe_4)[I_9]\,(\text{crystalline})$$

are $\Delta G^0_{298} = -8.9 \pm 0.4$ kJ mole^{-1}, $\Delta H^0_{298} = -1.3 \pm 0.8$ kJ mole^{-1}, and $\Delta S^0_{298} = 25.9 \pm 2.5$ J mole^{-1} K^{-1}.[41]

The reported existence of the polyiodo-iodate $(NMe_4)[I_{10}]$ [33] in the $(NMe_4)I-I_2-C_6H_5Me$ system at 6 °C appears doubtful.

VI. UNDECA-IODIDES

The possible formation of a polyiodo-iodate containing the $[I_{11}]^-$ anion has been demonstrated in only one paper,[33] describing a study of the $(NMe_4)I-I_2-C_6H_5Me$ system at 6–25 °C. According to these data,[33] a phase with the composition $(NMe_4)[I_{11}]$ crystallises over a fairly wide iodine concentration range: 2.27–9.41 mass % at 6 °C, and 3.53–14.7 mass % at 25 °C. In aqueous ethanol (95%) solutions, tetramethylammonium undeca-iodide is stable only in an extremely narrow iodine concentration range.

The structure of the $[I_{11}]^-$ anion has not been determined, but it may be assumed that it is similar to that of the $[I_9]^-$ anion, except that the inner sphere contains four iodine molecules, two on each end of the $[I_3]^-$ ion.

A study of the $[Ln(ur)_5]I_3-I_2-H_2O$ † systems (0 °C and 25 °C), where Ln represents various lanthanides, detected [85–88] the formation of only one new phase, with the composition $[Ln(ur)_5]I_3.4I_2.10H_2O$, which separated as large acicular hexagonal crystals, incongruently soluble in water. The suggestion that this compound contains the $[I_{11}]^-$ anion has not been confirmed. The new phase apparently contains either the $[I_5]^-$ ion ($[Ln(ur)_5I][I_5]_2.10H_2O$) or chain anions built into the cation matrix.

Anions with the composition $[I_{13}]^-$ have not been detected in any of the polyiodo-iodates synthesised. The preparation of substances with anions containing more than 13 iodine atoms is even less likely. The reaction of iodine with ferrocene in acetone or chloroform gives a black powder with the composition $[Fe(C_5H_5)_2].10I_2$, which decomposes when heated to 170 °C to give iodine and ferrocene, [19] but the actual nature of this substance is still not known.

Thus discrete polyiodo-iodate anions contain not more than 5–7 iodine atoms. The $[I_9]^-$ and $[I_{11}]^-$ anions are rather oligomeric chain anions. If conditions are created for a further increase in the number of iodine atoms in the anion, the latter becomes polymeric, and consists chiefly of $[I_3]^-$ and $[I_5]^-$ ions.

VII. POLYIODO-IODATES WITH CHAIN ANIONS

The tendency for iodine molecules to form chain polyiodo-iodate anions $[I_x]^-_\infty$ (x = 3, 5, or 7) is often observed when the molecules of substances reacting with iodine have a planar configuration and are able, after oxidation, to form a "stacked" structure containing cavities and channels with dimensions and geometry comparable with those of the polyiodo-iodate chain. [89]

When the chains are not commensurate with the framework of the substance, the latter contains solvent molecules in its channels, as established [90] for the crystals of $[(TMA).0.09H][I_5].0.7H_2O$.# The polyiodo-iodate chains in this complex consist of $[I_5]^-$ ions (Fig.12), and do not have a fixed position. In other polyiodo-iodates, some of the channels are occupied by iodine chains, and some by solvent molecules, for example $[Pd(bqd)_2][I_x].0.5C_6H_4Cl_2$.§ [91]

In various organic and inorganic polymers containing cavities of appropriate size, the cavities can be occupied by quasi-one-dimensional chains of iodine atoms.

A polyiodo-iodate chain generally consists of $[I_3]^-$ or $[I_5]^-$ ions or their various combinations. Less frequently, the chains contain $[I_7]^-$ ions. If the chains containing $[I_3]^-$ ions are represented as ...I(1)–I(2)–I(3)...I(1)–I(2)–I(3)..., it may be assumed that the distance I(1)–I(2) and I(2)–I(3) vary in the range $R - \delta$, and the distances I(3)...I(1) in the range $R + 2\delta$, where R = 2.95–3.28 Å, and δ = 0.15–0.35 Å. The most stable structure is that with linear chains, in which R = 3.2 Å and δ = 0.15 Å. [92] For linear chains containing $[I_5]^-$ ions, ...I(1)–I(2)–I(3)–I(4)–I(5).....I(1)–I(2)–....., the interatomic distances I(1)–I(2) are $R - \varepsilon$, and the distances I(2)–I(3) and I(3)–I(4) are $R + \delta$, and the most stable structure is that with ε = 0.5 Å. [92]

The channels of the stacked structures are not always completely filled by the chain anions. For example, in $(TTF)[I_x]$¶ they occupy only 40–50% of the volume, [93] so that the chain anions have little influence on one another.

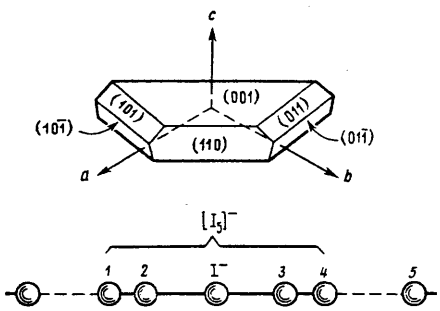


Figure 12. Crystal habit of $[(TMA).0.09H][I_5].0.7H_2O$ and a fragment of a polyiodo-iodate chain; [90] interatomic distances (Å): 1–2 = 2.74; 2–I^- = 3.26; I^-–3 = 3.26; 3–4 = 2.74; 4–5 = 3.50; 1–5 = 15.5.

Ordered regions ($[I_3]^-$ and $[I_5]^-$ ions) and disordered regions (the intermediate regions between the chains) alternate in the quasi-one-dimensional polyiodo-iodate chains. The disordered regions can be regarded as amorphous one-dimensional formations. [51,94–97]

Phase transformation to a completely ordered structure throughout the chain is not observed above 20 K. [95,98]

Three types of polyiodo-iodate with polymeric anions are examined below: polyiodo-iodates of heterocyclic compounds (mainly aromatic), coordination compounds of *d* elements with macrocyclic ligands, and polymeric carbohydrates.

1. Polyiodo-iodates of Heterocyclic Compounds

Many heterocyclic compounds react with iodine or its mixtures with KI in inorganic solvents or aqueous solutions: tetrathiofulvalene, tetrathiotetracene, tetraselenotetracene, tetracyanoquinodimethane, thiopyranylidene, phenazine, thiophenazine, etc. The reaction products are isolated by isohydric or isothermal crystallisation as acicular crystals containing polyiodo-iodate chains.

In the compound $(TTT)_2[I_3]_{1+x}$ † (x = 0.012–0.1), [99–114] the stacked cations with an interplanar distance of 3.32 Å [103,109,110] contain channels occupied by linear chains of symmetric $[I_3]^-$ ions joined to one another; the interionic distance is 3.00–3.64 Å (Fig.13). The non-stiochiometry of the compound is due to the appearance of iodine molecules in the chain. The greatest non-stoichiometry of the polyiodo-iodate chain is observed when $(TTT)_2[I_3]_{1+x}$ is recrystallised from a solution, heated to 95 °C, in nitrobenzene containing 3×10^{-3} M TTT at a molar ratio iodine/TTT = 1 and a cooling rate of 3 K h^{-1}. [101] Crystals with the stoichio-

† ur = urea.

TMA = trimesic acid, $C_6H_3(COOH)_3$.

§ bqd = o-benzoquinone dioximate.

¶ TTF = tetrathiofulvalene.

† TTT = tetrathiotetracene.

metric composition can be obtained by decreasing the TTT concentration, the molar ratio iodine/TTT, and the cooling rate.

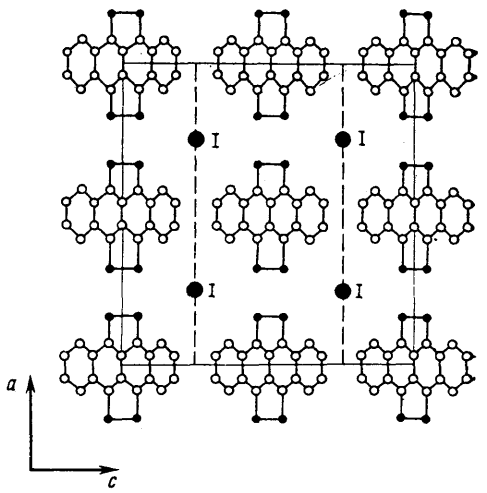


Figure 13. [010] projection of the compound $(TTT)_2[I_3]$;[102, 110] the small black and open circles represent the atoms of sulphur and carbon respectively; the polyiodo-iodate chains lie at right angles to the plane of the Figure and are denoted by large black circles.

To obtain single crystals of $(TTT)_2[I_3]$, it is recommended[114] that the substance be crystallised from a gaseous mixture of TTT and iodine, passed in separate streams into a special crystallisation vessel.

In another method, aqueous solutions of TTT acetate and potassium or sodium iodide are mixed.[113]

When the sulphur atoms in the TTT molecule are replaced by selenium atoms (tetraselenotetracene, TSeT), the structure of the polyiodo-iodate chain is altered; in addition to $[I_3]^-$ ions, it also contains $[I_5]^-$ ions.[108,115–119] Three homogeneity ranges have been detected for the compound $(TSeT)_2[I_3]_x$ ($x = 0.17–0.40$):[118] a phase (A) ($x = 0.17$), a phase (B) ($x = 0.24$), and a phase (C) ($x = 0.26$). It is considered[118] that only the phases (B) and (C) contain $[I_3]^-$ and $[I_5]^-$ ions in the chains. Complete charge transfer to the polymeric anion has been established for the phase (A), which is also the phase with the highest electrical conductivity.

The reaction of iodine with tetrathiofulvalene (TTF) in benzene or acetonitrile gives four new phases, depending on the original component ratio: two stoichiometric, $(TTF)_3.[I_3]_2$ and $(TTF)[I_3]$, and two non-stoichiometric, $(TTF).[I_3]_x$ ($x = 0.24–0.26$) and $(TTF)[I_3]_x$ ($x = 0.77–0.87$).[120–128] The syntheses almost always give a mixture of these phases, which are difficult to separate. In the solid-phase synthesis, the number of new phases formed decreases to two: $(TTF)[I_3]$ and $(TTF)[I_3]_x$ ($x = 0.23$).[129]

In all TTF polyiodo-iodates, the stacked structure of the cation contains zigzag chains consisting of $[I_3]^-$, $[I_5]^-$, and I^- ions and iodine molecules.[120,122,124,126] This non-uniform composition of the chains is apparently due to the presence in the new phases of an appreciable number of different trace components and to the difficulty of separating the reaction products.

For the reaction

$$(TTF)(\text{crystalline}) + 3/2\ I_2(\text{crystalline}) = (TTF)[I_3]\,(\text{crystalline})$$

the quantities ΔG^0_{298}, ΔH^0_{298}, and ΔS^0_{298} are -5.4 ± 0.4 kJ mole^{-1}, -15.1 ± 0.8 kJ mole^{-1}, and 32 ± 1.3 J mole^{-1} K^{-1} respectively.[130]

Tetraselenofulvalene polyiodo-iodates $(TSeF)[I_3]_x$ have been synthesised, but the chain structure of the anions has not yet been studied in detail.[131]

Quasi-one-dimensional polyiodo-iodate chains have been detected in $(TPDTP)[I_x]$# ($x = 2.2–3.4$).[132,133] The polymeric anions consist of either $[I_3]^-$ ions ($x = 2.2$) or a combination of $[I_3]^-$ and $[I_5]^-$ ions ($x = 3.4$). The interionic distances in the $[I_3]^-...[I_3]^-$ chains are 5.49 Å.[132] in the reaction with iodine, the TPDTP molecule loses 0.76–0.90e.

Phenazine (P), phenothiazine (PT), and their derivatives can be oxidised by iodine either in solution in benzene or ether or by thoroughly grinding the starting materials in small quantities of these solvents.[94,95,133–136] The oxidation products have the composition $P[I_x]$ ($x = 1.5–1.6$) and $(PT)[I_3]$, and have polyiodo-iodate chains containing asymmetric $[I_3]^-$ ions and $[I_5]^-$ ions.[134,136] The distance between the $[I_3]^-$ ions in the chain is 3.7–3.9 Å.[95]

Quasi-one-dimensional chains consisting of $[I_3]^-$ anions, with an interionic distance of 3.68 Å,[133] have been detected in the crystal structure of $(NMe_4)^+(TCNQ)^{-2/3}[I_3]^-_{1/3}$ § and its derivatives.[137–141] When the tetramethylammonium cation is replaced by the isopentyldimethylammonium cation, the chains acquire quasi-three-dimensional character.[133] The phase transformation of $(NMe_3H)(TCNQ)[I_3]$ at 150 K does not influence the structure of the polyiodo-iodate chains, and alters only the order in which they are arranged.[141]

All the above polyiodo-iodates have cations with a stacked structure, and belong to the group of radical-cation salts.

2. Polyiodo-iodates of Polymeric Carbohydrates and Hydrocarbons

Macromolecular carbohydrates (amylose, cyclodextrins, polyvinyl alcohol) and hydrocarbon (polyacetylene, etc.) react in aqueous solution with iodine or its mixtures with KI to form strongly coloured products containing chains of $[I_3]^-$, $[I_5]^-$, and $[I_7]^-$ ions in the channels and cavities of their matrices.

In the channels of amylose (Am), the chains consist chiefly of $[I_5]^-$ ions.[49,142–155] When the solid complexes $Am[I_5]_\infty$ are heated slightly, partial decomposition of the anions to $[I_3]^-$ and iodine takes place.[150] The interionic distance in the chain (3.1–3.5 Å) indicates appreciable interaction of the anions along the chain. The complex with the composition $Am[I_5]_\infty$ contains 50–500 iodine atoms, if there are 3.9 glucose units for every iodine atom.[148,151] Depending on the degree of polymerisation of amylose (the length of its spirals), the concentrations of iodine and iodide ions in the chain may include other ions: $[I_7]^-$, $[I_8]^{2-}$, and $[I_6]^{2-}$. With increase in the length of the chains,

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TPDTP = tetraphenyldithiopyranylidene.

§ TCNQ = 7,7,7,6-tetracyanoquinodimethane.

the maximum of the absorption band in the electronic spectra at 580 nm is displaced to 630 nm with a simultaneous increase in the molar absorptivity.[146]

The average decrease in enthalpy in the formation of $Am[I_5]_\infty$, calculated for one glucose structural unit and one mole of combined iodine, is −5.2 kJ mole^{-1}.[149]

The polyiodo-iodates of cyclodextrins (CD) have different compositions, depending on the synthesis conditions: $(\alpha\text{-CD})_2M[I_5].8H_2O$ (M = Li, Na, Tl), $(\alpha\text{-CD})_2M[I_5].27H_2O$ (M = K, NH_4, Ca, Sr, Zn, Cd), $(\alpha\text{-CD})_2M[I_5].(12\text{–}19)H_2O$ (M = K, NH_4, Rb, Cs).[149,143,150,156–158] The units of the almost linear polyiodo-iodate chain are $[I_5]^-$ ions.

The central I^- atom of each ion of this type is situated between the dimeric molecules of (α-CD) and does not occupy a definite structural position; the amplitude of its movement is about 1.7 Å.[155,156,159]

The metal cations and water molecules are situated outside the channels of the (α-CD) structure, and are separated from the $[I_5]^-$ anions by a distance of about 6 Å, so that their influence on the polyiodo-iodate anion is slight.[45,143]

In the (β-CD)–iodine complexes, the channels of diameter 6.2 Å are occupied by zigzag chains of $[I_7]^-$ ions.[156]

When iodine is added to polyacetylene during its formation in n-hexane, black polymers with the composition *cis*-$(CHI_{0.06})_\infty$ and *trans*-$(CHI_{0.22})_\infty$ separate. The *trans*-isomer was isolated by heating the mixture of polymers in a vacuum or in argon at 180 °C.[160,161] Polyacetylene film is iodinated by treating it with iodine vapour[161] or by immersing it in CCl_4 saturated with iodine.[162,163]

Polyacetylene polyiodo-iodates with other compositions, for example $(CHI_x)_\infty$, where x = 0.12–0.23, can also be obtained.[164–168]

According to Ref.168, the surface layer of the polymer fibres contains $[I_7]^-_\infty$ ions. In a vacuum, these ions decompose, leaving only $[I_5]^-$ ions in the chains, and the composition of the polymer approaches $(CHI_{0.15})_\infty$.

Thus each $[I_5]^-$ ion of the linear chain accepts one electron per 33 carbon atoms of the polyacetylene. Other charge-transfer ratios are also observed.

The polyiodo-iodate chains are arranged between the fibres of the polymer[169] in different ways.[168–171]

The chains of *cis*-$(CHI_{0.23})_\infty$ contain 93% $[I_5]^-$ ions and 7% $[I_3]^-$ ions;[162] the $[I_5]^-$ ion is linear, with a symmetrical charge distribution. When the substance is kept for a long time in a vacuum, the concentration of $[I_3]^-$ ions in the chain increases. An interesting feature is that the ratio of $[I_3]^-$ and $[I_5]^-$ ions in the chains alters when the polyacetylene films are stretched.[98] According to Ref.163, the ions predominating in the polymer $(CHI_x)_\infty$ are $[I_3]^-$ and $[I_5]^-$ at $x \leq 0.1$, $[I_5]^-$ at $x \geq 0.12$, and $[I_7]^-$ at $x > 0.3$.

In the spiral structure of polyvinyl alcohol, the polyiodo-iodate chains consist of $[I_3]^-$ ions.[172–175]

The iodination of polycyclic aromatic compounds (perylene, pyrene, flavone, etc.) gives chain polyiodo-iodates.[176,177] The nature of the chain anions in this case has not been finally established, although the presence of $[I_7]^-$ ions has been assumed.[178,179]

3. Polyiodo-iodates of *d* Elements with Macrocyclic Ligands

Polyiodo-iodate chains may be formed in a large number of complex compounds of *d* elements with chelating macrocyclic ligands with a planar configuration (phthalocyanines, tetrabenzoporphyrinates, diphenylglyoximates, benzoquinone dioximates, ethylenediamine complexes of metals, etc.) when these compounds are oxidised by iodine.

Polyiodo-iodate chains are formed in the stacked structure of the cations only when the complex-forming metals are arranged above one another at a relatively short distance of 3.15–3.40 Å.[180] The influence of the iodine atoms on the production of the channels in the stacked structure of the cations has not been proved.

In most cases these polyiodo-iodates are charge-transfer complexes.

The following six groups of complex have been studied in detail: I) diphenylglyoximates with the composition $[M(Hdpg)_2][I_x]$,¶ where x = 0.58–0.68, and M = Ni and Pd;[51,91,181–184] II) benzoquinone dioximates with the composition $[M(Hbqd)_2][I_x]$, where x = 0.5–0.7, and M = Ni and Pd;[91,96,185–188] III) phthalocyanines with the composition $[M(pc)_n][I_x]_n$,† where $x \geq 3$, and M = Cu, Zn, Al, Ga, Si, Cr, Fe, Co, Ni, Pt;[188–195] IV) ethylenediamine complexes with the composition $[M(en)_2][I_3]_2$, where M = Zn, Cd, Ni, Co, Pd;[23,67,89,196–198] V) tetrabenzoporphyrinates with the composition $[Ni(tbp)_2]_2.[Ni(tbp)]^+[I_3]^-$; #[199–201] VI) tetra-azoazulenes with the composition $[M(taa)][I_x]$,§ where x = 0.8–1.9, and M = Cu, Co, Ni, Pd.[202–204]

Polyiodo-iodates with macrocyclic ligands are usually prepared by the same method: the metal chelate and iodine are dissolved in an organic solvent (toluene, dichlorobenzene) with heating, sometimes in the presence of small quantities of KI, followed by slow isohydric crystallisation.[91,185,190,205]

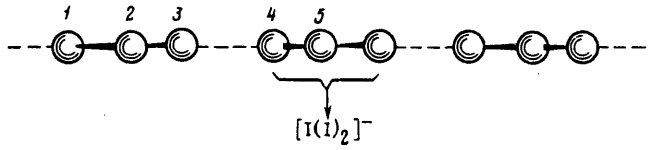


Figure 14. Structure of the polyiodo-iodate anion in $[Ni(Hbqd)_2][I_{0.5-0.7}]$; interatomic distances (Å): 1–2 = 2.96; 2–3 = 2.90; 3–4 = 3.80; 4–5 = 2.90.[96,186]

$[I_5]^-$ anions predominate in the polyiodo-iodate chains of the complexes of the first group, and $[I_3]^-$ ions in the complexes of the second group (Fig.14). Group III also includes the polyiodo-iodates of phthalocyanines with partly oxidised metal-containing macro-rings with the composition $[M(pc)O][I_x]$, where x = 0.5–5.5, and M = Sn, Ge, and Si.[206,207] These substances are stable in air, and lose iodine only when heated above 100°. The anions of the phthalocyanines contain symmetrical $[I_3]^-$ ions with an interionic distance of 3.72 Å.

¶ dpg = 1,2-diphenylglyoximate.

† pc = phthalocyanine.

tbp = tetrabenzoporphyrinate.

§ taa = tetra-azoazulene.

The energy characteristics of the formation of phthalocyanine polyiodo-iodates in the reaction

$$[M(pc)]\,(crystalline) + 1/2\,I_2(crystalline) = [M(pc)]\,[I]\,(crystalline)$$

are, for M = Cu, Co, and Ni, $\Delta H^0_{298} = -13.0$, -16.7, and -18.8 kJ mole^{-1} respectively, and $\Delta S^0_{298} = -24.3$, -15.5, and -33.9 J mole^{-1} K^{-1} respectively.[130]

Thus the thermodynamic stability of the phthalocyanine polyiodoiodates decreases with increase in the atomic number of the complex-forming element.

In polyiodo-iodates containing ligands with large rings (pc, tbp, tmp,¶ etc.), the chain anion consists of $[I_3]^-$ ions; when the ligands contain small rings, however, the chains contain $[I_5]^-$ ions, for example in the compounds of Ni and Cu with oep.†[208]

Partial oxidation of the metal-containing macro-rings does not alter the nature of the polyiodo-iodate chains. $[I_5]^-$ ions appear in the chains only at a high iodine concentration.[206,207]

In the complexes of groups IV and V, the chains contain asymmetric $[I_3]^-$ ions with an interionic distance of 3.598 Å.[89] Analysis of the Raman and Mössbauer spectra showed that the chains in the compounds of these groups do not contain iodine molecules or $[I_5]^-$ ions.[181,187,199,200]

In recent years, another class of chain polyiodo-iodates has appeared, namely inorganic polymers. Treatment of the polymer $(SN)_\infty$ with iodine vapour (20 mmHg, 350 °C) gives $(SNI_{0.14})_\infty$. In this product, the polyiodo-iodate chains consist of $[I_3]^-$ and $[I_5]^-$ ions, and also strongly polarised iodine molecules.[209,210]

VIII. SUMMARY

The above data show that the size, configuration, and composition of the polyiodo-iodate anion are determined not only by the cation environment but also by the synthesis conditions.

Sodium, potassium, and rubidium polyiodo-iodates containing more than five iodine atoms are extremely unstable, and it has not yet been possible to isolate them from aqueous solutions as individual solid phases, although a complex with the composition $(NH_4)[I_5]$ has been obtained. This branch of the chemistry of the alkali metal polyiodo-iodates requires further study.

In $(NR_4)I-I_2-H_2O$–organic solvent systems, polyiodo-iodates with all anions from $[I_5]^-$ to $[I_{11}]^-$ may be formed, but there is no system containing tetra-alkylammonium iodides in which a range of crystallisation of octa-iodides has been detected, or in which the crystallisation ranges of all other polyiodo-iodates coexist.

Non-aqueous solvents often stabilise polyiodo-iodate anions and convert the adducts into ionic compounds, but nevertheless, in the $RbI-I_2-C_6H_6$ system, only the tri-iodide, hepta-iodide, and nona-iodide crystallise, but there is no penta-iodide crystallisation range (see Fig.4). If rubidium iodide in this system is replaced by caesium iodide, the hepta-iodide crystallisation range disappears, but a penta-iodide crystallisation range does not appear.

The fact that the number of iodine atoms in the anions of most polyiodo-iodates is odd is noteworthy. This anion composition is determined by the fact that the complex-forming species is always either an iodine atom with positive, negative, or zero charge, or the tri-iodide ion $[I_3]^-$, and the ligands are iodine molecules or iodide ions. In the $[I_8]^{2-}$ anion, the complex-forming species is an iodine molecule. The coordination number in the polyiodo-iodates is 2. The appearance of coordination numbers of 3 in the $[I_9]^-$ ion and 4 in the $[I_{11}]^-$ ion is unusual, and the distorted chain structure of these anions does not agree with the usual ideas about the conformation of ions with analogous coordination numbers. Nona-iodides and undeca-iodides are rather oligomers.

The influence of the crystal field on the geometry, bond order, and charge distribution in the anions is slight. The stability of the anions is greater when the crystal lattice contains large cations. In an asymmetric crystal field, with a rigid non-deformable cation environment, the anions become angular and asymmetric. For example, the $[I_5]^-$ anion is linear only in a vacuum and in the polyacetylene–iodine system, and in other cases it is V-shaped.

The polyiodo-iodate anions being considered are apparently stereochemically non-rigid structures. The determination of their conformation requires allowance for interatomic vibrations which may bring about rearrangement of the nuclei in the chain. The concepts of "equilibrium structure" and "point symmetry of the nuclear configuration" are therefore inapplicable to these anions.

Polyiodo-iodate chains are ordered only in one direction, and even in this case there are appreciably extended disordered regions (the regions between the anions), as is typical of liquids or amorphous solids. Thus these chains are sometimes regarded[94,95] as one-dimensional liquids. The ordered range along the chains increases with decrease in temperature, but complete ordering is not achieved even at 10–30 K.[94]

All chain polyiodo-iodates can be divided into three types. In compounds of the first type, the chains are stabilised by the presence of spiral and cyclic organic molecules with a closed configuration (amylose, α-cyclodextrin, etc.). The channels in compounds of this type may contain two chains, with different interionic distances.[211] In polyiodo-iodates of the second type, the chains are situated in the channels of stacked cations with an open atom configuration (TTT, TTF, etc.). The chains are stabilised by the planar aromatic system containing donor molecules with π electrons, α-pyrone rings, etc. In compounds of the third type, in which the structure of the cations somewhat resembles that of the polyiodo-iodates of the second type, the chains are stabilised by the oxidation of different functional parts of the inner sphere, and by the arrangement of the chelates in a "stack", in which the complex-forming species form a quasi-one-dimensional chain with the minimum possible interionic distance.

In any case, the presence of a stacked cation structure does not necessarily mean that chains of iodine atoms can be produced in it.[212–215]

Polyiodo-iodates have recently been attracting considerable attention. They include substances with metallic conductivity, some of which may be promising for the product of new semiconductors and high-temperature superconductors.[121,184,185,216] Polyiodo-iodates are being tested as components of future hydrogen energy systems[217,218] and opto-electronic devices,[158] and for the production of organic polymers with controllable composition-dependent electrical properties.[219] Polyiodo-iodates are used in medicinal and antimicrobial preparations,[220] in analytical chemistry,[221] and in the separation

¶ tmp = 5,10,15,20-tetramethylporphyrinate.

† oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate.

of materials and the preparation of extremely pure substances.[222]

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Lomonosov Moscow
Institute of Fine
Chemical Technology