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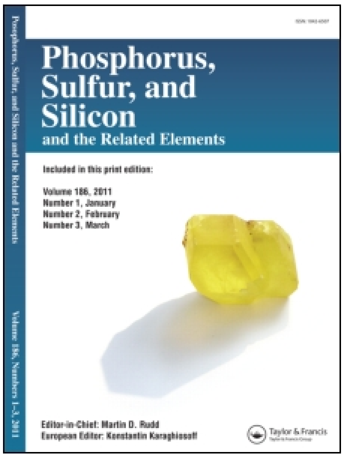

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1,3,2-Dithiazolylium Cations with Various Anions; Syntheses and Solid State Structures

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A versatile method for preparing 1,3,2-dithiazolylium cations is demonstrated for the parent compound. Crystal structures for two examples with transition metal halides as anions are discussed.

Keywords: heterocyclic compounds; sulfur-nitrogen compounds; crystal structures.

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INTRODUCTION

1,3,2-Dithiazolylium cations were synthesised for the first time by Passmore et al.[1]. Subsequently a variety of derivatives were published by the same authors[2] and others. Rees et al. have found this type of heterocyclic cation to be an unexpected by-product for the reaction of 1,2-disulfenyl dichlorides with bis(timethylsilyl)sulfurdiimide[3]. Independently we have elaborated a distinct but simple and versatile route that offers an enormous synthetic potential. It allows for preparation of monocyclic as well as condensed ring systems. The only limitation for the presented method is the availability of the corresponding 1,2-disulfenyl dichloride as a starting material. To overcome these limits, we have developed an alternative route based on 1,2-dithioles as educts[4]. Accordingly, the analogous 1,3,2-diselenazolylium cations are accessible by reaction of 1,2-diselenenyl dichlorides with trimethylsilyl azide.

DISCUSSION

A typical example for the suggested reaction pathway is the preparation of the parent 1,3,2-dithiazolylium cation[1,2] (DTA^+).

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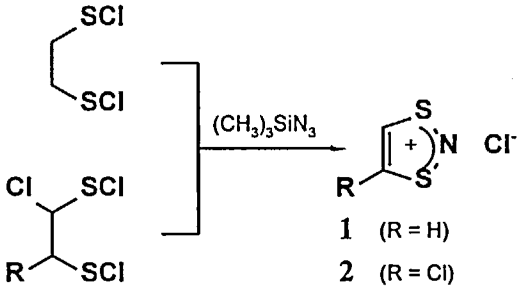

1 (R = H)
2 (R = Cl)

The educt 1,2-ethenedisulfenyl dichloride is not accessible immediately. However, reaction of 1,2-ethanedisulfenyl dichloride or 1-chloro-1,2-ethanedisulfenyl dichloride with trimethylsilyl azide affords $DTA^+ Cl^-$ **1**-Cl in 72% or 63% yield, respectively. The latter reaction is obvious. Ring closure reaction is accompanied by elimination of HCl. The former reaction with 1,2-ethanedisulfenyl dichloride should lead to the dihydro derivative of **1**-Cl. Though such compounds are known[5] we have never observed them from the reaction of 1,2-disulfenyl dichlorides with trimethylsilyl azide. Most likely, the oxidation to **1**-Cl is driven by the creation of a cyclic 6-π system. The underlying redox reaction was not studied in detail. However, no hydrogen was produced. After extraction of the reaction mixture with liquid sulfur dioxide some ammonium chloride and a polymeric gumlike material remained. Further chlorination of 1,2-ethanedithiol yields 1,2-dichloro-1,2-ethanedisulfenyl dichloride which affords 4-chloro-1,3,2-dithiazolylium chloride **2**-Cl upon reaction with trimethylsilyl azide.

Formally dithiazolylium cations can be regarded as cyclic 6-π Hückel-systems. Thus, in principle, electrophilic aromatic substitution is feasible. Due to the positive charge such a reaction is highly unlikely. Consequently, e.g. chlorination or nitration failed. Bromination with *N*-bromosuccinimide, probably progressing via a radical mechanism, yields a product with an elemental composition of $C_2Br_2ClNS_2$. This is consistent with the expected 4,5-dibromo-1,3,2-dithiazolylium chloride. The IR spectrum shows only a few peaks and differs fundamentally from those of other 1,3,2-dithiazolylium salts. To complicate matters the mass spectra exhibit peaks for $C_2Br_2NS_2^+$, $C_2BrClNS_2^+$, and $C_2Cl_2NS_2^+$. All crystals obtained so far were multiply twinned.

The high conductivity measured for the CT-complex BDTA · TCNQ[6] prompted us to prepare analogous CT-complexes with the parent 1,3,2-dithiazolyl system. Mixing **1**-Cl with Li^+ $TCNQ^-$ affords a black amorphous material with the composition DTA · TCNQ. Its powder conductivity of ca. 2.7×10^{-4} indicates a fully ionic compound DTA^+ $TCNQ^-$.

Exchange of the chloride by bulky anions or formation of complex anions by addition of metal halides greatly enhances the solubility

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of the product. For transition metal halides in low oxidation states the question arises if a redox reaction takes place with DTA^+ being reduced to the neutral radical state. This aspect is particularly stimulating in view of the potential conductivity of the material. Previously we have shown that benzo-bis-dithiazolylium dication $BBDTA^{2+}$ is reduced to the radical cation state when $FeCl_2$ is added[7]. Thus we have reacted 1 with Cu(I)Cl and with Fe(II)Cl_2. In both cases we attained a 1:1 complex that could be crystallised to give well-shaped single crystals suitable for X-ray structure determination.

We have added anhydrous $FeCl_2$ to **1**-Cl in absolute ethanol that afforded dark blue plates of $DTA_2 \cdot FeCl_4$ **1**-Fe. Accordingly addition of CuCl to **1**-Cl, dissolved in a mixture of acetonitrile and sulfur dioxide yields $DTA_2 \cdot CuCl_3$ **1**-Cu as black needles. A decision has to be made between $[DTA^+]_2$ $[FeCl_4^{2-}]$ and $[DTA^+]_2$ $[CuCl_3^{2-}]$ or $[DTA \cdot DTA^+]$ $[FeCl_4^-]$ and $[DTA \cdot DTA^+]$ $[CuCl_3^-]$ respectively. The concluding answer is expected from X-ray structure determinations carried out for both compounds. Experimental data for these studies are summarised in Table II. The crystal structure of **1**-Fe (Fig. 1) consists of two independent flat DTA rings and tetrahedral $FeCl_4$. The solid state architecture shows two distinct types of stacks, both running along the crystallographic *b*-axis: mixed stacks of alternating DTA and $FeCl_4$ and homomolecular DTA stacks. Due to the tetrahedral geometry of $FeCl_4$ only one chlorine atom is intercalated between parallel DTA rings. In the homomolecular stacks only the carbon moieties of DTA are interlaced thus minimising interaction between the sulfur atoms. Comparison of the bond parameters with the corresponding values for neutral

DTA species and cationic DTA^+ structures as well as the metal-chlorine distances for $[FeCl_4^-]$ and $[FeCl_4^{2-}]$ (Table I and III) clearly shows that the compound must be described as $[DTA^+]_2$ $[FeCl_4^{2-}]$. This result is further supported by a Mößbauer study[8] being exclusively consistent with the presence of $[Fe(II)Cl_4^{2-}]$. Intermolecular S····Cl contacts, crosslinking the stacks, are well below the Van der Waals separation.

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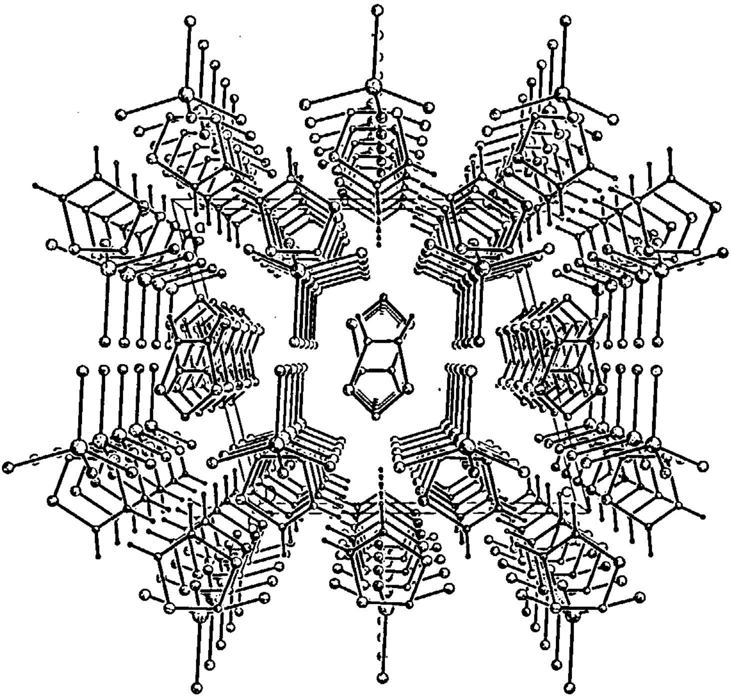

FIGURE 1 Packing for **1**-Fe. Viewed down the *c*-axis

1-Cu (Fig. 2) with 2 independent formula units adopts a different packing pattern. Again, there are homomolecular DTA stacks running along

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the crystallographic *c*-axis. Staggering of the centrosymmetrically related DTA units is even more pronounced than in **1**-Fe. Mixed stacks of DTA and $CuCl_3$ are arranged in a similar manner as in **1**-Fe run along the *b*-axis. Additionally the stacks are crosslinked via S···Cl contacts. A comparison of bond lengths with those of model substances unambiguously reveals that the oxidation state of the educts is preserved in **1**-Cu.

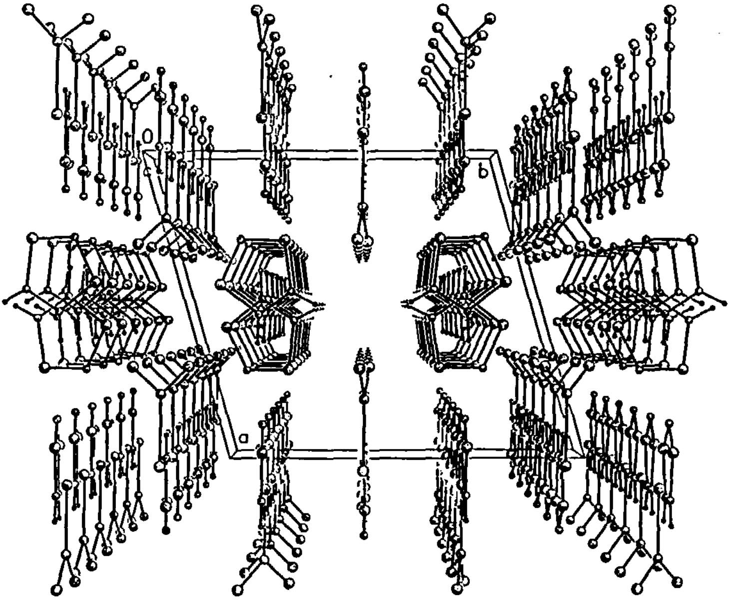

FIGURE 2 Packing for **1**-Cu. Viewed down the *c*-axis

EXPERIMENTAL

Satisfactory elemental analyses were obtained for all substances.

1,3,2-Dithiazolylium chloride **1**-Cl — 5,2 g (61,4 mmol) Trimethylsilyl azide, dissolved in 25 ml methylene chloride, are slowly added to an ice-cooled solution of 10g (61,4 mmol) 1,2-ethanedisulfenyl dichloride in 250 ml methylene chloride. After stirring over night the yellow precipitate is collected on a frit, washed several times with methylene chloride, and dried *in vacuo*. Extraction of the precipitate with liquid sulfur dioxide yields 6,21 g (72%) of **1**-Cl. IR (KBr) 3050(br),1385(s), 1220(s), 1210(m), 1005(s), 940(m), 840(m), 810(m), 755(vs), 640(s), 600(w), 555(w), 420(s) [cm^{-1}].

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4-Chloro-1,3,2-dithiazolylium chloride **2**-Cl — Procedure as for 1-Cl. Recrystallisation from acetonitrile yields 71% **2**-Cl as a yellow powder. IR (KBr) 3000(m), 2980(m), 1375(s),1170(s), 990(m), 935(w), 870(w), 830(m), 815(m), 765(s), 680(w), 585(m) [cm^{-1}].

1,3,2-Dithiazolylium tetracyanoquinodimethane **1**-TCNQ — 42 mg (0,19 mmol) LiTCNQ was dissolved in 3 ml water and this solution was added to a solution of 27,2 mg (0,19 mmol) **1**-Cl in 5 ml water. The mixture was stirred at ambient temperature for 1 h. The resulting black precipitate was filtered off, washed 10 times with small portions of water washed with ether, and dried *in vacuo*. **1**-TCNQ is obtained in 93% yield. IR (KBr) 3080(br), 2190(s), 2180(w), 2165(s), 1580(s), 1560(w), 1510(m), 1390(w), 1365(m), 1340(vs), 1255(w), 1180(s), 1010(w), 985(w), 820(m), 760(m), 720(w), 640(w), 615(w), 590(m) [cm^{-1}].

Bis(1,3,2-dithiazolylium) tetrachloroferrat(II) **1**-Fe — A solution of 0,34 g (5,4 mmol) anhydrous $FeCl_2$ in 30 ml ethanol is dropped into a solution of 0,75 g (5,4 mmol) **1**-Cl in 50 ml ethanol. After stirring for

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½ h the dark blue precipitate is collected on a frit, washed with ethanol, and dried *in vacuo*. The yield is 79%. Suitable crystals for X-ray structure determination can be obtained by slow diffusion of both educt solutions. IR (KBr) 3085(s), 3060(s), 3020(s), 2990(s), 1375(s), 1365(m), 1270(m), 1250(s), 1225(w), 1085(w), 1045(m), 965(w), 955(w), 965(m), 825(m), 785(m), 775(s), 760(s), 650(w) [$\mathrm{cm^{-1}}$].

Bis(1,3,2-dithiazolylium) trichlorocuprat(I) **1-Cu** —To a solution of 0,62g (4,44 mmol) **1-Cl** in 20 ml acetonitrile/ sulfur dioxide (3:1) 0,22 g (2,22 mmol) CuCl, dissolved in 10 ml of the same solvent, are added under stirring at ambient temperature. The mixture is set aside and the SO_2 content is reduced by slowly bubbling argon through the solution. 0,76 g (90,5%) **1-Cu** is obtained as black needles. IR (KBr) 3050(m), 2970(s), 2310(m), 1380(m), 1370(m), 1360(m), 1250(m), 1235(s), 1060(w), 1045(m), 1005(s), h), 940(m), 855(w), 845(m), 810(m), 780(s), 770(s), 755(s), 640(w), 600(w) [$\mathrm{cm^{-1}}$].

TABLE I Selected bond length and angels in **1-Fe** and **1-Cu**

	$\bar{d}$ (S-N) [Å]	$\bar{d}$ (S-C) [Å]	$\bar{d}$ (C-C) [Å]	S-N-S [°]	C-C-S [°]
1-Cl	1.594	1.697	1.355	114.9	112.9
4-Me-DTA$^+$ AsF_6^- [9]	1.601	1.675	1.365	112.2	112.1
1-Fe*	1.587	1.660	1.370	114.4	113.0
1-Cu*	1.594	1.677	1.348	115.0	113.5
R_2DTA; R = CN[10]	1.641	1.727	1.370	115.3	114.0
TTTAP*[11]	1.650	1.727	1.426	116.8	113.6

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* TTTAP = 1,3,2-Trithia-2,4,6-triazapentalenyl.

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TABLE II Crystal data[12] for **1-Cu** and **1-Fe**

Formula	$C_4H_4Cl_3CuN_2S_4$	$C_4H_4Cl_4FeN_2S_4$
Molecular weight	378.22	405.98
Radiation	Mo $K\alpha$ (0.71073 Å)	
Scan type	Ω–θ–scans	Ω–scans
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Cell dimensions	a = 11.6643(5) Å	a = 11.462(3) Å
	b = 13.0027(8) Å	b = 10.321(4) Å
	c = 8.2601(6) Å	c = 11.994(3) Å
	α = 91.114(7)°	α = 90°
	β = 90.744(6)°	β = 104.58(2)°
	γ = 73.837(6)°	γ = 90°
Cell volume	1203.01(13) $Å^3$	1373.2(7) $Å^3$
Cell formula units Z	4	4
Calculated density	2.088 Mg/m^3	1.964 Mg/m^3
Absorption coefficient	3.135 mm^{-1}	2.452 mm^{-1}
Crystal size [mm]	0.30 x 0.25 x 0.21	0.23 x 0.21 x 0.05
θ-Range	1.82 to 22.45°	1.84 to 22.46°
Independent reflections	2775	1782
Absorption correction	Semi-empirical	
Max. / min. transmission	0.45 / 0.33	0.86 / 0.69
Diffractometer	Enraf Nonius CAD4	
Structure solution[13]	Direct Methods	
Structure refinement[13]	Full-matrix least-squares against F^2	
Data/ Parameter	2775 / 253	1782 / 137
Final R-values [$I>2\sigma(I)$]	R1 = 0.0349,	R1 = 0.0430,
	wR2 = 0.0930	wR2 = 0.1003
R-values (all Data)	R1 = 0.0463,	R1 = 0.1000,
	wR2 = 0.0959	wR2 = 0.1070

A riding model was assumed for the H-atoms during refinement and the thermal parameters were fixed at 1.1 times U_{eq} of the corresponding C-atom.

TABLE III Mean bond lengths for the anions in **1**-Fe and **1**-Cu

	1-Cu	$[PMe_4]^+_2$ $CuCl_3^{2-}$ [14]	**1**-Fe	$[NMe_4]^+_2$ $FeCl_4^{2-}$ [15]	$BBDTA^+$ $FeCl_4^-$ [7]
d (M-Cl) [Å]	2,236	2,221	2,306	2,309	2,183

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