

along which the Cu ions can move. The temperature factors for the Cu atoms in octahedral sites were appropriately large.

In our single-crystal X-ray study of CuI 12R no electron density is found in octahedral sites. The possibility of the crystal containing domains with the layered kind of structure proposed by Kurdyumova & Baranova (1961) is considered unlikely and we prefer the local ordering indicated in Fig. 2, where each I atom is surrounded by a tetrahedron of Cu atoms, or perhaps a completely random distribution over the tetrahedral sites. The temperature factors for Cu are somewhat larger than those for I (see Table 1). The thermal motion is essentially isotropic. Unfortunately the conductivity of polytype 12R could not be determined because the crystals obtained were too small.

Clearly techniques for obtaining good single crystals of CuI in its various phases and polytypes are desirable in order to clarify the role of structure in determining ionic conductivity. The use of PH₃-saturated solvents may prove useful in the synthesis of single crystals of metal iodides.

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Structure of Magnesium Isothiocyanate Tetrahydrate

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Abstract. Mg(NCS)₂·4H₂O, monoclinic, $P2_1/a$, $a = 7.488$ (2), $b = 9.030$ (2), $c = 7.869$ (2) Å, $\beta = 113.63$ (1)°, $V = 487.5$ (2) Å³, $Z = 2$, $D_c = 1.45$ Mg m⁻³. The structure has been determined by Patterson and Fourier methods and has been refined to $R = 0.029$ for 807 observed reflections. The structure consists of Mg(NCS)₂(H₂O)₄ molecules which are interconnected by three kinds of O—H···S and one kind of O—H···O hydrogen bonds. Mg has a centrosymmetric octahedral coordination with Mg—N 2.102 (2), Mg—O 2.047 (2) and 2.126 (2) Å.

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Introduction. This study was stimulated by our interest in hydrogen bonds between water molecules and sulphur (Mereiter, Preisinger, Baumgartner, Heger, Mikenda & Steidl, 1982). Colourless platy crystals of the title compound were obtained by mixing two equimolar aqueous solutions of MgSO₄·7H₂O and Ba(SCN)₂·3H₂O, filtering off the precipitated BaSO₄, and evaporating the solution obtained at room temperature.

Intensity data for a crystal 0.3 × 0.2 × 0.1 mm were collected on a Philips PW 1100 four-circle

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diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. One half of the reflection sphere with $\theta < 28^\circ$ (2360 reflections) was measured by the ω - 2θ scan method with a scan speed of 1° min^{-1} and a scan width of 1.2° . The three standard reflections were constant with time. The equivalent reflections were averaged [$R = \sum \langle I \rangle - I / \sum I = 0.012$] and yielded 807 independent observed reflections with $I_o > 3\sigma(I_o)$. Systematic absences were consistent with space group $P2_1/a$.

The positions of Mg and S atoms were derived from a Patterson map, those of N, C and O atoms from a Fourier map. The structure was then refined with anisotropic temperature factors to $R = 0.04$. At this stage approximate positions of the H atoms could be taken from a difference map. In the subsequent calculations the H atoms were refined as parts of rigid H_2O molecules adopting $\text{H}-\text{O}-\text{H} = 108^\circ$, $\text{O}-\text{H} = 0.96 \text{ \AA}$ for the nuclear H positions and $\text{O}-\text{H} = 0.8 \text{ \AA}$ for the centre of the spherical scattering function of Stewart, Davidson & Simpson (1965). All other scattering functions were taken from *International Tables for X-ray Crystallography* (1974). The final refinement, which included a correction for extinction, adjusted 60 parameters and converged with weights $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$ to $R = 0.029$ ($R_w = 0.029$) for the 807 observed reflections. When the 373 reflections with $I < 3\sigma(I)$ were included, $R = 0.052$ ($R_w = 0.033$). The final difference map showed no unusual features. Calculations were carried out at the Interuniversitares Rechenzentrum Wien with the program system *SHELX 76* (Sheldrick, 1976).*

Discussion. The structure is illustrated in Fig. 1. Positional parameters are in Table 1. Bond lengths and angles are given in Table 2. The structure is built up from *trans*-tetraaquabis(isothiocyanato)magnesium molecules which are interconnected exclusively by hydrogen bonds. The thiocyanate groups are N-bonded to Mg, unlike in $\text{Co}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ (Cano, Garcia-Blanco & Guerrero-Laverat, 1976) where they are N- and S-bonded to hexacoordinated Co. The MgN_2O_4 octahedron is centrosymmetric and almost regular. The $\text{Mg}-\text{O}(2)$ bond is significantly longer than $\text{Mg}-\text{O}(1)$ because O(2) receives a hydrogen bond, but O(1) does not. The $\text{Mg}-\text{N}-\text{C}$ linkages are almost straight, as is usual with M^{2+} and M^{3+} thiocyanates (Brattas, Jagner & Ljungstrom, 1978). The dimensions of the NCS group agree well with those previously found in N-bonded thiocyanate complexes (Norbury, 1975). The two independent water molecules of the structure

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36514 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

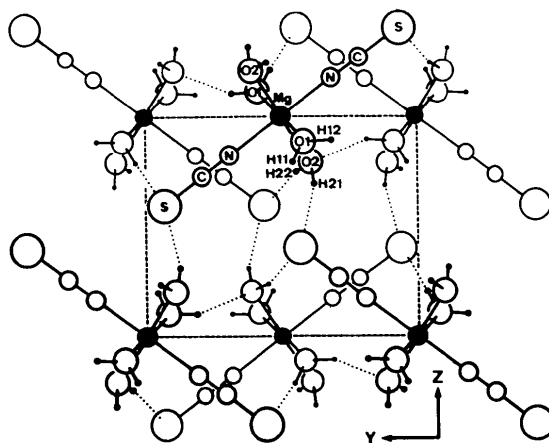


Fig. 1. $\text{Mg}(\text{NCS})_2 \cdot 4\text{H}_2\text{O}$ in a view parallel to $[100]$. The Mg atoms at the top are located at $x = \frac{1}{2}$ and $x = 1$, those at the bottom at $x = 0$ and $x = \frac{1}{2}$.

Table 1. Atomic coordinates ($\times 10^5$, for H $\times 10^4$) and thermal parameters (Å^2)

Hydrogen atoms were refined as parts of rigid H_2O molecules with the corresponding O atoms as reference points and with $\text{H}-\text{O}-\text{H} = 108^\circ$ and $\text{O}-\text{H} = 0.96 \text{ \AA}$ as fixed values. The average standard deviation of the H_2O rotation angles is 1.8° . One overall B_{iso} was refined for the H atoms. $B_{\text{eq}} = \frac{1}{3}\pi^2(U_{11} + U_{22} + U_{33})$.

| | x | y | z | $B_{\text{iso}}/B_{\text{eq}}$ |
|-------|------------|------------|-------------|--------------------------------|
| Mg | 0 | 0 | 0 | 2.30 (4) |
| S | 18192 (8) | 43514 (6) | 40256 (7) | 3.32 (2) |
| C | 13681 (26) | 28832 (22) | 26841 (25) | 2.5 (1) |
| N | 10137 (24) | 18579 (19) | 17314 (22) | 3.2 (1) |
| O(1) | 27585 (20) | -8646 (15) | 10702 (20) | 3.1 (1) |
| O(2) | 6424 (21) | 11067 (17) | -20732 (18) | 3.1 (1) |
| H(11) | 3775 | -371 | 2076 | 5.1 (3) |
| H(12) | 3157 | -1871 | 1037 | |
| H(21) | -565 | 1183 | -3144 | |
| H(22) | 1551 | 577 | -2427 | |

Table 2. Interatomic distances (Å) and angles ($^\circ$)

Symmetry code: none x, y, z ; (i) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, -z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z - 1$.

| | | | |
|---------|-----------|--------------|-----------|
| Mg-N | 2.102 (2) | N-Mg-O(1) | 89.7 (1) |
| Mg-O(1) | 2.047 (2) | N-Mg-O(2) | 89.3 (1) |
| Mg-O(2) | 2.126 (2) | O(1)-Mg-O(2) | 89.6 (1) |
| N-C | 1.153 (3) | N-C-S | 178.7 (2) |
| C-S | 1.643 (2) | Mg-N-C | 172.4 (2) |
| N-S | 2.796 (2) | | |

Hydrogen bonds (H_2O geometry fixed at $\text{O}-\text{H} = 0.96 \text{ \AA}$ and $\text{H}-\text{O}-\text{H} = 108^\circ$)

| A | B | C | B-C | A-C | $\angle A-B-C$ |
|---------------|--|---|------------|-----------|----------------|
| O(1)-H(11)... | S ⁱ | | 2.365 (9) | 3.294 (2) | 162.8 (24) |
| H(12)... | O(2 ⁱⁱ) | | 2.054 (11) | 2.963 (2) | 157.2 (24) |
| O(2)-H(21)... | S ⁱⁱⁱ | | 2.352 (10) | 3.278 (2) | 161.9 (25) |
| H(22)... | S ⁱⁱ | | 2.351 (8) | 3.290 (2) | 166.0 (25) |
| | S ⁱ -O(1)-O(2 ⁱⁱ) | | | 92.0 (1) | |
| | S ⁱⁱⁱ -O(2)-S ⁱⁱ | | | 87.3 (1) | |

possess different coordinations, H₂O(1) having a flat pyramidal threefold one, and H₂O(2) a distorted tetrahedral one. The three different O—H...S bonds of the structure are approximately at right angles to the acceptor NCS groups (O...S—C = 89–112°) and have similar dimensions (Table 2). H...S and O...S distances are slightly shorter than for the 'average' O—H...S bond between water and sulphur, for which O...S = 3.324 Å was reported (Mereiter, Preisinger & Guth, 1979). Two O—H...S bonds similar in lengths to those of the title compound have been found by neutron diffraction in Mg₂S₂O₃·6H₂O (O...S = 3.26 and 3.25 Å, H...S = 2.28 and 2.34 Å; Elerman, Fuess & Joswig, 1982). Judged from its length, the O(1)—H(12)...O(2) bond seems to be weaker than the O—H...S bonds of the structure.

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Structure of Iron(II) Molybdenum(IV) Oxide Fe₂Mo₃O₈*

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Abstract. Fe₂Mo₃O₈, *P6₃mc*, *a* = 5.7732 (6), *c* = 10.0542 (11) Å at 298 K with *Z* = 2 giving *d*_{calc} = 6.03 Mg m⁻³. The structure was refined to *R_F* = 0.029 for 966 reflections observed with Mo *K*α radiation. The compound is isostructural with Zn₂Mo₃O₈ with Mo—Mo distances of 2.5296 (6) Å inside the clusters and 3.2436 (6) Å from cluster to cluster. The so-called FeMoO₃ (JCPDS pattern #19-611) is likely to be Fe₂Mo₃O₈.

Introduction. Large crystals of the phase Fe₂Mo₃O₈ were grown in the course of a study of mixed oxides in the FeO—MoO₂ system (Strobel, McAlister & Le Page, 1982). This substance was first synthesized by McCarroll, Katz & Ward (1957) who prepared a series of isostructural oxides *M*₂^{II}Mo₃^{IV}O₈ (*M* = Mg, Mn, Fe, Co, Ni, Zn and Cd). They indexed the Fe₂Mo₃O₈ powder pattern in the space group *P6₃mc* with *a* = 5.782 ± 0.005 and *c* = 10.046 ± 0.010 Å by similarity with the single-crystal studies of the Zn and Mg analogues. The

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JCPDS file contains no data on Fe₂Mo₃O₈, but the observed powder pattern from crushed crystals obtained in the present study fitted quite well the JCPDS pattern #19-611 following the description by Rusakov, Novokhatskii, Lenev & Savinskaya (1965) of a hexagonal phase FeMoO₃ with cell parameters *a* = 4.67 and *c* = 15.03 Å. A single-crystal study was therefore undertaken in order to investigate the interesting structural features of Fe₂Mo₃O₈, especially the Mo₃ clusters, and to clarify the ambiguity about its identification.

The diffraction intensities of a 0.36 mm diameter sphere of Fe₂Mo₃O₈ were measured at 298 K. Graphite-monochromatized Mo *K*α radiation generated at 50 kV and 8 mA was used in a *θ/2θ* scan with line-profile analysis (Grant & Gabe, 1978). A total of 1265 intensity measurements were made up to 2*θ* = 90°. They reduced to 969 unique reflections (including Friedel equivalents), of which 966 had *I*_{net} > 3σ(*I*_{net}) and were considered to be observed. The agreement ⟨*ΔI*⟩/⟨*I*⟩ of the measurements of the symmetry-related intensities was 1.1%. Only 41 of the 100 unique