The Crystal Structure of Bis(thiourea)iodine(I) Iodide

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The yellow compound of composition (thiourea)$_2$.I$_2$, formed from thiourea and iodine in methylene chloride, crystallizes in the monoclinic space group $C2/c$ with $a = 22 \cdot 27$ (2), $b = 5 \cdot 290$ (5), $c = 9 \cdot 808$ (5) Å, $\beta = 115 \cdot 31$ (3)°. There are four units of $\{I[SC(NH_2)_2]_2\}^+ I^-$ in the unit cell. Zirconium-filtered Mo $K\alpha$ data were measured on a Picker automatic diffractometer. The structure was solved by Fourier techniques and refined by full-matrix least-squares methods. All variable parameters were refined, including ansiotropic temperature factors for nonhydrogen atoms, and isotropic ones for hydrogen. The final R index is 0·025 for 851 reflections. Bond distances: I^+–$S = 2 \cdot 629$, S–C $= 1 \cdot 724$, C–N $= 1 \cdot 317$ and 1·296 Å. Bond angles: I^+–S–C $= 106 \cdot 3$, S–C–N (*cis* to I^+) $= 123 \cdot 0$, S–C–N (*trans* to I^+) $= 117 \cdot 4$, N–C–N $= 119 \cdot 5$°. The centrosymmetric cation is not planar; the fold angle I–S–C–N is 17°.

Introduction

The interaction of thiourea with iodine can result in a variety of different compounds, depending on the conditions under which the reaction takes place.

Spectrophotometric studies of solutions of iodine and thiourea in dichloromethane have indicated the presence of a 1:1 molecular complex (Lang, 1962). We have succeeded in growing deep red-brown crystals of a complex of this composition, but owing to the instability of the crystals we have not been able to complete the structure determination.

A compound with a thiourea-iodine mole ratio of 2:1 was obtained by McGowan (1886) by reacting thiourea with iodine in alcohol–water solution. Later X-ray studies showed the colorless compound to be formamidine disulfide diiodide monohydrate, $[(NH_2)_2C–S–S–C(NH_2)_2]^{2+} 2I^-$. H_2O (Foss, Johnsen & Tvedten, 1958). However, if thiourea and iodine are mixed in a 2:1 molar ratio in benzene or dichloromethane at room temperature, a light-yellow solution results from which a yellow solid may be obtained by evaporation of the solvent. A compound fitting this description was described by Werner in 1912, but its structure remained unknown. The color of the compound suggested that it did not contain an I–I bond of the type normally found in X. I$_2$ complexes, but beyond that we were unable to propose any structural properties. The X-ray crystallographic study reported here was begun in the expectation that an unusual type compound would be discovered. (A preliminary report of our findings has been given earlier; Hope & Lin, 1970.)

Experimental

The yellow compound of composition $[(NH_2)_2CS]_2$. I$_2$ was prepared by adding a solution of 0·01 mole of iodine in a minimum amount of dichloromethane, in small portions, to 0·02 mole of finely powdered thiourea in a mortar; for each portion of solution the mix-

ture was ground until all iodine color disappeared. The resulting solid was recrystallized from methylene chloride solution. Specimens for the X-ray study were grown by slow evaporation of the solution. The compound decomposes very rapidly in water, yielding a colorless solution, presumably of the formamidine disulfide iodide mentioned above. The substance is readily soluble in acetone, the solution showing a deep reddish-brown color.

The crystals are clear, yellow monoclinic prisms elongated along the *b* axis. Oscillation and Weissenberg photographs indicated monoclinic symmetry. Based on the systematic absence of reflections other than hkl: $h + k = 2n$, $h0l$: $h = 2n$, $l = 2n$, the space group can be either Cc or $C2/c$. The results of the structure analysis indicate the space group to be $C2/c$.

Cell dimensions were obtained by a least-squares fit to 12 sets of χ, φ, 2θ angles measured on a Picker diffractometer equipped with a full-circle goniostat using Cu $K\alpha_1$ radiation. The cell dimensions are $a = 22 \cdot 27$ (2), $b = 5 \cdot 290$ (5), $c = 9 \cdot 808$ (5) Å; $\beta = 115 \cdot 31$ (3)° ($t = 24$ °C, λCu $K\alpha_1 = 1 \cdot 54051$ Å). Estimated standard deviations (in parentheses) apply to the least significant figures. The density measured by flotation is 2·55 g.cm^{-3}, and the density calculated for four units of $C_2H_8N_4S_2I_2$ per cell is 2·58 g.cm^{-3}.

The crystal used for intensity measurements had dimensions $0 \cdot 1 \times 0 \cdot 1 \times 0 \cdot 25$ mm, and was mounted with the long direction, **b**, within a few degrees of the goniostat φ axis. Intensity data were collected with a Picker automatic diffractometer, using Zr-filtered Mo $K\alpha$ radiation with a NaI(TlI) scintillation detector and pulse-height analyzer. The intensities of 914 unique reflections accessible below $2\theta = 51°$ were measured with the θ–2θ scan technique at a scan speed of 2° min^{-1}, with the scan range given by $[2\theta(\alpha_1) - 0 \cdot 8°] - [2\theta(\alpha_2) + 0 \cdot 8°]$; 20-sec background counts were taken at each end of the scan range. Attenuators were used to keep the count rate below 10,000 counts per sec. Measurements of one monitor reflection were repeated

at 80-reflection intervals. The intensity of this reflection showed no systematic variation.

The intensities were corrected for Lorentz and polarization effects. An e.s.d. for a recorded number of counts was calculated from the expression $\sigma(N) = [N + (0 \cdot 01N)^2]^{1/2}$. An e.s.d. for the net intensity was derived from $\sigma(N)$ for scan and background counts, resulting in 851 reflections for which I_{net} exceeded 3σ (I_{net}). The linear absorption coefficient was calculated to be 60 cm^{-1} for Mo $K\alpha$. The maximum variation in the absorption factor for the crystal used was about 5%. No absorption correction was made.

Solution and refinement of the structure

A three-dimensional sharpened Patterson function could be readily interpreted in terms of one iodine atom, I(1), placed at the center of symmetry at $(\frac{1}{4}, \frac{1}{4}, 0)$ and the other, I(10), on the twofold axis at $(0, y, \frac{1}{4})$. The position of a sulfur atom associated with I(1) was also obtained. The carbon and two nitrogen atoms were located from a subsequent Fourier map. Four cycles of least-squares refinement with anisotropic temperature factors for all included atoms reduced R to 0·03. A difference Fourier synthesis was then calculated with all I, S, N, and C atoms subtracted. All four H atoms were found near their expected positions.

Two additional least-squares cycles, where all variable parameters were refined (isotropic temperature factors for the H atoms), converged with $R = 0·026$. At this stage we noticed that a few of the low-order reflections showed some irregularities, the cause of which was not readily apparent, and we decided to exclude all data with $\sin \theta/\lambda < 0·15$ Å^{-1}. Two final least-

Table 1. *Final positional and thermal parameters with e.s.d.'s*

The anisotropic temperature factor is of the form $\exp\left[-\frac{1}{4}(h^2a^{*2}B_{11} + \ldots + klb^*c^*B_{23})\right]$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I(1)	0.25000	0.25000	0.00000	2.67(2)	2.87(3)	1.83(2)	-0.33(2)	1.15(2)	-0.26(1)
S(2)	0.32357(8)	-0.09202(28)	0.19065(15)	4.30(7)	2.82(6)	2.36(6)	0.48(5)	0.83(5)	-0.16(5)
C(3)	0.37019(20)	0.0645(10)	0.35802(55)	2.75(22)	3.12(23)	2.20(21)	0.04(19)	1.29(18)	0.24(18)
N(4)	0.35353(31)	0.2892(10)	0.36829(60)	3.95(25)	3.48(23)	2.58(21)	0.78(20)	0.83(19)	-0.33(18)
N(5)	0.42105(28)	-0.0511(12)	0.45901(68)	3.51(25)	3.94(28)	3.15(24)	0.72(21)	0.38(21)	0.26(21)
I(10)	0.50000	0.45838(10)	0.75000	3.56(3)	3.20(3)	2.41(2)	0.00	0.67(2)	0.00
H(6)	0.3205(41)	0.374(15)	0.3402(90)	5.(1)					
H(7)	0.3829(37)	0.399(13)	0.4657(88)	5.(1)					
H(8)	0.4458(38)	-0.014(16)	0.5377(87)	5.(2)					
H(9)	0.4362(39)	-0.207(17)	0.4397(90)	5.(1)					

Table 2. *Observed and calculated structure factors for bis(thiourea)iodine(I) iodide*

Columns are h, $10F_o$, $10F_c$, and $100/\sigma(F)$. 'U' means 'unobserved', 'X' means 'not included in final least-squares cycles' ($\sin \theta/\lambda < 0·15$ Å^{-1}).

squares cycles resulted in some minor shifts, and converged with $R = 0.025$.

The final parameters with their e.s.d.'s are listed in Table 1, and a comparison of observed and calculated structure amplitudes is given in Table 2. (Including all 'observed' and 'unobserved' reflections, R is 0.028.)

All calculations were performed on an IBM 7044 computer using locally developed or adapted programs. The least-squares program (originally written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood) was used to minimize the sum $\sum w(\Delta F)^2$, where $w = 1/\sigma^2(F)$. The anisotropic temperature factor is of the form $\exp[-\frac{1}{4}(a^{*2}h^2B_{11} + \ldots + 2b^*c^*klB_{23})]$ and the isotropic temperature factor is of the form $\exp(-B\sin^2\theta/\lambda^2)$. Atomic scattering factors were those of Hanson, Herman, Lea & Skillman (1964) for I, S, N, and C (values for I^0 were used for both I atoms) and those of Stewart, Davidson & Simpson (1965) for H. Anomalous scattering corrections ($\Delta f'$ and $\Delta f''$) given by Cromer & Liberman (1970) were used for I and S. E.s.d.'s were derived from the diagonal elements of the least-squares normal equation matrix.

Discussion

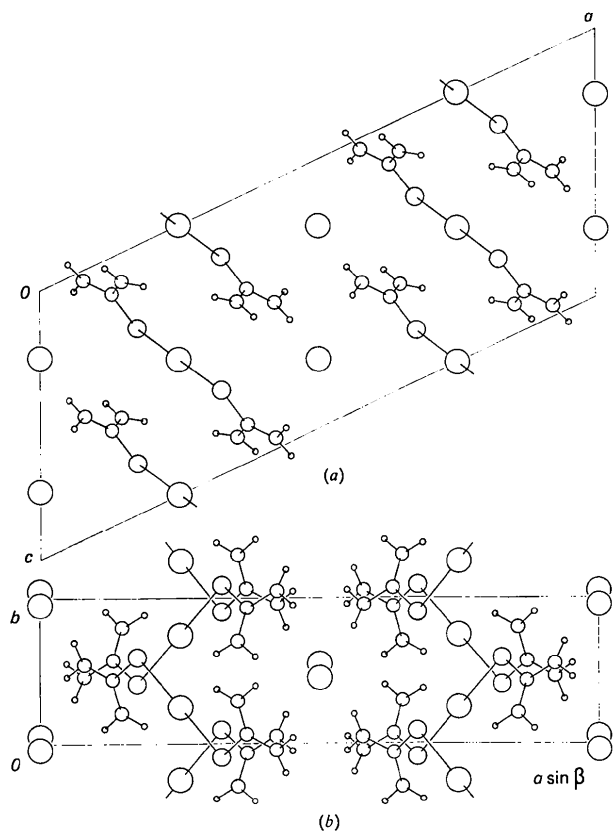Evidence for the existence of the iodine(I) cation, I^+, has been cited by different investigators (Arotsky &

(a)

(b)

Fig. 1. Projections of the structure of $\{I[SC(NH_2)_2]_2\}I$; (a) along **b**; (b) along **c**.

Symons, 1962; Garrett, Gillespie & Senior, 1965). The I^+ ion is a powerful electrophile and can exist only in media with weak nucleophilic properties. In solvents containing a stronger nucleophilic agent, complexes of I^+ are formed. For example, when iodine is dissolved in pyridine it gives the (pyridine)$_2I^+$ ion. The existence of the (pyridine)$_2I^+$ ion was suggested by Carlsohn (1932) and later confirmed from its crystal structure (Hassel & Hope, 1961).
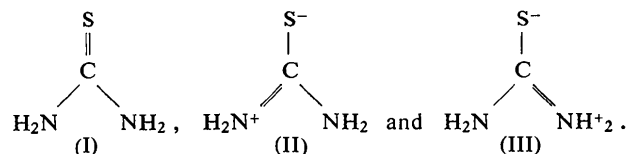
The I^+ ion has the electronic configuration $(5s)^2(5p)^4$ for the outermost shell. In the ground state, the four electrons in the $5p$ orbitals are arranged in a spin-free form as $(5p_x)^2(5p_y)^1(5p_z)^1$. In a strong ligand field, however, these electrons are rearranged in a spin-paired form as $(5p_x)^2(5p_y)^2$, and the $5p_z$ orbital is therefore available for sp hybridization with the $6s$ orbital which occupies the next higher energy level.

The ionic character of the present compound is readily established from the crystal structure, shown in Fig. 1, projected along b and c, respectively. The compound consists of bis(thiourea)iodine(I) cations, $I[SC(NH_2)_2]_2^+$, and iodide anions.

Thiourea is known to form coordination complexes with most of the transition metals and acts as a strong ligand. In the structure of the bis(thiourea)iodine(I) ion, the I^+ ion behaves in a manner very similar to transition metal cations such as Ag^+, Cu^+, Au^+, Hg^{2+}, etc. The linear configuration around I^+ indicates that the bis(thiourea)iodine(I) ion is formed by the coordination of two thiourea ligands with sp hybridization with I^+.

Bond distances and angles are given in Fig. 2. The S–I distance of 2.63 Å appears to be the shortest S–I distance observed to date; the next shortest (2.69 Å) is that found in the dithiane.2IBr complex (Knobler, Baker, Hope & McCullough, 1971). In the present structure the distance is only 0.26 Å longer than the sum of the single-bond covalent radii, and one might expect that the formation of this strong bond would be accompanied by marked changes in the geometry of the thiourea moiety.

Thiourea has been found to be planar [Elcombe & Taylor, 1968 (neutron); Truter, 1967 (X-ray)]. Accordingly, it can be represented by the three resonance structures:

$$
\begin{array}{ccc}
S & S^- & S^- \\
\| & | & | \\
C & C & C \\
/ \backslash & /\!\!/ \backslash & / \backslash\!\!\backslash \\
H_2N \quad NH_2, & H_2N^+ \quad NH_2 \text{ and} & H_2N \quad NH^+_2. \\
(I) & (II) & (III)
\end{array}
$$

Complexation with sulfur as the donor site would enhance (II) and (III). The two C–N bond distances in the present structure do appear somewhat shorter than in thiourea itself. But the C–S distance gives no indication of a corresponding lengthening relative to that reported by Truter (1967), although relative to the room-temperature results ('uncorrected') of Elcombe

& Taylor (1968) a slight lengthening is observed. Apparently, a more rigorous interpretation must await data of higher precision. However, in this connection we note that in the complex (X.I–I type) formed with 1 mole of I_2 to 1 mole of N-phenyl-N'-benzoylselencurea, a definite lengthening of the C–Se bond has been observed (Lin, 1969).

Normally, bond angles at sulfur are found to be in the range 97–103°, and in thiourea complexes the preferred orientation of the bond would be in the plane of the molecule. However, a model constructed from these premises, with a symmetrical thiourea moiety, shows that the steric requirements of I(1) and N(4)–H(6) cannot be satisfied without serious strain. The actual geometry of the complex gives a very graphic impression of how the strain is relieved through the various modes of distortion available: widening of the angles I$^+$–S–C (106·3°) and S–C–N(4) (123·0°) with concomitant narrowing of S–C–N(5) (117·4°), and finally a twist about the S–C direction to a dihedral angle I–S–C–N(4) of 17°. Nothing is to be gained by making the thiourea moiety non-planar, in keeping with the exact planarity of this group (maximum deviation from the least-squares plane is 0·01 Å).

The packing contacts between anions and cations occur via the hydrogen atoms. I$^-$ at ($\frac{1}{2}$,0·46,$\frac{3}{4}$) is near the plane of the thiourea group, making contacts of 2·9 and 3·1 Å with H(7) and H(8), respectively; the distance from H(9) to I$^-$ at ($\frac{1}{2}$, −0·46,$\frac{1}{4}$) is also 3·1 Å.

The ultraviolet absorption spectrum of thiourea in dichloromethane shows a band with maximum at about 250 nm. For bis(thiourea)iodine(I) iodide this maximum shows a slight shift towards longer wavelengths,

and a new band ('charge transfer') appears at about 300 nm. A similar description applies to N-phenyl-N'-benzoylselenourea and its I_2 complex, which is known to be of the type X–I–I (Lin, 1969). The two bands occur at about 260 and 325 nm, respectively. It seems that the assignment of molecular geometry from spectral data of this kind alone is hazardous indeed.

To our knowledge the bis(thiourea)iodine(I) cation represents only the second case of an iodine(I) complex found in a crystal structure, the first being bis(pyridine)iodine(I) (Hassel & Hope, 1961). Further expansion of the list, however, should be quite straightforward.

In order not to confuse the iodine(I) complexes with 'iodonium' ions it is sufficient to point out that the former consist of I$^+$ ions and two complexing groups, each with a lone pair of electrons, whereas the latter are made up from I$^+$ and two radicals, each contributing a single electron.

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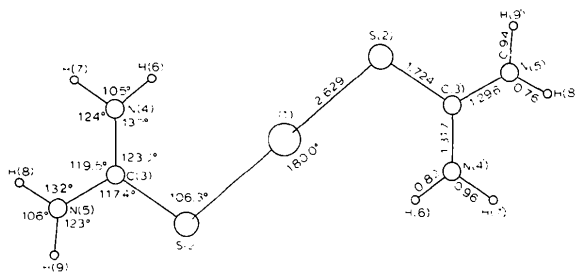WERNER, E. A. (1912). *J. Chem. Soc.* **101**, p. 2166.

Fig. 2. Bond distances and angles in the I[SC(NH₂)₂]₂⁺ ion. E.s.d.'s: I–S = 0·001, S–C = 0·005, C–N = 0·008, N–H = 0·08 Å; I–S–C = 0·2°, other angles with no H = 0·5°, with one H = 5–6°, with two H = 7–8°.