

X-Ray Crystallographic Data on Certain Substituted 1,2- and 1,3-Dithiolium Salts, and two Substituted 1,2-Dithioles

ASBJØRN HORDVIK*

X-Ray Crystallography Department, The Weizmann Institute of Science, Israel

In connection with an X-ray crystal structure study of unsaturated five-membered cyclic disulphides, which so far comprises the structures of xanthan hydride¹ and rhodan hydrate², the author became interested in the structure of the 1,2-dithiolium cation. This ion is also an unsaturated five-membered cyclic disulphide, and a pseudoaromatic system. It would be of interest to determine the dimensions of the 1,2-dithiolium ion, and to find to which degree the different bonds are shortened through π -bonding. The results may then be compared with the theoretical bond orders, which have been calculated by Bergson³ by a molecular orbital method.

In recent years the synthesis of several differently substituted 1,2-dithiolium salts have been reported⁴⁻⁷, but so far no X-ray crystallographic data have been available. A survey of unit cells and space groups of some substituted 1,2-dithiolium salts is given here; it also comprises two substituted 1,3-dithiolium salts and two substituted 1,2-dithioles.

Oscillation and Weissenberg photographs were taken using copper radiation, λ (CuK α) = 1.542 Å. The cell dimensions given below are believed to be correct to within 1 %. Densities were determined by flotation.

*3,5-Diamino-1,2-dithiolium chloride monohydrate*⁴ crystallizes from water by slow evaporation as thin colourless plates with {001} predominant. Monoclinic, $a = 5.72$ Å, $b = 8.71$ Å, $c = 15.45$ Å, $\beta = 90.4^\circ$. Four formula units per unit cell; density, calc. 1.61, found 1.59 g/cm³. Systematic absences, $0k0$ when k is odd. The space group is thus $P2_1$ or $P2_1/m$.

*3,5-Diamino-1,2-dithiolium bromide monohydrate*⁴. The salt crystallizes from water

as yellowish-brown needles, elongated along the a axis. Monoclinic, $a = 5.74$ Å, $b = 9.03$ Å, $c = 31.71$ Å, $\beta = 91^\circ$. Eight formula units per unit cell; density, calc. 1.87, found 1.89 g/cm³. Systematic absences, $h0l$ when l is odd, $0k0$ when k is odd. The space group is thus $P2_1/c$.

Except for the doubling of the c axis, the cell dimensions of the bromide are very nearly the same as those of the chloride above. In the $h0l$ zone the c axis of the bromide is halved and thus like that of the chloride. The intensity distributions in the $h0l$ zones also show similarities.

*3,5-Diamino-1,2-dithiolium iodide*⁴. Crystallization from a series of different solvents always resulted in twinned crystals. Some untwinned ones were eventually obtained from butanol. These were orthorhombic, but of rather poor quality. The cell dimensions are, $a = 5.46$ Å, $b = 9.23$ Å, $c = 14.17$ Å, and there are four formula units per unit cell; density, calc. 2.33, found 2.20–2.30 g/cm³. Systematic absences, $0kl$ when $k + l$ is odd, $hk0$ when h is odd. Of the two possible space groups with these absences, the centrosymmetric one, $Pnma$, has been found to be the correct one through Fourier projection along the a axis⁸. The crystals are isomorphous with those of thiuret hydroiodide⁹.

*3,5-Diacetamido-1,2-dithiolium chloride*⁵ crystallizes from water by slow evaporations as colourless needles, elongated along b and with {100} predominant. There is perfect cleavage along a plane parallel to [010]. Monoclinic, $a = 24.36$ Å, $b = 4.73$ Å, $c = 20.86$ Å, $\beta = 112.5^\circ$. Eight formula units per unit cell; density, calc. 1.51, found 1.51 g/cm³. Systematic absences, hkl when $h + k$ is odd, $h0l$ when l is odd. The space group is thus either $C2/c$ or C/c . The salt was prepared, according to Schmidt⁵, by dissolving the base (3-acetylmino-5-acetamido-1,2-dithiole) in slight excess of warm dilute hydrochloric acid and allowing the solution to cool.

*3,5-Diacetamido-1,2-dithiolium bromide and iodide*⁵ crystallize from water by slow evaporation as yellowish-brown and yellow needles respectively. The crystals are isomorphous with those of the chloride and are developed in the same way. Bromide, $a = 24.38$ Å, $b = 4.87$ Å, $c = 21.02$ Å, $\beta = 113.4^\circ$; density, calc. 1.71, found 1.72 g/cm³. Iodide, $a = 24.68$ Å, $b = 5.05$ Å, $c = 21.41$ Å, $\beta = 115.2^\circ$; density, calc. 1.89, found 1.89 g/cm³. The bromide was prepared in the same way as the chloride, from dilute hydro-

* Present address: Chemical Institute, University of Bergen, Norway.

bromic acid, and the iodide was obtained by adding potassium iodide to a warm aqueous solution of the chloride.

4-Phenyl-1,2-dithiolium bromide⁶. The salt crystallizes from ethanol as yellow needles and thin flakes elongated along *c* and with {100} predominant. Orthorhombic, *a* = 26.41 Å, *b* = 8.27 Å, *c* = 4.72 Å. Four formula units per unit cell; density, calc. 1.67, found 1.70 g/cm³. Systematic absences, *Ok**l* for *k* + *l* odd, *h**k*0 for *h* odd. The centrosymmetric space group, *Pnma*, has been found to be the correct one through Patterson and Fourier projections along the *a* axis¹⁰.

4-Phenyl-1,2-dithiolium iodide⁶. Crystallization from ethanol yields orange crystals which are isomorphous with those of the bromide and also developed in the same way. The cell dimensions are, *a* = 26.02 Å, *b* = 8.53 Å, *c* = 4.78 Å, and the density, calc. 1.93, found 1.93 g/cm³.

4-Phenyl-1,2-dithiolium perchlorate⁶. The crystals are light yellow laths, elongated along *c* and with {100} predominant. Orthorhombic, *a* = 18.29 Å, *b* = 10.75 Å, *c* = 11.30 Å. Eight formula units per unit cell; density, calc. 1.67, found 1.67 g/cm³. The systematic absences are those of the space group *Pbca*.

3-Phenyl-1,2-dithiolium iodide⁶. Orange crystals from ethanol, needles and flakes elongated along *b* and with {001} predominant. Monoclinic, *a* = 8.32 Å, *b* = 5.60 Å, *c* = 22.57 Å, β = 98.2°. Four formula units per unit cell; density, calc. 1.95, found 1.98 g/cm³. The space group, from systematic absences, is *P2*₁/*c*.

3-Phenyl-1,2-dithiolium perchlorate⁶. The crystals are light yellow laths, elongated along *c* and with {100} predominant. Orthorhombic, *a* = 18.23 Å, *b* = 11.06 Å, *c* = 11.24 Å. Eight formula units per unit cell; density, calc. 1.63, found 1.65 g/cm³. The systematic absences are those of the space group *Pbca*. The space group is the same as that of 4-phenyl-1,2-dithiolium perchlorate, and the unit cell dimensions are very similar. It is thus likely that the phenyl group has the same position in the two crystals, and also the 1,2-dithiolium ring except for the rotation of the latter corresponding to the different position of attachment of the phenyl group. The difference would roughly correspond to an exchange of a sulphur and a carbon atom. The intensity distributions of the reflections are accordingly different.

3-Methyl-5-phenyl-1,2-dithiolium perchlorate⁷. The salt crystallizes from acetic acid as light yellow needles elongated along the *c* axis. Orthorhombic, *a* = 11.07 Å, *b* = 16.06 Å, *c* = 7.10 Å. Four formula units per unit cell; density, calc. 1.54, found 1.55 g/cm³. The systematic absences are those of the space group *P2*₁2₁2₁.

2,4-Diphenyl-1,3-dithiolium perchlorate⁷. Crystallization from acetic acid yielded both orthorhombic and monoclinic crystals. The orthorhombic ones were thin yellow flakes, elongated along *a* and with {010} predominant. The cell dimensions are, *a* = 8.54 Å, *b* = 16.87 Å, *c* = 10.70 Å. Four formula units per unit cell; density, calc. 1.53, found 1.54 g/cm³. The systematic absences are those of the space groups *Pnma* or *Pn*2₁/*a*. Considerations of molecular dimensions and axial lengths show that a mirror plane can not be present, since then all the atoms of the cation must lie in the mirror plane provided a non-statistical structure.

The monoclinic crystals were yellow needles of rather poor quality, and elongated along *a*. Photographs were taken around the needle axis only: *a* = 11.57 Å, *b* = 10.14 Å, *d*₀₀₁ = 13.04 Å. Four formula units per unit cell; density, calc. 1.54, found 1.54 g/cm³. The space group, from systematic absences, is *P2*₁/*n*.

2,4,5-Triphenyl-1,3-dithiolium perchlorate⁷. The salt crystallizes from acetic acid as flat prisms, elongated along *b* and with {001} predominant. There is a pronounced tendency of twinning. Monoclinic, *a* = 15.12 Å, *b* = 7.20 Å, *c* = 19.24 Å, β = 107°. Four formula units per unit cell; density, calc. 1.43, found 1.43 g/cm³. The systematic absences are those of the space group *P2*₁/*c*.

1,2-Dithiole-3-thione¹¹ crystallizes from ethanol as square or rectangular prisms, elongated along *c* and bounded by {110}. Tetragonal, *a* = 10.67 Å, *c* = 9.38 Å. Eight molecules per unit cell; density, calc. 1.66, found 1.67 g/cm³. Systematic absences, *h**h**l* when *l* is odd, *Ok**l* when *k* is odd. The space group is thus either *P4*₃/*mbc* or *P4*₂/*bc*. The former one would demand that the molecule lie with all its atoms in a crystallographic mirror plane. The distance between layers of molecules would then be $\frac{1}{2}c$ = 4.69 Å which is too long for van der Waals contacts. Of the two space groups, *P4*₂/*bc* is therefore probably the correct one. These crystals

have earlier been reported to be tetragonal¹².

The compound was prepared according to Mayer and Kubasch¹¹, but was purified over the mercuric chloride adduct instead of by sublimation.

*3-Acetylrimino-5-acetamido-1,2-dithiole*⁵ crystallizes from butanol as light brownish-yellow needles elongated along *b*. Orthorhombic, $a = 17.41$ Å, $b = 10.54$ Å, $c = 15.64$ Å. Twelve molecules per unit cell; density, calc. 1.50, found 1.51 g/cm³. The systematic absences are those of the space groups $Pnma$ or $Pn2_1a$. The intensities of the $h0l$ reflections are normal for $l = 3$, but are very weak for the remainder. This implies that a pattern of four molecules is repeated three times in the c -axis direction as seen along the b axis, and may indicate that the asymmetric unit consists of three molecules, one from each pattern of four; this would correspond to the space group $Pn2_1a$.

Further work on the crystal structures of some of the compounds will be made.

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An Isoselenocyanate Complex of Chromium(III)

Preparation and Absorption Spectrum

KIRSTEN MICHELSEN

*Department I. Inorganic Chemistry.
The H. C. Ørsted Institute, University of
Copenhagen, Copenhagen, Denmark*

The selenocyanate- like the thiocyanate ion has, when acting as a ligand, the special characteristic of being able to bind through either end of the group. It looks as if there is a correlation between the division of metals into class (a) and class (b) acceptors proposed by Ahrland, Chatt and Davies¹ and the type of binding, the class (a) metals tending to form isothiocyanate complexes, the class (b) metals to form thiocyanate complexes^{2,3}.

In the last years great interest has been taken in thiocyanate complexes, whereas little work has been done on the corresponding seleno-cyanate compounds. This work has mainly been concerned with complexes of the class (b) metals as platinum and mercury^{4,5}. Recently, however, Cotton *et al.*⁶ and Turco *et al.*⁷ have investigated some selenocyanate complexes of cobalt(II) and by means of spectral and magnetic data concluded that the selenocyanate groups are co-ordinated to cobalt through the nitrogen atoms in the $[\text{Co}(\text{NCSe})_6]^{3-}$ ion.

The intention of this work has been to investigate a selenocyanate complex of chromium(III) of the type $[\text{Cr}(\text{NCSe})_6]^{3-}$ and from spectral data to find out which end of the selenocyanate group is bound to the metal.

Chromium(III) is a class (a) acceptor, and in analogy with a thiocyanate complex,⁸ $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^+$, co-ordination through the nitrogen atoms should be expected. The spectral data obtained here seem to confirm this.

Experimental. Anhydrous CrCl_3 and KSeCN were prepared by methods described in the literature^{9,10}. All other chemicals were reagent grade and used without further purification.

Preparation of $((\text{CH}_3)_4\text{N})_3[\text{Cr}(\text{NCSe})_6]$. To the boiling solution of 43 g of KSeCN (0.3 mole) in 175 ml of 99.9 % ethanol 5 g of CrCl_3 (0.03 mole) is added. The mixture is heated to reflux with constant stirring for 4 h. During