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Main Group Metal Halide Complexes with Sterically Hindered Thioureas
X. Complexes of Antimony(V) Chloride and 1,3-Dimethyl-2(3H)-Imidazolethione

DANIEL J. WILLIAMS*, PATRICIA H. POOR, GUILLERMO RAMIREZ
Department of Chemistry, Kennesaw State College, Marietta, GA 30061 (U.S.A.)
and DONALD VANDERVEER
School of Chemistry, Georgia Institute of Technology, Atlanta, GA 30332 (U.S.A.)

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Abstract

Four complexes resulting from the interaction of $SbCl_5$ and dmit (dmit = 1,3-dimethyl-2(3H)-imidazolethione) are synthesized and characterized. Previously reported $SbCl_5$dmit (**I**) is shown to be the dithiouronium disulfide ($dmit_2^{2+}$) salt of $[Sb_2Cl_{10}]^{2-}$. Refluxing **I** in CH_3CN yielded $[dmit_2][SbCl_4]_2$ (**II**) while refluxing **I** in dimethylformamide yielded a salt containing a unique dithiouronium monosulfide dication in combination with $[SbCl_6]^{2-}$ (**III**). A fourth salt was characterized via X-ray crystallography in an attempt to determine the structure of **I**. Selection of a non-representative crystal revealed a new compound also containing the monosulfide dication observed in **III** but in combination with the $[Sb_2Cl_{10}]^{2-}$ anion made up of zigzag chains of $SbCl_6$ octahedra sharing disordered Cl vertices and alternating Sb(III) and Sb(V) units with chlorine bridges *trans* to each other in the latter and *cis* in the former. Bulk quantities of **IV** could not be synthesized for further characterization. Crystallographic parameters were determined for **II**, **III** and **IV**, but only the structure of **IV** was solved. Crystallographic data for **II**: space group $P2_1/c$; $Z = 4$; $a = 16.25(1)$, $b = 12.94(1)$, $c = 11.93(1)$ Å, $\beta = 99.47°$; $V = 2474$ Å^3; $D_c = 2.103$ g/cm^3, $D_o = 2.09$ g/cm^3 (flotation in $CH_2I_2/C_2H_2Cl_4$). **III**: space group $Cmcm$; $Z = 8$; $a = 17.56(1)$, $b = 29.15(1)$, $c = 12.65(1)$ Å; $V = 6475$ Å^3; $D_c = 1.606$ g/cm^3, $D_o = 1.59$ g/cm^3 (flotation in $CH_2Cl_2/CH_2I_2/C_2H_2Cl_4$). **IV**: space group $C2/c$; $Z = 4$; $a = 16.131(4)$, $b = 12.161(3)$, $c = 18.862(4)$ Å, $\beta = 92.16°$; $V = 3697$ Å^3; D_c 1.476 g/cm^3, D_o indeterminate.

Introduction

Several reports of $SbCl_5$ acting as a Lewis acid have appeared in the literature [1]. Most of the reported complexes are those with oxygen or nitrogen based donors in addition to the well known hexachloroantimonate(V) anion. This is consistent with the hard–soft acid base (HSAB) concept of Pearson [2]. Notably absent in the literature are thiourea complexes with $SbCl_5$ while a few have been reported for $SbCl_3$ [3] – again consistent with the HSAB approach. In our laboratory, an attempt to synthesize a complex of thiourea and $SbCl_5$ yielded no isolable product, but reaction of a unique aromatic heterocyclic thiourea, 1,3-dimethyl-2(3H)-imidazolethione (dmit, Fig. 1), produced three complexes. In Part IX of this series, we reported preliminary results for the synthesis, characteristics and properties of these three new complexes [4]. This paper gives a more detailed account of the characterization of these complexes and the results of a single crystal X-ray study revealing a fourth new complex containing a unique monosulfide dication.

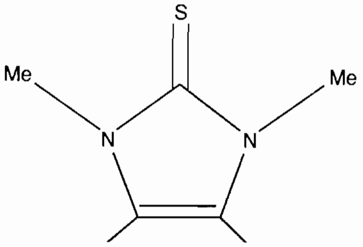

Fig. 1. 1,3-Dimethyl-2(3H)-imidazolethione (dmit).

Experimental

General

Specific conductivity and other physical properties were all obtained as previously reported [4].

Chemicals

Electrical grade anhydrous CH_3CN (Fisher) was used as obtained without further purification ($L = 6$ μmhos). All other solvents and chemicals were

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*Author to whom correspondence should be addressed.

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reagent grade and used as purchased without further purification. Dmit was synthesized as previously reported [5].

Analytical

Elemental analysis was done by Galbraith Laboratories, Inc. and Atlanta Microlabs, Inc.

Synthesis

The synthesis of $SbCl_5$dmit (**I**) has already been reported [4]. Other complexes reported in this paper were prepared as follows.

$[(C_5H_8N_2)_2S_2][SbCl_4]_2$ *(II)*

A suspension of **I** (*c.* 1.0 g) was refluxed in 50 ml CH_3CN for *c.* 1 h. The mixture was filtered and then allowed to cool to room temperature. Yellow crystals resulted after cooling the mixture to 10 °C, melting point (m.p.) 180–183 °C. *Anal.* Calc. for $C_{10}H_{16}N_4S_2Sb_2Cl_8$: C, 15.32; H, 2.06; N, 7.15; S, 8.18; Sb, 31.08; Cl, 36.20. Found: C, 15.70; H, 2.06; N, 7.22; S, 8.42; Sb, 30.21; Cl, 35.96%. Crystallographic data: space group $P2_1/c$; $Z = 4$; $a = 16.25(1)$, $b = 12.94(1)$, $c = 11.93(1)$ Å, $\beta = 99.47°$; $V = 2474$ Å^3; $D_c = 2.103$ g/cm^3, $D_o = 2.09$ g/cm^3 (flotation in $CH_2I_2/C_2H_2Cl_4$). $\Lambda_M = 218$ mho cm^2/mol.

$[(C_5H_8N_2)_2S]_2[SbCl_6]$ *(III)*

A suspension of 1.0 g of **I** was refluxed for 2 h in 30 ml *N,N*-dimethylformamide (DMF). The solution turned deep ruby red in color. The reaction was allowed to cool to room temperature and an equal volume of CH_3CN was added. After 48 h at −10 °C, orange crystals had separated, m.p. 187–190 °C. *Anal.* Calc. for $C_{20}H_{32}N_8S_2SbCl_6$: C, 30.68; H, 4.11; N, 14.36; Cl, 27.16. Found: C, 30.88; H, 4.15; N, 14.39; Cl, 26.97%. Crystallographic data: space group *Cmcm*; $Z = 8$; $a = 17.56(1)$, $b = 29.15(1)$, $c = 12.65(1)$ Å; $V = 6475$ Å^3; $D_c = 1.606$ g/cm^3, $D_o = 1.59$ g/cm^3 (flotation in $CH_2Cl_2/CH_2I_2/C_2H_2Cl_4$). $\Lambda_M = 254$ mho cm^2/mol.

$[(C_5H_8N_2)_2S][Sb_2Cl_{10}]$ *(IV)*

This compound appears to have been co-generated with **I** in the original synthesis. Microscopic examination of a sample of **I** revealed a few well-formed darker yellow crystals mixed in the much lighter yellow crystals of **I**. One of these darker yellow crystals was isolated and mounted in a fashion described below for X-ray structural analysis. The only proof of stoichiometry for **IV** is from the X-ray structure since enough crystals could not be isolated to characterize, and attempts to duplicate the synthesis of **IV** generated the other compounds reported above. Crystallographic data: space group $C2/c$; $Z = 4$; $a = 16.131(4)$, $b = 12.161(3)$, $c = 18.862(4)$ Å, $\beta = 92.16°$; $V = 3697$ Å^3; $D_c = 1.476$ g/cm^3, D_o indeterminate.

X-ray Crystallographic Data

Suitable crystals of **II**, **III** and **IV** were mounted on a glass fiber using epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis. Unit cell parameters were determined on a Syntex $P2_1$ four circle diffractometer equipped with a graphite monochrometer (Bragg 2θ angle = 12.2°) using Mo Kα ($\lambda = 0.71069$ Å) radiation at a takeoff angle of 6.75°. Fifteen reflections were machine centered and used in least-squares refinement of the lattice parameters. Omega scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.24 Å, indicating a satisfactory mosaic spread for each crystal examined.

Axial photographs were used to determine the space group for each crystal with zero and upper level intensity data being examined for systematic absences in the usual fashion.

Intensity data for **IV** were collected using ω scans with X-ray source and monochromator settings identical to those used for determination of the unit cell parameters. A variable scan rate of 3.91 to 29.3° min^{-1} was used, and a scan width of 1.0° was sufficient to collect all the peak intensity. Stationary background counts were measured at the beginning and at the end of each scan with a total background-to-scan time ratio of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (008, 060, 800) measured every 97 reflections. Intensities were calculated from the total scan count and background counts by the usual relationship.

The intensities were assigned standard deviations in the usual manner, and from a total of 3236 reflections collected in a complete quadrant ($\pm h + k + l$) of data out to $2\theta = 50°$, 2832 were accepted as statistically above background on the basis that F was greater than $3\sigma(F)$. Lorentz and polarization corrections were made in the usual way. Absorption corrections were not applied.

Solution and Refinement of the Structure

Computations were performed using the standard programs [6] and were carried out on the CDC Cyber 74 System. For structure factor calculations, the scattering factors were taken from the International Tables for X-Ray Crystallography [7]. The agreement factors are defined in the conventional way. In all least-squares refinements, the quantity minimized has been previously defined [8]. The weighting schemes based on counting statistics are also as previously defined for the calculation of R_w and in least-squares refinement [8].

The structure was solved using a Patterson map. Disorder was observed in the chlorine atoms labelled C16 and C16′, and the structure was further refined by assigning half occupancy to these atoms. Hydrogen atoms were not added. Final calculated values

TABLE 1. Final positional parameters for non-hydrogen atoms with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Sb1	0.5000	0.5000	0.0000
Cl1	0.54762(8)	0.3486(1)	-0.09068(7)
Cl2	0.65505(7)	0.5421(1)	0.04170(7)
Sb2	0.5000	0.20347(3)	0.2500
Cl4	0.47129(8)	0.0546(1)	0.33518(7)
Cl5	0.34348(7)	0.1966(1)	0.20955(7)
S1	0.26777(7)	0.4072(1)	0.10857(6)
N1	0.1624(2)	0.3535(3)	0.2170(2)
N2	0.2682(2)	0.4534(3)	0.2506(2)
N3	0.1857(2)	0.5959(3)	0.0618(2)
N4	0.1437(2)	0.4467(3)	0.0087(2)
C1	0.2277(3)	0.4074(4)	0.1945(2)
C2	0.1600(3)	0.3664(4)	0.2889(3)
C3	0.2254(4)	0.4277(4)	0.3094(2)
C4	0.3463(4)	0.5141(5)	0.2515(3)
C5	0.1045(3)	0.2882(4)	0.1728(3)
C6	0.1941(3)	0.4869(4)	0.0608(2)
C7	0.1035(3)	0.5340(5)	-0.0231(2)
C8	0.1287(3)	0.6255(4)	0.0104(3)
C9	0.1342(4)	0.3325(5)	-0.0146(3)
C10	0.2289(3)	0.6726(4)	0.1098(3)
Cl6	0.4972(2)	0.3677(2)	0.0915(1)
Cl6′	0.5240(2)	0.3311(3)	0.1372(2)

TABLE 2. Interatomic angles (°) with e.s.d.s in parentheses

Cl2-Sb1-Cl1	91.9(0.0)	Cl6-Sb1-Cl1	90.7(0.1)
Cl6-Sb1-Cl2	87.6(0.1)	Cl5-Sb2-Cl4	87.9(0.0)
Cl6′-Sb2-Cl4	167.7(0.1)	Cl6′-Sb2-Cl5	87.3(0.1)
Cl4-Sb2-Cl4	86.0(0.1)	C6-S1-C1	101.9(0.2)
C2-N1-C1	108.3(0.4)	C5-N1-C1	125.7(0.4)
C5-N1-C2	125.9(0.4)	C3-N2-C1	107.4(0.4)
C4-N2-C1	127.7(0.4)	C4-N2-C3	124.7(0.4)
C8-N3-C6	108.8(0.4)	C10-N3-C6	126.7(0.4)
C10-N3-C8	124.6(0.4)	C7-N4-C6	107.6(0.4)
C9-N4-C6	128.2(0.4)	C9-N4-C7	124.1(0.4)
N1-C1-S1	128.1(0.4)	N2-C1-S1	122.6(0.4)
N2-C1-N1	108.7(0.4)	C3-C2-N1	107.4(0.4)
C2-C3-N2	108.1(0.4)	N3-C6-S1	127.6(0.3)
N4-C6-S1	123.6(0.3)	N4-C6-N3	108.2(0.4)
C8-C7-N4	107.9(0.4)	C7-C8-N3	107.6(0.4)
Cl6′-Cl6-Sb1	150.6(0.3)	Cl6-Cl6′-Sb2	146.3(0.3)
Cl6′-Sb2-Cl6′	109.1(0.1)		

were $R = 0.035$ and $R_w = 0.036$. Table 1 lists final positional parameters for the non-hydrogen atoms, and interatomic angles and distances are listed in Tables 2 and 3 respectively. See also 'Supplementary Material'.

Results and Discussion

In Part IX of this series we reported a complex with the stoichiometry of $SbCl_5dmit$ (**I**) [4] which would have been an unprecedented example of a molecular adduct of Sb(V) chloride with a sulfur-based donor. Based on the results cited above, however, this is an unlikely conclusion. As was previously indicated, the specific conductivity for **I** falls into the range of a 2:1 electrolyte (253 mho cm^2/mol) in acetonitrile. This was rationalized on the basis of the fact that considerable heating had to be applied to dissolve a sufficient amount of **I** for the conductivity study, and in doing so, the structure may have been altered. It was speculated that perhaps the dithiouronium disulfide cation $[dmit_2]^{2+}$ (Fig. 2) may be forming as a result of a redox couple between Sb(V) and dmit. Based on the data presented above, this now seems likely since refluxing **I** in CH_3CN for a prolonged period resulted in the isolation of **II** containing the dithiouronium disulfide cation. Furthermore, it seems more likely that the actual structure of **I** is $[dmit_2][SbCl_5]_2$. This is based on the crystallographic data for **IV** formed as a by-product of **I**. The observed anion in the solid state structure of **IV** has the stoichiometry $[Sb_2Cl_{10}]^{2-}$ with 1:1 Sb(III)/Sb(V) ratio as previously reported by Kruger and Schmidt [9]. This anion is stable apparently only in the solid state [9], and thus the observed conductivity data for **I** can be attributed to dissociation in solution phase probably to generate $[SbCl_6]^-$ and

TABLE 3. Interatomic distances (Å) with e.s.d.s in parentheses

Sb1-Cl1	2.646(0.001)	Sb1-Cl2	2.644(0.001)
Sb1-Cl6	2.361(0:002)	Sb2-Cl4	2.476(0.001)
Sb2-Cl5	2.611(0.001)	Sb2-Cl6′	2.674(0.003)
S1-C1	1.767(0.004)	S1-C6	1.755(0.005)
N1-C1	1.324(0.006)	N1-C2	1.366(0.006)
N1-C5	1.464(0.006)	N2-C1	1.345(0.006)
N2-C3	1.363(0.006)	N2-C4	1.460(0.007)
N3-C6	1.333(0.006)	N3-C8	1.358(0.006)
N3-C10	1.460(0.006)	N4-C6	1.344(0.006)
N4-C7	1.371(0.006)	N4-C9	1.463(0.006)
C2-C3	1.337(0.007)	C7-C8	1.335(0.007)
Cl6-Cl6′	1.048(0.004)		

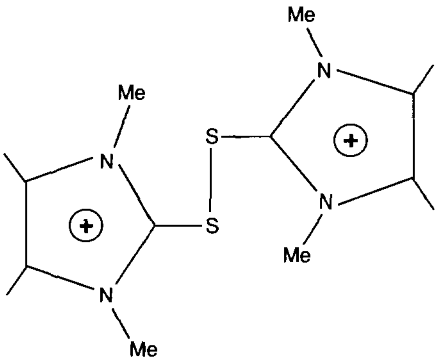

Fig. 2. Dithiouronium disulfide dication of dmit.

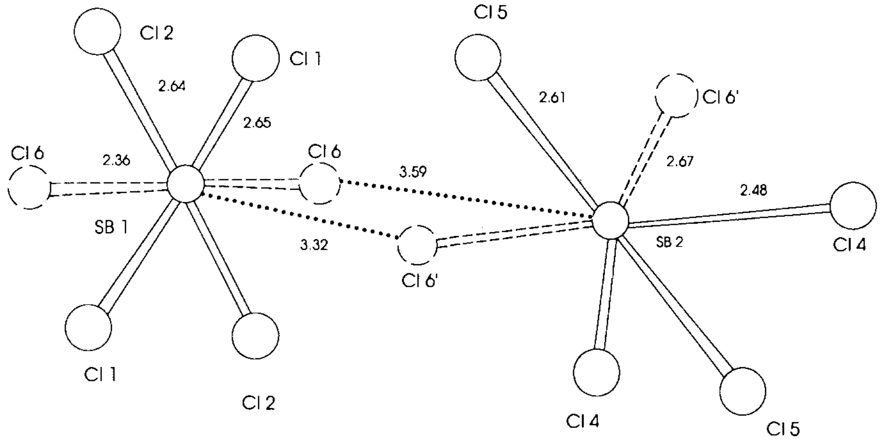

Fig. 3. Structure of $[Sb_2Cl_{10}]^{2-}$. Dashed lines represent disordered chlorine atoms (Cl6 and Cl6′) in half-occupancy positions. Dotted lines represent interionic contacts.

$[SbCl_4]^-$. Further evidence for the proposed structure of **I** is given by Arduengo and Burgess [10] who reported the formation of $[dmit_2]^{2+}$ by the addition of elemental Br_2 to a non-aqueous solution of dmit. It seems likely that Sb(V) chloride, although a milder oxidizing agent based on aqueous standard reduction potentials (1.0 V for Br_2/Br^- versus 0.6 V for Sb(V)/Sb(III) [11], would produce similar results. The dithiouronium cation would also help explain the large deviation for the λ_{max} of $SbCl_5$dmit relative to known molecular adducts of dmit with other post-transition elements (206 versus *c.* 270 nm respectively) [4].

In the process of further characterizing **I**, a single crystal for X-ray study was chosen. However, as indicated above, a non-representative crystal was obtained, and the results indicated a new compound **IV** containing the $[Sb_2Cl_{10}]^{2-}$ anion (Figs. 3 and 4) and a unique unprecedented dithiouronium monosulfide cation (Fig. 5) in 1:1 stoichiometry as deduced from the crystallographic data. Although further characterization of this compound could not be done due to lack of bulk quantities of this substance, the results are significant and are supported by the other substances reported above.

As seen in Figs. 3 and 4, the $[Sb_2Cl_{10}]^{2-}$ anion is made up of zigzag chains of octahedra sharing common vertices through long chlorine bridges *cis* to each other on Sb2 and *trans* to each other on Sb1. With regard to bond angles (Table 2), the localized geometry about Sb1 appears to be more regular than Sb2 with angles ranging from 87.6° to 91.9°. The largest Cl–Sb–Cl angle observed is 109.1° while the smallest is 86.0°, both observed around Sb2. Based on the degree of angular distortions, oxidation states are assigned as +5 for Sb1 and +3 for Sb2. There is good evidence for a stereoactive lone pair of electrons in the valence shell of Sb2 since 109.1° is a significant departure from the ideal value of 90.0°.

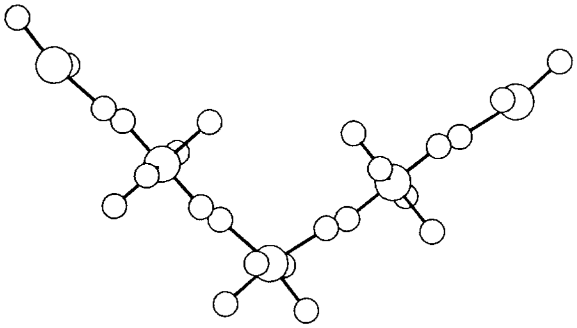

Fig. 4. Polymeric chain in $[Sb_2Cl_{10}]^{2-}$. Spheres in close proximity are the disordered chlorine atoms.

The disordered chlorine atoms, Cl6 and Cl6′, are positionally offset from each other by about 1.0 Å (Table 3). The bridging distances are 3.32 Å for Sb1---Cl6′ and 3.59 Å for Sb2---Cl6 both of which are well within the sum of the van der Waal's radii (4.0 Å) [12]. Table 4 lists reported Sb–Cl minimum and maximum bond distances including intermolecular contacts for a few octahedral hexachloroantimony(III) and (V) complexes. The bridging distances listed above for **IV** are comparable to the maxima noted in Table 4. Non-bridging Sb–Cl bond distances also fall within the range of those noted for other complexes [13]. Sb1–Cl bond distances are somewhat longer than those noted for most chloroantimonate(V) complexes [13a, b, c], but Sb1–Cl6 does fit into the observed range.

Both octahedral configurations around Sb1 and Sb2 are highly distorted with respect to bond distances when chlorine bridges are considered. Statistical distortion factors (Δ) completed via the method of Shannon [14] are 1.15×10^{-2} for Sb1 and 1.98×10^{-2} for Sb2. For comparative purposes, the perfectly centrosymmetric $[SnCl_6]^{2-}$ is the standard with Δ equal to zero, and Abriel [15] reports several

TABLE 4. Bond distance minina (R_i min.), maxima (R_i max.), means $\bar{R}_i$ in A (e.s.d.s in parentheses) and statistical distortion factors (Δ) for octahedral chloro–Sb(III) and Sb(V) complexes[a]

Complex	R_i min.	R_i max.	$\bar{R}_i$	$\Delta \times 10^5$	Reference
Sb(III)					
$[C_5H_5NH][SbCl_4]$	2.380(3)	3.126(4)*	2.712(15)	1310	13d
$[(CH_3)NH]_3[Sb_2Cl_9]$	2.408(3)	3.189(5)*	2.757(9)	1510	13e
	2.411(3)	3.330(5)*	2.752(9)	1520	
$(CH_3)_3SbCl_2 \cdot SbCl_3$	2.380(3)	3.308(3)*	2.798(7)	2310	13f
$[(CH_3)_3NH]_3[Sb_3Cl_{14}]$	2.37(nr)	3.90(nr)*	2.83	3450	9
IV	2.476(1)	3.594(3)*	2.740(4)	1985	
Sb(V)					
$[(CH_3)_3NH]_3[Sb_3Cl_{14}]$	2.33(nr)	2.33(nr)	2.33	0	9
$[NH_4][SbCl_6]$	2.360(2)	2.369(2)	2.364(5)	0.37	13c
$[CH_3CO][SbCl_6]$	2.362(2)	2.367(2)	2.365(5)	0.10	13a
$[(CH_3)_2CH][SbCl_6]$	2.347(1)	2.389(1)	2.372(3)	3.80	13b
IV	2.361(2)	3.315(3)*	2.740(4)	1149	

[a] nr = not reported; intermolecular contacts denoted with asterisk.

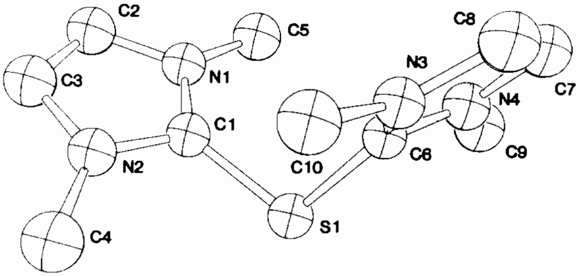

Fig. 5. Molecular structure of dithiouronium monosulfide dication with thermal ellipsoids drawn at the 50% probability level.

computed Δ values for hexahalo Se(IV) and Te(IV) complexes which range from zero to 1.86×10^{-3}. Table 4 shows how Δ values for IV compare to those calculated for other Sb(III) and Sb(V) complexes. Notably, all the Sb(III) complexes show high distortion factors due to bridging whereas the Sb(V) complexes tend to be much more regular with the exception of the one noted in this study.

The other interesting aspect of IV is the hitherto unprecedented monosulfide dication seen in Fig. 5. The bond angles and distances are very similar to those noted for dmit [16] and also for those observed for the dithiouronium disulfide dication reported by Pulcrano [17]. The only notable difference is the progressive lengthening of the C–S bond in going from dmit to the dithiouronium disulfide dication to the dithiouronium monosulfide dication – 1.695, 1.733 and 1.761 Å, respectively*. Dmit is one of the few thioureas that generally resists desulfurization [5], and compounds III and IV are apparently first examples of the exception to this rule [18]. Intensity data were collected for III, but the structure could not be solved presumably because of disorder. Nevertheless, the chemical composition for III does support the observed structure of IV. The monosulfide dication apparently requires high temperature conditions such as refluxing DMF to form, and the only explanation of it being a by-product in the formation of I could be due to localized thermal pockets in the resultant heterogeneous product mixture since the reaction is somewhat exothermic.

Supplementary Material

Additional tables of structure factors, thermal parameters, intermolecular contacts, and calculate positions of hydrogen atoms are available from the author for correspondence on request.

Acknowledgements

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*In Ref. 4, Table III had incorrectly reported the C=S bond distance for dmit as 1.79 A. The correct value rounded to three significant figures is 1.70 A.

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