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Structure, conductivity and Raman spectrum of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecanebis(diiodine)

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Abstract

The preparation, X-ray structure, Raman spectrum and conductivity of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecanebis(diiodine) ($2(C_{12}H_{24}O_4S_2)\cdot 5I_2$) are described. The title compound crystallizes in space group $P\bar{1}$ (No. 2) with $a=12.467(8)$, $b=14.097(7)$, $c=15.662(9)$ Å; $\alpha=75.53(4)$, $\beta=75.94(5)$, $\gamma=70.01(4)°$ and $Z=2$; $R=0.043$ for 5899 reflections. The I_2 units form a neutral polyhalogen network anchored at sulfurs. The Raman spectrum at 100 K shows one peak at 164 cm^{-1} assigned to the symmetric stretching mode of I_2. This compound has low electrical conductivity, which is attributed to the lack of continuous polyiodide chains in the structure.

Introduction

Iodine addition compounds crystallize in a wide variety of structures that frequently include I_2–I_2 interactions [1–5]. The present research was undertaken to explore the relation between electrical properties and structure of I_2 complexes. In previous work it has been shown that the interaction of iodine with a non-ionic donor such as a dialkylsulfide or polyether yields semiconducting materials [6–8]. The conduction process in the dialkylsulfide–iodine and polyether–iodine complexes is thought to involve the polyiodides formed. In its interactions with donors, I_2 may give simple I_2 complexes, extended I_2 complexes or polyiodides. In the later case the polyiodide is generated by a donor (D) promoted redox disproportionation that may be schematically represented by

$$2I_2+2D=[ID_2]^+ + I_3^- \qquad (1)$$

The selectivity towards simple I_2 donor complexes or, alternatively, $[ID_2]^+$ polyiodide complexes is determined by the nature of the donor. Diethyl ether and diglyme form simple I_2 complexes. Several authors report the formation of $[ID_2]^+$ polyiodides from the interaction between iodine and crown ethers, but none of these compounds have been characterized by single crystal X-ray structure determination [9–11]. In the present research, the reaction of a macrocyclic polyether sulfide and iodine was investigated for evidence of iodine dissociation, the thought being the thioether might be able to stabilize a soft acid like I^+ and yield a characterizable, crystalline product of the type: $[I\ crown^+][I_n^-]$.

Experimental

4,7,13,16-Tetraoxa-1,10-dithiacyclooctadecane (**1**) was prepared by the method of Dann *et al.* [12]. The product was recrystallized from boiling ether and judged to be pure by ^1H and ^{13}C NMR. FAB-MS for $1H^+$ $m/e=297$. Red crystals of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecanebis(diiodine) (**2**) were grown by evaporation of a solution of **1** and iodine in ethyl acetate. The resonance Raman spectrum was recorded at 100 K with Ar^+ (488 nm) excitation and a Spex 1401 monochromator with photon-counting detection. d.c. conductivity measurements were performed in the usual four-probe configuration using instrumentation and procedures described elsewhere [13].

Intensity data was collected with a Enraf-Nonius CAD-4 diffractometer at a temperature of 153 K. The radiation source was graphite monochromated Mo Kα radiation ($\lambda=0.7107$ Å). The red platelike crystal was mounted on a glass fiber and carefully centered. A set of twenty-five reflections in the range $22.41<2\theta<22.88°$ was used to generate a least-squares refined reduced unit cell corresponding to a triclinic cell. The average value of the normalized structure factor was consistent with a center of symmetry and accordingly the space group was determined to be $P\bar{1}$ (No. 2), which yielded successful solution and refinement. Axial photographs

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TABLE 1. Crystallographic data for $2(C_{13}H_{24}O_4S_2)\cdot 5I_2$

Empirical formula	$[C_{24}H_{48}I_{10}O_8S_4]$
Formula weight	1861.92
Crystal dimensions (mm)	$0.65\times 0.34\times 0.15$
Space group	$P\bar{1}$ (No. 2)
a (Å)	12.467(8)
b (Å)	14.097(7)
c (Å)	15.662(9)
α (°)	75.53(4)
β (°)	75.94(5)
γ (°)	70.01(4)
V (Å^3)	2467
Z	2
ρ_{calc} (g/cm^3)	2.506
μ (cm^{-1})	64.2
Transmission coefficient	0.13–0.42
Radiation	Mo Kα
T (K)	153
Secondary extinction coefficient	1.12×10^{-7}
$R(F)^a$	0.043
$R_w(F)^b$	0.054

$^aR(F)=[\Sigma|(|F_o|-|F_c|)|/\Sigma|F_o|]$. $^bR_w(F)=[(\Sigma w(|F_o|-|F_c|)^2)/\Sigma wF_o^2]^{1/2}$; $w=4F_o^2/\sigma(F_o^2)$.

were taken to verify the cell dimensions. The data were collected using the ω/θ scan technique over the range $2<2\theta<46.0°$ ($\pm h$, $\pm k$, $+l$). The intensities of three standard peaks were monitored at ninety minute intervals showing no appreciable decay. The data collection resulted in 7152 reflections of which 6855 were unique. A summary of the crystallographic data is given in Table 1. Corrections were applied to account for analytical absorption, secondary extinction, polarization and Lorentz effects.

The structure was solved using direct methods. Atomic scattering factors [14] and anomalous dispersion terms [15, 16] were taken from the literature. Final refinement was done using full matrix least-squares based on 5899 reflections ($I>3\sigma(I)$ and 561 variable parameters) and yielded residuals of: $R=0.043$, $R_w=0.054$. Hydrogen atoms were refined with group isotropic thermal parameters while all other atoms were anisotropically refined. The maximum and minimum peak intensities in the final difference map were 2.55 and -1.78 e$^-$/Å^3, respectively, and located in the vicinity of the iodines. All calculations were performed using the TEXSAN7 crystallographic software package [17].

Results and discussion

Structure description

The structure of **2** is shown in Fig. 1 and the final atomic fractional coordinates for the non-hydrogen atoms are given in Table 2. Comparison of these results with the structure of the iodine-free analogue, **1**, [18] shows that the addition of iodine results in no significant distortion of the ring geometry. Of the five I_2 units in the asymmetric unit, four are coordinated to sulfur atoms. Interestingly, the iodine atoms may be considered to form a neutral poly-dihalogen network anchored at sulfurs. This network can be thought of as two sets of nearly coplanar atoms as shown in Fig. 2(a). These two planes of atoms, (I) and (II), intersect at approximately a 65° angle with the atoms S(10B*), I(3B*) and I(4B*) lying at their intersection.

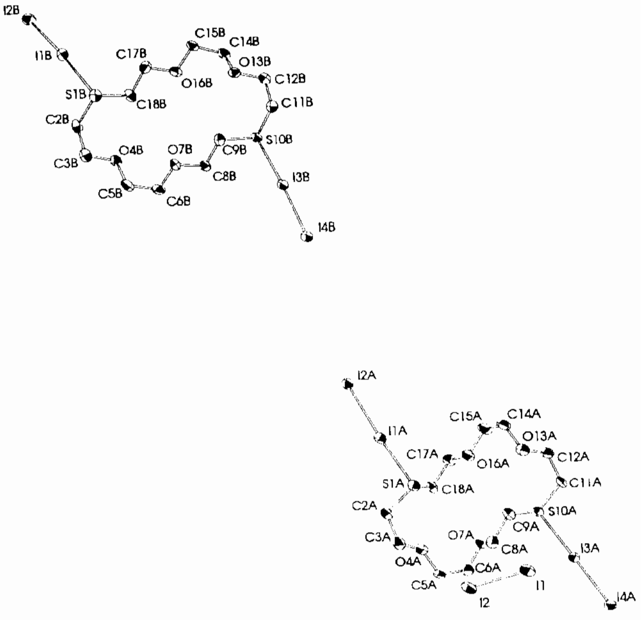

Fig. 1. ORTEP drawing of **2** with thermal ellipsoids drawn at 50% probability level. The hydrogens are omitted for clarity.

Three of the sulfur-coordinated diiodine moieties interact forming a wishbone-like structure in plane (I). The distances at which these interact are as follows: $d(I(2B^*)\cdots I(4A^*))=3.783(3)$ Å and $d(I(4B^*)\cdots I(4A^*))=3.719(2)$ Å. In crystalline I_2, interaction between diiodine units is implicated as causing the lengthening of the I–I bond distance (2.715 Å at 110 K) [19] relative to that found in the gas phase (2.662 Å) [20]. The shortest non-bonded distance in crystalline I_2, however, is 3.50 Å at 110 K [19] which is significantly shorter than $d(I(2B^*)\cdots I(4A^*))$ and $d(I(4B^*)\cdots I(4A^*))$. These longer interaction distances, however, are similar to those found in structures containing coordinated diiodine interactions in the absence of a bridging I_2. For example, dithia[3.3.1]propellane-$2(I_2)$ exhibits a distance of 3.720(1) Å between sulfur coordinated diiodines [1].

The final sulfur-coordinated diiodine is connected via a bridging I_2 extending from I(4B*). This forms an I_6 moiety anchored at each end by sulfur atoms in plane (II). The interaction distances between the bridging I_2 and the coordinated diiodines are similar to those found in polyiodides [21, 22] and other organosulfur

TABLE 2. Atomic fractional coordinates for non-hydrogen atoms in $2(C_{12}H_{24}O_4S_2)\cdot 5I_2$

Atom	x	y	z
I(1)	−0.09016(7)	0.29246(6)	0.25522(5)
I(1A)	0.27712(6)	0.42104(5)	0.69199(5)
I(1B)	1.35763(6)	1.26052(5)	1.04011(5)
I(2)	0.12923(7)	0.17545(6)	0.28112(5)
I(2A)	0.35996(6)	0.54552(6)	0.76764(5)
I(2B)	1.44441(7)	1.30182(6)	1.16944(5)
I(3A)	−0.36336(6)	0.25348(5)	0.49745(4)
I(3B)	0.63572(6)	1.09519(5)	0.77656(5)
I(4A)	−0.44475(7)	0.17336(5)	0.38719(5)
I(4B)	0.59720(6)	0.98465(5)	0.66550(5)
S(1A)	0.1875(2)	0.3179(2)	0.6225(2)
S(1B)	0.2786(3)	1.1940(2)	0.9159(2)
S(10A)	−0.2781(2)	0.3342(2)	0.6008(2)
S(10B)	0.6834(2)	1.1884(2)	0.8934(2)
O(4A)	0.1853(7)	0.1024(5)	0.6182(5)
O(4B)	1.2338(6)	0.9926(5)	0.9033(5)
O(7A)	−0.0518(6)	0.1734(5)	0.6113(5)
O(7B)	1.0210(6)	1.0479(6)	0.8502(5)
O(13A)	−0.2315(7)	0.5486(5)	0.5750(5)
O(13B)	0.7342(6)	1.3844(5)	0.9147(5)
O(16A)	−0.0529(7)	0.4407(6)	0.6747(5)
O(16B)	0.9432(7)	1.3151(5)	0.9817(5)
C(2A)	0.306(1)	0.200(1)	0.618(1)
C(2B)	1.356(1)	1.0621(9)	0.9471(8)
C(3A)	0.286(1)	0.130(1)	0.5677(8)
C(3B)	1.351(1)	0.993(1)	0.8892(8)
C(5A)	0.139(1)	0.0517(8)	0.5738(8)
C(5B)	1.215(1)	0.9421(9)	0.8444(8)
C(6A)	0.016(1)	0.0678(9)	0.6148(9)
C(6B)	1.091(1)	0.9438(8)	0.8669(9)
C(8A)	−0.062(1)	0.2295(9)	0.5230(7)
C(8B)	0.900(1)	1.0571(8)	0.8745(8)
C(9A)	−0.139(1)	0.3367(8)	0.5304(7)
C(9B)	0.838(1)	1.1679(8)	0.8520(7)
C(11A)	−0.370(1)	0.4680(8)	0.5761(8)
C(11B)	0.621(1)	1.3226(9)	0.8519(7)
C(12A)	−0.341(1)	0.5375(9)	0.6197(8)
C(12B)	0.620(1)	1.388(1)	0.9143(8)
C(14A)	−0.183(1)	0.5981(9)	0.617(1)
C(14B)	0.745(1)	1.412(1)	0.9919(8)
C(15A)	−0.138(1)	0.5311(9)	0.7017(8)
C(15B)	0.865(1)	1.4162(8)	0.9841(8)
C(17A)	−0.005(1)	0.3749(8)	0.7497(7)
C(17B)	1.060(1)	1.3083(9)	0.9755(8)
C(18A)	0.085(1)	0.2801(9)	0.7183(7)
C(18B)	1.131(1)	1.2000(8)	0.9723(7)

iodine addition compounds that possess bridging diiodines such as 2(dithizone)–7(I_2) [4] and triphenylphosphine sulfide–3(I_2) [3]. Also typifying these compounds and polyiodides [21, 22], is a slight lengthening of the bridging I_2 over that found in crystalline iodine. This lengthening is also seen in **2** with *d*(I(1)–I(2)) = 2.736(3) Å.

Herbstein and Schwotzer invoke ionic resonance contributions to explain the significant shortening of the S–I bond and corresponding lengthening of the SI–I bond [4]. For instance, in 2(dithizone)–7(I_2) they propose that RSI^+I^- contributes to the resonance hybrid. They also point to 2(ethylenethiourea)–3(I_2) where bond length data is consistent with the formulation $C{=}S\cdots I^+I_4^{2-}I^+\cdots S{=}C$. Although **2** possesses a similar I_6 moiety, it does not exhibit significant shortening of any S–I bond. There is some variation but the shortest S–I bond in **2**, *d*(S(1A*)–I(1A*)) = 2.654(3) Å, is still significantly longer than that observed in 2(ethylenethiourea)–3(I_2), 2.580 Å, and 2(dithizone)–7(I_2), 2.506 Å.

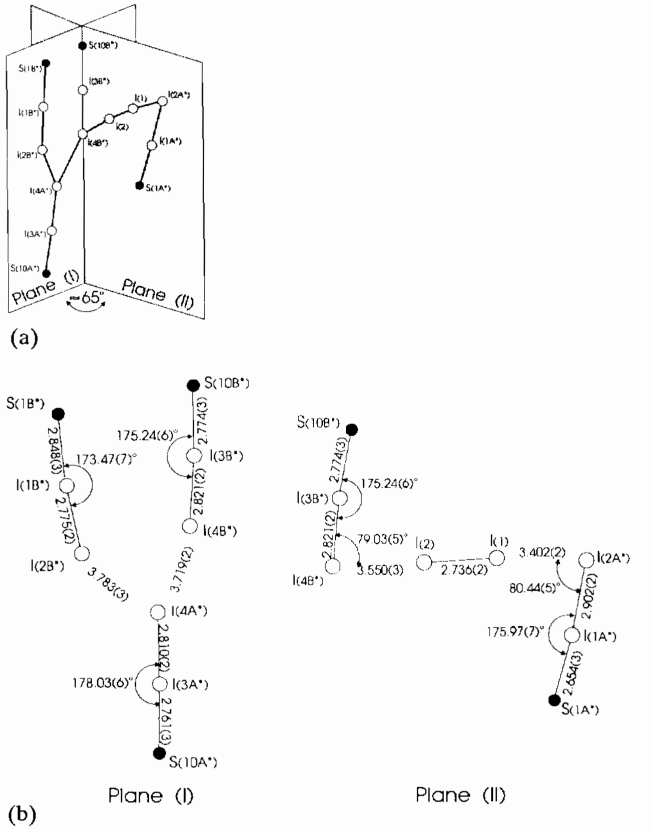

Fig. 2. The structure of **2** can be thought of as two sets of nearly coplanar atoms that intersect at roughly a 65° angle as shown in (a). The bond lengths (Å) and angles for the atoms within each plane are shown in (b).

The coordination of I_2 to sulfur is not linear. There are significant angular distortions with the smallest S–I–I angle being ∠S(1B*)–I(1B*)–I(2B*) = 173.47(7)°. These distortions appear to result from the interactions between diiodine moieties, as inspection of Fig. 2 reveals.

The expected product of the reaction between **1** and iodine was of the type: [I crown$^+$][I_n^-]. Instead a neutral polyiodine network anchored at the sulfurs of the macrocyclic polyether sulfide formed. In retrospect, **1** would be unable to stabilize an I^+ by the macrocyclic effect if the sulfur donor atoms point out of the ring as they do in the crystal structure of **1** [18]. Examination of the crystal structures of three similar macrocyclic polyether sulfides, 1,4,7-trithia-12-crown-4, 1,4-dithia-15-crown-5 and 1,4-dithia-18-crown-6, reveals similar conformations with all the sulfur atoms pointing out of the ring and most of the oxygen atoms pointing inward [18]. However, the crystal structure of **1** coordinating lanthanum(III) demonstrates that the ring is flexible enough that all six sulfur and oxygen atoms may point in to coordinate a cation [23].

These observations are similar to those found for other macrocycles where coordination results in a conformational change [24]. Molecular mechanics calculations of various conformations of all oxygen analog of **1**, 18-crown-6, have been previously performed by Bovill *et al.* [25]. These authors calculate the energy of four conformations of 18-crown-6 adopted upon coordination. They find that these conformations range from 16–33 kJ/mol higher than the conformation corresponding to the uncoordinated crown.

There are three structurally characterized compounds in which an I^+ bridges two sulfur atoms. The first two, bis(thiourea) iodine (I) iodide and μ-iodo-bis(4-iodo-*cyclo*-heptasulfur), exhibit linear S–I–S arrangements and S–I bond lengths of 2.629 and 2.674(7) Å, respectively [26, 27]. The S–I–S array in the third compound $\{[(en)_2Co(SCH_2CH_2NH_2)]_2I\}(NO_3)_5 \cdot 4H_2O$ is nearly linear (173.0(1)°) with an S–I bond length of 2.619(2) Å [28]. These S–I bond lengths are shorter than all but one S–I bond in **2**, $d(S(1A^*)\text{–}I(1A^*)) = 2.654(3)$ Å. A linear S–I–S linkage is expected for a five-electron pair, trigonal-bipyramidal, I^+ center in which the two sulfur atoms occupy axial positions and three lone pairs occupy equatorial positions. It is not clear if an analogous linear intramolecular bond is possible with **1**. In this case and others, it is difficult to predict whether a donor will promote the redox disproportionation of iodine.

Raman spectrum and conductivity

The Raman spectrum of **2** at 100 K shows one peak at 164 cm^{-1} with a high wavenumber shoulder assigned to the symmetric stretching mode of I_2. The shift in the peak from 216 cm^{-1} in the case of I_2 vapor to 164 cm^{-1} in **2** is attributed to electron density donated from the sulfur and neighboring iodine moieties to an antibonding orbital in I_2, lengthening and weakening the bond. Nour *et al.* [29] and Marks [30] have reported similar decreases in the ν_1 mode of I_2 when it is part of a larger iodine network. The electrical conductivity of **2** at room temperature is less than 10^{-8} S/cm. In comparison, solid iodine also has a low conductivity of 5×10^{-12} S/cm perpendicular to the *bc* plane and 1.7×10^{-8} S/cm within the plane at room temperature [31]. These values are far lower than those for polyether–iodine or dialkylsulfide–iodine complexes with similar iodine concentrations to **2** [6, 7]. The poor conductivity of **2** is consistent with the structure. An ion relay conduction mechanism is unlikely because there is no continuous polyiodide chain and some of the iodine atoms are coordinated to sulfur, pinning them down. Band-gap calculations predict that even a linear I_2 chain would be an insulator because of the localized single bonds [32, 33]. This type of distortion is clearly seen in the alternating of long and short bonds within the polyhalogen network studied here.

Supplementary material

Atomic coordinates, bond lengths, bond angles, anisotropic temperature factors and observed and calculated structure factors for **2** are available from the authors on request.

Acknowledgements

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