SHORT COMMUNICATIONS

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

A S H J O R N H O R D V I K *

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In connection with an X-ray crystal structure study of unsaturated five-membered cyclic disulphides, which so far comprises the structures of xanthan hydride 1 and rhodan hydrate 2, 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 Bergson 3 by a molecular orbital method.

In recent years the synthesis of several differently substituted 1,2-dithiolium salts have been reported 4, 5, 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-dithiololes.

Oscillation and Weissenberg photographs were taken using copper radiation, λ (CuKα) = 1.54 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, β = 90.4°. 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 P2₁, or P2₁/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, β = 91°. 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 P2₁/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, 0k0 when k and l are odd, h0l 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 axis 5. The crystals are isomorphous with those of thiuret hydroiodide 5.

3,5-Diacetamido-1,2-dithiolium chloride 5 crystallizes from water by slow evaporation 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, β = 112.5°. 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 C1/c. The salt was prepared, according to Schmidt 5, by dissolving the base (3-acetylimino-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 = 21.62 Å, β = 113.4°; density, calc. 1.71, found 1.72 g/cm³. Iodide, a = 24.68 Å, b = 5.05 Å, c = 21.41 Å, β = 115.2°; density, calc. 1.89, found 1.89 g/cm³. The bromide was prepared in the same way as the chloride, from dilute hydro-

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Acta Chem. Scand. 17 (1963) No. 6
bromic acid, and the iodide was obtained by adding potassium iodide to a warm aqueous solution of the chloride.

4-Phenyl-1,2-dithiolium bromide. The salt crystallizes from ethanol as yellow needles and thin flakes elongated along c and with (100) predominant. Orthorhombic, $a = 26.41 \, \text{Å}$, $b = 8.27 \, \text{Å}$, $c = 4.72 \, \text{Å}$. Four formula units per unit cell; density, calc. 1.67, found 1.70 g/cm$^3$. Systematic absences, 0kl for $k + l$ odd, hh0 for h odd. The centrosymmetric space group, Pnma, has been found to be the correct one through Patterson and Fourier projections along the a axis.

4-Phenyl-1,2-dithiolium iodide. 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, $a = 26.02 \, \text{Å}$, $b = 8.53 \, \text{Å}$, $c = 4.78 \, \text{Å}$, and the density, calc. 1.93, found 1.93 g/cm$^3$.

4-Phenyl-1,2-dithiolium perchlorate. The crystals are light yellow laths, elongated along c and with (100) predominant. Orthorhombic, $a = 18.29 \, \text{Å}$, $b = 10.75 \, \text{Å}$, $c = 11.30 \, \text{Å}$. Eight formula units per unit cell; density, calc. 1.67, found 1.67 g/cm$^3$. The systematic absences are those of the space group Pnca.

3-Phenyl-1,2-dithiolium iodide. Orange crystals from ethanol, needles and flakes elongated along b and with (001) predominant. Monoclinic, $a = 8.32 \, \text{Å}$, $b = 5.60 \, \text{Å}$, $c = 22.57 \, \text{Å}$, $\beta = 98.2^\circ$. Four formula units per unit cell; density, calc. 1.95, found 1.98 g/cm$^3$. The space group, from systematic absences, is $P2_1/c$.

3-Phenyl-1,2-dithiolium perchlorate. The crystals are light yellow laths, elongated along c and with (100) predominant. Orthorhombic, $a = 18.23 \, \text{Å}$, $b = 11.06 \, \text{Å}$, $c = 11.24 \, \text{Å}$. Eight formula units per unit cell; density, calc. 1.63, found 1.65 g/cm$^3$. The systematic absences are those of the space group Pnca. 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 perchlorate. The salt crystallizes from acetic acid as light yellow needles elongated along the c axis. Orthorhombic, $a = 11.07 \, \text{Å}$, $b = 16.06 \, \text{Å}$, $c = 7.16 \, \text{Å}$. Four formula units per unit cell; density, calc. 1.54, found 1.55 g/cm$^3$. The systematic absences are those of the space group P2$_2$2$_1$2$_1$.

2,4-Diphenyl-1,3-dithiolium perchlorate. 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, $a = 8.54 \, \text{Å}$, $b = 16.87 \, \text{Å}$, $c = 10.70 \, \text{Å}$. Four formula units per unit cell; density, calc. 1.53, found 1.54 g/cm$^3$. The systematic absences are those of the space groups Pnma or Pn2$_1$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: $a = 11.57 \, \text{Å}$, $b = 10.14 \, \text{Å}$, $d_{001} = 13.04 \, \text{Å}$. Four formula units per unit cell; density, calc. 1.54, found 1.54 g/cm$^3$. The space group, from systematic absences, is P2$_2$/a.

2,4,5-Triphenyl-1,3-dithiolium perchlorate. The salt crystallizes from acetic acid as flat prisms, elongated along b and with (001) predominant. There is a pronounced tendency of twinning. Monoclinic, $a = 15.12 \, \text{Å}$, $b = 7.20 \, \text{Å}$, $c = 19.24 \, \text{Å}$, $\beta = 107^\circ$. Four formula units per unit cell; density, calc. 1.43, found 1.43 g/cm$^3$. The systematic absences are those of the space group P2$_2$/c.

1,2-Dithiole-3-thione crystallizes from ethanol as square or rectangular prisms, elongated along c and bounded by (110). Tetragonal, $a = 10.67 \, \text{Å}$, $c = 9.38 \, \text{Å}$. Eight molecules per unit cell; density, calc. 1.66, found 1.67 g/cm$^3$. Systematic absences, $hk0$ when $l$ is odd, 0kl when $k$ is odd. The space group is thus either $P4_1/mnc$ 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 $\frac{1}{2}c = 4.69 \, \text{Å}$ 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
Short Communications

An Isoselenocyanate Complex of Chromium(III)

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The isoselenocyanate-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 Ahrlund, Chatt and Davies \(^1\) and the type of binding, the class (a) metals tending to form iso-thiocyanate complexes, the class (b) metals to form thiocyanate complexes \(^5\).

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 \(^5\). 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 \([\text{Co(NCSe)}]^{2-}\) ion.

The intention of this work has been to investigate a selenocyanate complex of chromium(III) of the type \([\text{Cr(NCSe)}]^{2-}\) 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, \([\text{Cr(NH}_3)_2(\text{NCS})_3]^{2-}\), co-ordination through the nitrogen atoms should be expected. The spectral data obtained here seem to confirm this.

Experimental. Anhydrous \(\text{CrCl}_3\) and \(\text{KSeCN}\) were prepared by methods described in the literature \(^8\). All other chemicals were reagent grade and used without further purification.

Preparation of \([\text{Cr(NCSe)}]_{\text{d}}\). To the boiling solution of 45 g of \(\text{KSeCN}\) (0.3 mole) in 175 ml of 99.9% ethanol 5 g of \(\text{CrCl}_3\) (0.03 mole) is added. The mixture is heated to reflux with constant stirring for 4 h. During

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