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Received June 13, 1956.

X-Ray Crystallographic Data on Certain Five-membered Cyclic Disulphides

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A survey has been made of unit cells and space groups of some simple 1,2,4-dithiazolidine derivatives. The compounds studied are, xanthan hydride [1-3] (3-imino-1,2,4-dithiazolidine-5-thione), rhodan hydrate [4,5] (3-imino-1,2,4-dithiazolidine-5-one), and three thiuret (3,5-diimino-1,2,4-dithiazolidine) hydrohalides. The latter compounds are oxidation products of dithiobiuret; the hydrochloride [6] and hydroiodide [7] have been mentioned in literature earlier, but apparently not the hydrobromide. The hydrobromide and hydroiodide used in the present work were obtained by adding an excess of aqueous potassium bromide or iodide to a warm aqueous solution of the hydrochloride.

Oscillation and Weissenberg photographs were taken using copper radiation, $\lambda(\mathrm{Cu}K\alpha)$ = 1.542 Å. The axial lengths given below are believed to be correct to within 0.5 %. Densities were determined by flotation in bromoform-carbon tetrachloride mixtures.

Xanthan hydride, $S_2(C:NH)(C:S)NH$. Monoclinic prismatic, $a = 4.05$ Å, $b = 10.59$ Å, $c = 12.78$ Å, $\beta = 97°$. Four molecules per unit cell; density, calc. 1.83, found 1.84 g/cm³. Systematic absences, $h0l$ when l is odd, $0k0$ when k is odd. The space group is thus $C_{2h}^5 - P2_1/c$.

From 60 % acetic acid the compound crystallized as long prisms, extended along the a axis and flattened along the b axis.

Rhodan hydrate, $S_2(C:NH)(C:O)NH$. Monoclinic, $a = 12.50$ Å, $b = 5.24$ Å, $c = 14.67$ Å, $\beta = 95\frac{1}{4}°$. Eight molecules per unit cell; density, calc. 1.86, found 1.87 g/cm³. Systematic absences, hkl when $h + k$ is odd, $h0l$ when l is odd. The space group is thus either $C_{2h}^6 - C2/c$ or $C_s^4 - C/c$.

From water, the compound crystallized as flat prisms, extended along the b axis and with {100} predominant. There is perfect cleavage along (001). The morphology of the crystals indicates the presence of a twofold axis and thus the correctness of the centrosymmetric space group, $C_{2h}^6 - C2/c$.

Thiuret hydrochloride, $S_2(C:NH)_2NH \cdot HCl \cdot \frac{1}{2}H_2O$. Monoclinic, $a = 19.58$ Å, $b = 5.47$ Å, $c = 14.34$ Å, $\beta = 114\frac{1}{2}°$. Eight formula units per unit cell; density, calc. 1.70, found 1.71 g/cm³. Systematic absences, hkl when $h + k$ is odd, $h0l$ when l is odd. Space group, $C_{2h}^6 - C2/c$ or $C_s^4 - C/c$.

The density, and the statement by Preisler and Bateman [6] that 5 % water remain after drying over calcium chloride, point to the presence of half a mole of crystal water per mole of hydrochloride.

From water, the compound crystallized as prisms extended along the b axis. As in the case of rhodan hydrate, the morphology is in favour of the former of the two possible space groups. The water molecules would then lie on twofold axes.

Thiuret hydrobromide, $S_2(C:NH)_2NH \cdot HBr$. Monoclinic prismatic, $a = 5.11$ Å, $b = 12.76$ Å, $c = 10.47$ Å, $\beta = 110°$. Four formula units per unit cell; density, calc. 2.22, found 2.22 g/cm³. Systematic absences, $h0l$ when l is odd, $0k0$ when k is odd. The space group is thus $C_{2h}^5 - P2_1/c$.

The compound crystallized from water as large plates {010} or as prisms extended along the a axis with, also here, {010} predominant.

Thiuret hydroiodide, $S_2(C:NH)_2NH \cdot HI$. Orthorhombic bipyramidal, $a = 5.38$ Å, $b = 9.24$ Å, $c = 13.98$ Å. Four formula units per unit cell; density, calc. 2.50, found 2.49 g/cm³. Systematic absences, $0kl$ when $k + l$ is odd, $hk0$ when h is odd. Of the two space groups compatible with these absences, the centrosymmetric one, $D_{2h}^{16} - Pnma$, has been found to be the correct one through Patterson and Fourier projections along the a axis [8]. The thiuret-H^+ ion lies across a crystallographic mirror plane of symmetry, and also the iodide ion is located in the mirror plane.

From water, the compound crystallized as prisms extended along the a axis and bounded by {001} and {011}. There is perfect cleavage along (001), and a rather pronounced tendency of irregular growth and twinning.

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

The author wishes to express his thanks to the American Cyanamid Company, New York, for a sample of thiuret hydrochloride.

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Fig. 1. Time-concentration curves showing the inhibiting effect of copper ions.

O: No active copper present
●: $2 \cdot 10^{-7}$ moles copper/l
▲: 10^{-5} » »

Kinetics of the Heterogeneous Reaction of Calcium Bicarbonate Formation, with Special Reference to Copper Ion Inhibition

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The system $CaCO_{3(s)} - CO_{2(g)} - H_2O_{(l)}$ is of considerable geological, physiological and technical importance. The reaction between solid calcium carbonate and aqueous carbon dioxide has therefore been discussed extensively in literature [1]. However, the published papers deal mainly with the thermodynamics of the reaction whereas the kinetic aspects seem to have been largely neglected.

Calcite of natural origin was used in the present investigation. When giving the ground material a repeated treatment with aqueous carbon dioxide, the reactivity of the calcite particles used for the experiment, did not change from one run to another. The experiments were carried out at 25° C in an agitated vessel made of stainless steel and designed to keep the solid particles well suspended in the liquid during the runs. The carbon dioxide-air mixture was blown into the suspension of calcite particles, and the reaction was followed by conductivity measurements.

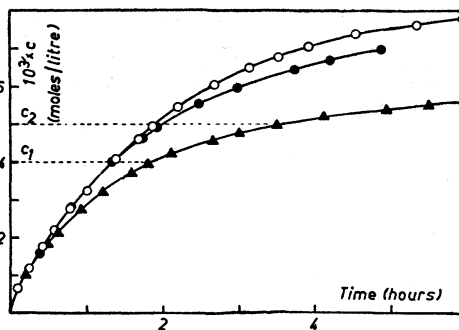The reaction was found to be strongly inhibited by very small amounts of copper ions. In Fig. 1 are shown the results of three runs, all carried out with 100 g of calcite suspended in 10 litres of distilled water. The particle size was 295—422 μ, corresponding to a surface area of approximately 125 cm² per g. The carbon dioxide pressure was 0.95 atm. In the first experiment traces of copper inevitably present in the solution were screened by adding 4×10^{-5} moles per litre of disodium - ethylenediamin - tetraacetic acid (EDTA) [3]. The middle curve shows that less than 2×10^{-7} moles per litre of copper ions, accidentally present due to contamination of the surface of the particles and the distilled water, has a significant effect on the reaction rate. The third run was carried out in the presence of 10^{-5} moles per litre of cupric chloride. The inhibition was now so strong that the reaction gave the appearance of approaching a new equilibrium concentration, 20—30 % below the real one.

With the object of investigating whether the bulk of the added copper ions was adsorbed on the calcite surface or remained dissolved in the water, the following experiment was carried out: Initially, the liquid contained 10^{-5} moles per litre of cupric chloride, but when the concentration of calcium bicarbonate reached c_1 in Fig. 1, the experiment was stopped, the liquid decanted and used for another run with a fresh portion of calcite. The concentration then continued to rise along the lower curve. At c_2 this experiment was stopped, the solution removed by decantation and