Crystal structure of 3-methylrhodaninedecopper(I) iodide

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Abstract
The crystal structure of the copper(I) complex CuI(CH₃--N--CO--CH₂--S--CS) has been determined by a three-dimensional X-ray analysis. The monoclinic unit cell, space group \( P_{2_1}/c \), \( a = 4.195(1) \), \( b = 15.581(2) \), \( c = 13.885(2) \) \( \text{Å} \) and \( \beta = 114.9(1)^\circ \), contains four formula-units. Intensities were collected on an automatic diffractometer. The structural parameters were refined by full-matrix least-squares methods to a conventional \( R \) value of 0.07 for 1809 non-zero observed reflections.

In this complex, the copper atom is in tetrahedral coordination with three iodine atoms and the sulphur atom of the thiocarbonyl group of the ligand. The iodine atom is coordinated with three copper atoms. The Cu--I distances are 2.683(2), 2.627(2) and 2.665(2) \( \text{Å} \). The distances between neighbouring copper atoms are 3.008(3) and 2.960(3) \( \text{Å} \) and the corresponding Cu--I--Cu angles are 68.44(6) and 68.02(6)\( ^\circ \), suggesting weak copper-copper interactions in this complex.

Introduction
In a previous paper, the preparations and properties of rhodanine and 3-substituted rhodanine complexes of copper(I) were reported (Moers & Steggerda, 1968). From the properties of the copper complexes we proposed a polymeric structure for these complexes, and infrared spectra and nmr measurements indicated a coordination with the thiocarbonyl group of the ligand.

Polymeric copper(I) complexes are known in which thiourea and its derivatives act as ligands. The copper : ligand ratios are 1 : 2 in Cu(thiourea)₂ Cl (Spofford &
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Amma, 1968); 1:3 in Cu(thiourea)Cl (Okaya & Knobler, 1964) and 4:9 in Cu₄(thiourea)₉(ClO₄)₄ (Vranka & Amma, 1966). The present study describes the X-ray analysis of a polymeric copper(I) complex in which copper forms a 1:1 complex with the ligand 3-methylrhodanine:

\[ \begin{array}{c}
  \text{H}_3\text{C}^+ \\
  \text{N} \\
  \text{S} \\
  \text{O} \\
  \text{S} \\
  \text{CH}_2
\end{array} \]

In addition, this crystal structure determination is the first involving a complex with a rhodanine ligand.

**Experimental**

**Crystal data**

3-methylrhodaninecopper(I) iodide, CuI(C₄H₅NOS₂), \( FW = 337.67 \), crystallizes from ethanol with well-formed yellow needles elongated along \( a \). Weissenberg photographs showed that the crystals were monoclinic with space group \( P2_1/c \) (No. 14). From Pt-calibrated Weissenberg photographs around \( a \) and \( b \), using Ni-filtered CuK\( \alpha \) radiation (\( \lambda = 1.5418 \) \( \AA \)), application of a least-squares procedure yielded the unit cell dimensions:

\[ a = 4.195(1) \text{\( \AA \)}, \quad b = 15.581(2) \text{\( \AA \)}, \quad c = 13.885(2) \text{\( \AA \)}, \quad \beta = 114.9(1)\text{o}; \quad V_c = 823.1(5) \text{\( \AA \)}^3. \]

The calculated density is 2.72 g cm\(^{-3}\), with \( Z = 4 \). The measured density is 2.80 g cm\(^{-3}\) (pycknometric method). \( F(000) = 632 \). The linear absorption coefficient for molybdenum K\( \alpha \) radiation is \( \mu = 69.63 \text{\( cm \)}^{-1} \).

**Intensity data**

A crystal of approximately \( 0.06 \times 0.14 \times 0.34 \text{\( mm \)}^3 \) was mounted with the needle axis as rotation axis. Intensities were collected with an automatic Nonius diffractometer, using Zr-filtered Mo-radiation. The scan speed was 1.2°/min. After every 20 reflexions, a reference reflexion was measured to detect and allow corrections to be made for slow fluctuations in the primary beam. Of the 2680 attainable symmetry independent reflexions \( hkl \) (up to \( \sin \theta/\lambda = 0.80 \text{\( \AA \)}^{-1} \)), 1625 reflexions have been measured above background. Of the 2274 attainable symmetry related reflexions \( hkl \) (up to \( \sin \theta/\lambda = 0.70 \text{\( \AA \)}^{-1} \)), 1573 reflexions have been measured above background (a reflexion is considered ‘above background’ if its peak intensity exceeds an instrumentally fixed value set slightly above the average background). Absorption corrections were calculated according to the Busing & Levy (1957) procedure, using \( 8 \times 4 \times 10 \) volume components and 6 accurately located boundary planes (the absorption factors were in the range 1.4-1.8).

The two symmetry-related sets of reflexions were brought on the same scale and corrected for Lp factors. The disagreement factor for reflexions common in both sets is:

\[ R' = \frac{\sum |F_{hkl}|-|F_{hkl}|}{\sum \frac{1}{2}[|F_{hkl}| + |F_{hkl}|]} = 0.09. \]

After completion of the measurements, it became apparent that many reflexions were measured incorrectly because of malfunctioning of the instrument. At that