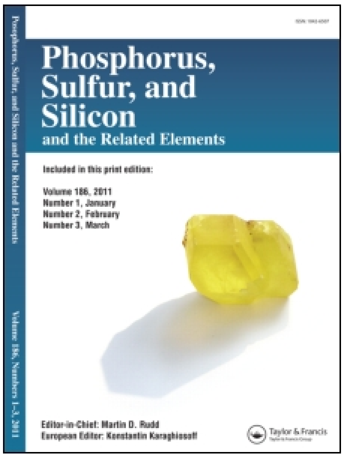

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SYNTHETIC, STRUCTURAL AND SPECTROSCOPIC STUDIES OF THE DONATING PROPERTIES OF SULPHUR-RICH MOLECULES TOWARDS I_2: X-RAY STRUCTURE OF 1,3-DITHIOLE-2-THIONE · DIIODINE

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SYNTHETIC, STRUCTURAL AND SPECTROSCOPIC STUDIES OF THE DONATING PROPERTIES OF SULPHUR-RICH MOLECULES TOWARDS I_2: X-RAY STRUCTURE OF 1,3-DITHIOLE-2-THIONE · DIIODINE

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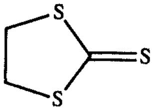
A study on the 1:1 complex between I_2 and 1,3-dithiole-2-thione (dtlt) in $CHCl_3$ solutions and in the solid state is reported. The refined formation constants ($K_{20°}$ = 89 ± 1 mol^{-1} dm^3) and molar extinction coefficients have been calculated simultaneously in the 260–550 nm range by means of a general computer program. The enthalpy change ($\Delta H° = -9.66 \pm 0.01$ Kcal mol^{-1}) falls in the range of moderately-strong thione donors. The features of the u.v.-vis. spectrum indicate that the complex is of charge-transfer type. The 1:1 complex has been isolated in the solid state and IR spectroscopic results suggest the thione sulphur donation. FT-Raman spectra on this solid compound show a very strong band attributed to $\nu(I\text{-}I)$ at 143 cm^{-1}. An X-ray structure of dtlt·I_2 has shown that the crystals are orthorhombic, space group $P2_12_12_1$, a = 11.413 (7), b = 10.038 (7), c = 7.760 (6) Å, V = 889.0 (1.1) $Å^3$, Z = 4. Solution and refinement of intensity data gave final residuals of R = 0.0537. A comparison with the donor behaviour of 1,3-dithiolane-2-thione shows that while in solution dtlt has values of K and enthalpy change higher than those found in the dtt case, in the solid state the more significant bond distances and angles are very similar.

Key words: Diiodine; C.T.-complexes; X-ray; trithiocarbonates; 1,3-dithiole-2-thione.

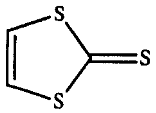
INTRODUCTION

Polyfunctional acyclic and heterocyclic thiones are potentially multisites donors towards transition metals and I_2.[1,2] In the course of our investigation in this field, we have found that thione-sulphur is usually involved in the donation even though the ligand contains other potential donor sites. A variety of inert or labile charge-transfer complexes with I_2 in the 1:1 and 1:2 ratios,[3,4] and mononuclear or polynuclear complexes with terminal[5] or bridging[6,7] ligands have been found.

In the case of trithiocarbonates 1,3-dithiolane-2-thione (dtt), and 1,3-dithiole-2-thione (dtlt) as shown:



dtt



dtlt

some differences in the donating properties of the two ligands are expected.[8] In fact while dtlt is a planar molecule, dtt has a puckered ring which should not allow stabilization by the *n*- and π-electrons.

In this paper we report a study on the reaction of dtlt with iodine in $CHCl_3$, structural results on the 1:1 adduct, isolated in the solid state and a comparison with the previously obtained data on the corresponding dtt reaction with I_2.[9]

RESULTS AND DISCUSSION

Dtlt ligand exhibits, in $CHCl_3$ solutions, a strong band at 360 nm ($\log \varepsilon = 4.2$) and a shoulder at 420 nm, which can be attributed to the $\pi \rightarrow \pi^*$ and to the $n \rightarrow \pi^*$ transition of the C=S group. Increasing additions of diiodine to dtlt produce a drastic change in the uv-visible spectrum of the solution: a new strong band with a shoulder at 305 nm appears at 295 nm, and the band near 400 nm grows up (Figure 1). The symmetrical measurements obtained by increasing additions of dtlt to diiodine allow to identify a well defined isosbestic point at 504 nm (Figure 2). This may be indicative of the existence of a 1:1 equilibrium between the reagents. By assuming that the 1:1 species is the only complex present, the spectrophotometric data have been used to calculate simultaneously the extinction coefficients and the formation constants in the whole wavelength range, by means of a computer program "SUPERQUAD" previously described.[10] A quite satisfactorily fitting of experimental data has been obtained. The refined molar extinction coefficients of

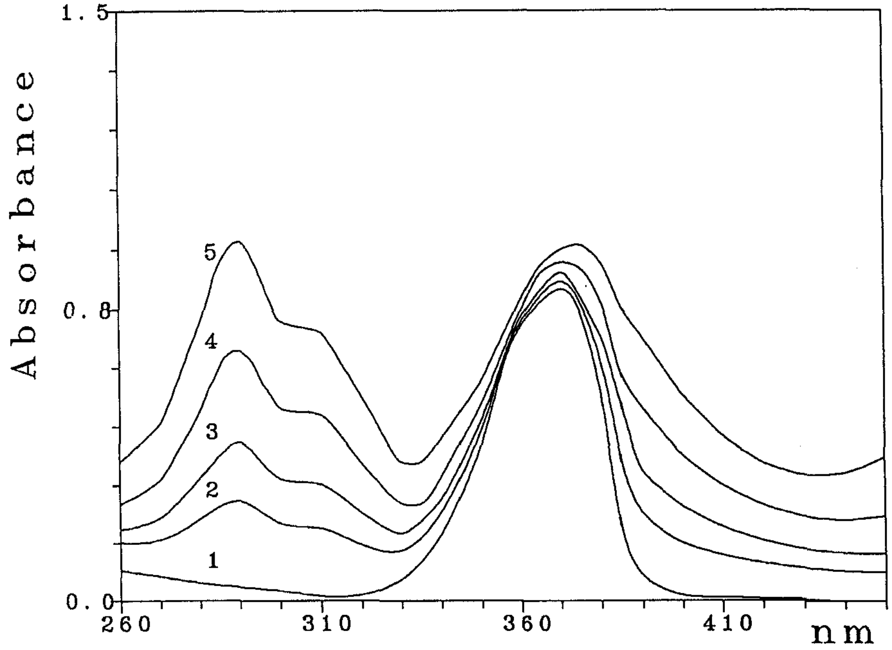


FIGURE 1 U.v.-visible spectra at 283 K in 0.1 cm cell of $CHCl_3$ solutions containing constant amounts of dtlt (5.0×10^{-4}mol dm^{-3}) and variable I_2 concentrations in the ratios: 1 = 1:0, 2 = 1:2.5, 3 = 1:5, 4 = 1:10, 5 = 1:20.

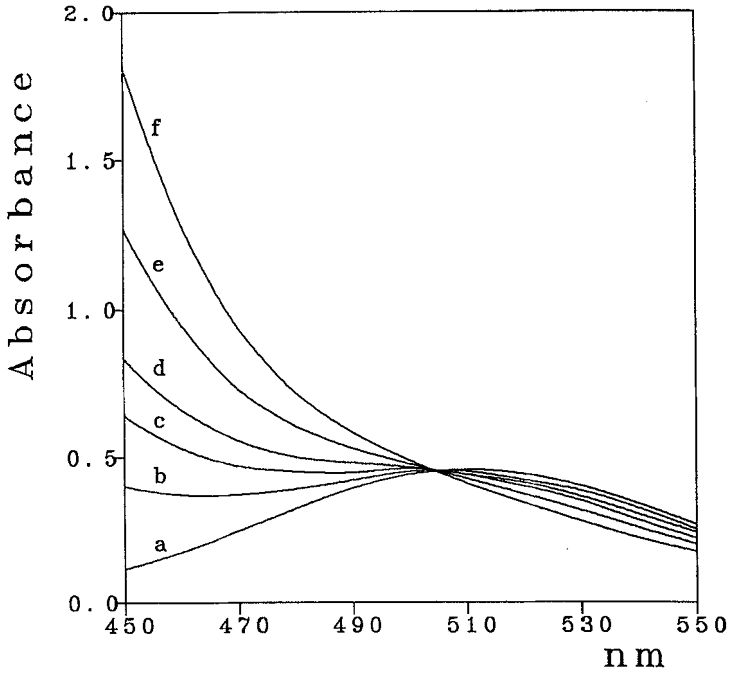


FIGURE 2 Visible spectra at 283 K in 1 cm cell of $CHCl_3$ solutions containing constant amounts of I_2 (5.0×10^{-4}mol dm^{-3}) and variable dtlt concentrations in the ratios: *a* = 1:0, *b* = 1:2.5, *c* = 1:5, *d* = 1:10, *e* = 1:20, *f* = 1:40.

the 1:1 complex are plotted in Figure 3. The strong band at 295 nm is the band of the charge-transfer type, the shoulder at 305 and the band at 385 nm are attributed to the blue-shifted ligand bands. The 385 nm band could seem too intense, however the contribution of the tails of the bands near 300 nm, and of the blue shifted diiodine band which appears on the low frequency side must be taken into account. The spectral features above described allow to classify the complex of the charge-transfer type.[11] The obtained log K values are listed in Table I. The interpolation of the plot of log K versus 1/T (correlation coefficient 1.00) allow to obtain the enthalpy and the entropy changes (reported in Table I) for the 1:1 complex formation. In the solid state a red-brown lustrous crystalline solid of elemental formula dtlt·I_2 has been isolated. The most characteristic i.r. absorptions are listed in Table II. The tentative assignments of the bands are based on those proposed by Klaboe *et al.* for the trithiocarbonate group.[12] The strong band at 1051 cm^{-1}, attributed to an out-of-phase combination of $\nu C{=}S$ and νSCS coupled with δCSS, is shifted 49 cm^{-1} towards lower frequencies, while the band at 508 cm^{-1}, mainly due to the symmetrical νCS_3 stretching, is shifted 14 cm^{-1} towards higher frequencies, as a consequence of the coordination. This suggests that a lowering of the exocyclic CS bond and an increase of the endocylic CS bonds occur. These shifts are to be expected when there is a coordination via exocyclic-sulphur,[5] in accordance with X-ray structural results reported below. The FT Raman spectrum in the region below 300 cm^{-1} shows a strong band at 143 cm^{-1}. This band is attributed to the symmetrical *I-I* stretching of diiodine coordinated to dtlt. In fact the strong Raman

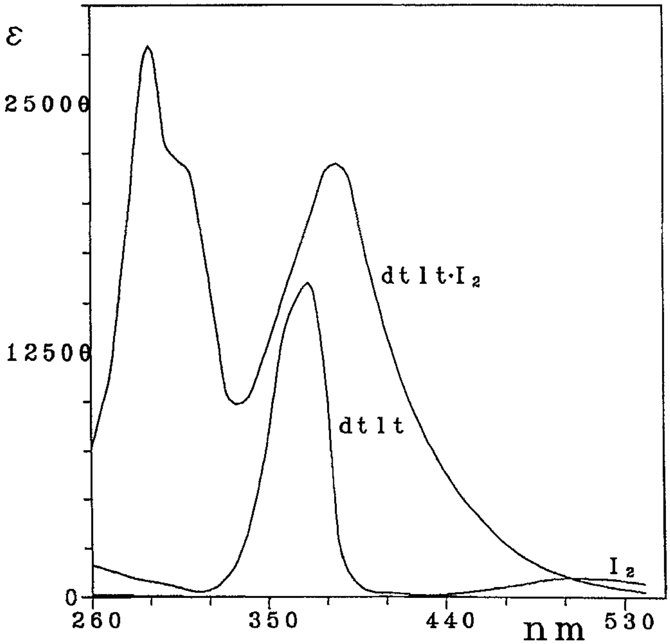


FIGURE 3 Calculated u.v.-visible spectra of the 1:1 complex between dtlt and I_2 at 283 K in $CHCl_3$ solutions. Spectra of the free reagents are reported for comparison.

TABLE I

Logarithms of the equilibrium constants, enthalpy (Kcal mol^{-1}) and entropy changes (cal K^{-1} mol^{-1}) for the formation of 1:1 complex between I_2 and dtlt in $CHCl_3$ solutions

T(°C)	log K
10	2.202 (1)
15	2.087 (2)
20	1.978 (5)
25	1.86 (1)
30	1.75 (1)
35	1.64 (2)

$\Delta H = -9.66 \pm 0.01$ Kcal mol^{-1}.
$\Delta S = -24.0 \pm 0.4$ cal K^{-1} mol^{-1}.

TABLE II

Selected infrared spectral data for dtlt and its diiodine adduct

Assignments	dtlt	dtlt·I_2
νC=S, ν_sSCS	1051 vs	1002 vs
ν_{as}SCS	885 m/817 ms	918 w/825 m
νC=S, ν_sSCS	508 ms	524 m

band at 180 cm^{-1} due to *I-I* vibration in solid diiodine is expected to decrease as a consequence of the lengthening of the *I-I* distance on coordination to donors[13] in agreement with a M.O. description, which shows that the HOMO has some extent of σ^* *I-I* antibonding character).[14]

TABLE III

Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

	X/a	Y/b	Z/c		X/a	Y/b	Z/c
I(1)	7564(1)	4195(1)	887(1)	S(3)	7796(4)	7616(6)	1266(8)
I(2)	9576(1)	2526(1)	899(2)	C(1)	6354(13)	7373(16)	958(20)
S(1)	5706(4)	5880(5)	742(9)	C(2)	6689(18)	9892(18)	1235(23)
S(2)	5549(4)	8804(5)	899(10)	C(3)	7773(18)	9307(23)	1402(26)

TABLE IV

Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

I(1)-I(2)	2.843(2)	I(2)-I(1)-S(1)	176.7(1)
I(1)-S(1)	2.715(5)	I(1)-S(1)-C(1)	102.0(6)
S(1)-C(1)	1.68(2)	S(1)-C(1)-S(2)	120.8(9)
S(2)-C(1)	1.71(2)	S(1)-C(1)-S(3)	125.1(1.0)
S(3)-C(1)	1.68(2)	S(2)-C(1)-S(3)	114.1(1.0)
S(2)-C(2)	1.72(2)	C(1)-S(2)-C(2)	97.1(9)
S(3)-C(3)	1.70(2)	C(1)-S(3)-C(3)	98.0(9)
C(2)-C(3)	1.38(3)	S(2)-C(2)-C(3)	115.1(1.5)
		S(3)-C(3)-C(2)	115.7(1.7)

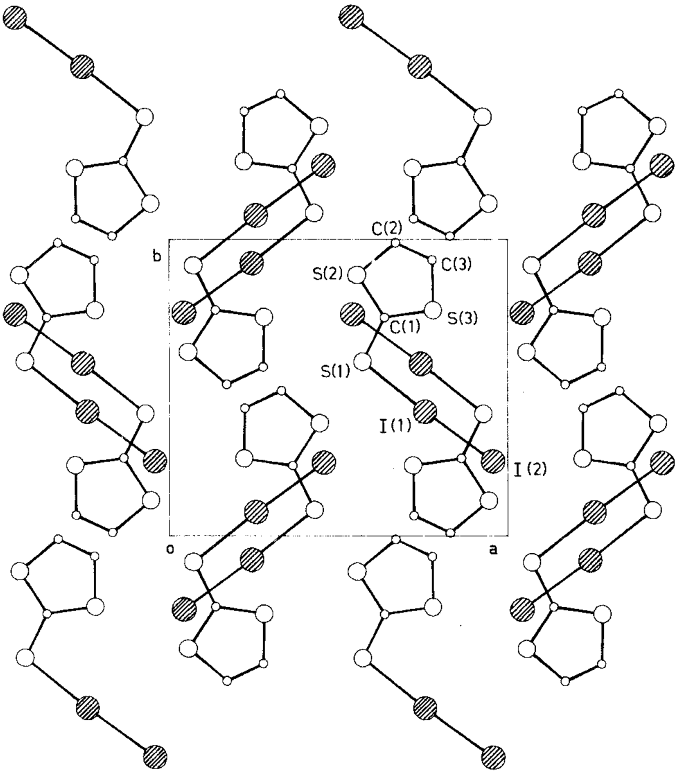


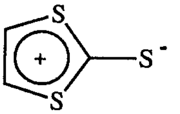
FIGURE 4 Projection of the structure viewed along [001].

Structural Results

Fractional atomic coordinates are given in Table III, bond distances and angles are reported in Table IV. The projection of the crystal structure along [001] and the atom labelling scheme for the molecule of the adduct are shown in Figure 4. The values of bond distances and angles are very similar to those observed in the corresponding adduct dtt$\cdot I_2$.[9] The organic molecule is obviously planar [maximum deviation from the mean weighted plane -0.023 (18) Å at $C(2)$]; the $I(1)$ and $I(2)$ atoms depart by 0.079 (1) and 0.288 (2) Å, respectively from the above cited plane. The most relevant contacts determining the packing are: $I(2)\cdots S(3)$ (2-x, 1-y, -z) 3.441 (5) Å, $I(2)\cdots C(3)$ (x, y-1, z) 3.851 (2) Å, $S(2)\cdots S(2)$ (1-x, 2-y, -z) 3.047 (8) Å. The existence of these contacts involving $I(2)$ contributes to the lowering of the I-I distance, which is slightly higher than the corresponding distance in dtt$\cdot I_2$.

Conclusions

A comparison with the corresponding dtt case shows that the situation appears to be different in solution and in the solid state: in $CHCl_3$ solutions, the formation constants of the 1:1 dtlt complex are almost twice as much and, more significantly, the value of the enthalpy of formation is $\approx$3 Kcal. mol^{-1} higher. According to that dtlt should be regarded a better donor than dtt towards I_2. That is not unexpected, given the structure of the donors (see Introduction). In fact in dtlt the carbon-carbon double bond may participate in bonding interactions by stabilization of the following dipolar structure:



In the solid state instead, the very similar $\nu(I\text{-}I)$ values in dtlt$\cdot I_2$ and in dtt$\cdot I_2$ (143 and 145 cm^{-1}, respectively), suggest a very similar interaction of the donor with I_2. X-ray structural results confirm this finding, being the S-I distances identical in both adducts.

EXPERIMENTAL

Materials and Methods. The dtlt compound has been furnished by Aldrich, and used as received. Well formed lustrous red-brown crystals of dtl$\cdot I_2$ suitable for X-ray analysis have been obtained by slow evaporation of a cyclohexane solution of the reagents in the 1:1 ratio.

Analytical Results: Found C 9.4 H 0.5 S 24.7
Calc. for $C_3H_2I_2S_3$ C 9.28 H 0.52 S 24.78

Spectroscopic Measurements. I.r. spectrum (cm^{-1}) was recorded on a Perkin Elmer mod 983 Spectrophotometer as KBr pellet: 3040 vw 3030 vw 1248 w 1073 m 1052 mw 1002 vs 930 w 918 w 868 w 825 m 750 w 682 s 627 w 524 m 445 mw 392 s 289 vs 241 s.

Raman spectra have been recorded by courtesy of Bruker Company (Milano), on IFS.66 Instrument using an exciting line of wavenumer 9394 cm^{-1} of a Nd:YAG-Laser.

The electronic spectra were measured at different temperatures (±0.1°C) in the range 10–35°C in $CHCl_3$ solutions with a Varian model Cary 5 spectrophotometer. A set of solutions was prepared with a constant dtlt (5.0×10^{-4} mol dm^{-3}) and variable diiodine concentrations ranging from 1.25×10^{-3} to 2.5×10^{-2} mol dm^{-3} in 1 mm silica cells, in the 260–450 nm range (Figure 1). Another set of solutions containing a constant diiodine (5.0×10^{-4} mol dm^{-3}) and variable dtlt concentrations, ranging from 1.25×10^{-3} to 2.5×10^{-2} mol dm^{-3} (Figure 2) was prepared and the spectra recorded between 400 and 550 nm using 1 cm silica cells.

Calculations. The experimental points used in the calculations have been taken from the recorded spectra at 10 nm intervals and the total number was always 160 readings for each system at each temperature. A general computer program, derived from "SUPERQUAD"[10] has been used to refine simultaneously equilibrium constants and molar extinction coefficients from the spectrophotometric data.

Structure Determination. The X-ray data collections were carried out at room temperature using a crystal of dimensions $0.19 \times 0.19 \times 0.39$ mm and Nb-filtered Mo-$k\alpha$ radiation. The cell parameters were determined by least-squares refinement from the Θ values of 30 reflections accurately measured. All diffraction measurements were made on a Siemens AED diffractometer using the $\Theta/2\Theta$ scan mode (with Θ in the range 3–27°) giving 2207 measurements of which 1173 having $I \geq 2.5\,\sigma(I)$ were considered observed and used in the analysis. The space group was $P2_12_12_1$ by control on the agreement between the intensities of symmetry equivalent reflections. Intensity data were corrected for the Lorentz and polarization factor; corrections for absorption (maximum and minimum values 1.4157, 0.8215) and extinction effects (maximum and minimum values 1.0628, 0.8748) were empirically applied[15] at the end of the isotropic refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares,[16] using anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms, placed at their geometrically calculated positions were refined riding on the corresponding atoms with an unique refined isotropic thermal parameters (U = 0.0694 (531) Å^2). Since the space group $P2_12_12_1$ leads to a chiral configuration in the structure, a complete refinement was unsuccessfully carried out using the coordinates $-x$, $-y$, $-z$. Convergence was reached at R = 0.0537.

Crystal Data. $C_3H_2I_2S_3$, M = 388.038. Orthorhombic, space group $P2_12_12_1$, a = 11.413 (7), b = 10.038 (7), c = 7.760 (6) Å, V = 889.0 (1.1) Å^3, Z = 4, μ[Mo-$k\alpha$] = 75.94 cm^{-1}, $F(000)$ = 696, λ = 0.71073 Å.

Note. The tables of experimental data for the crystallographic analysis, of coordinates for hydrogen atoms, and of anisotropic thermal parameters are deposited with the Cambridge Crystallographic Data Center (CCDC), U.K.

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