The structure was refined by full-matrix least squares using *SHELXTL-Plus* (Sheldrick, 1990). All non-H atoms were assigned anisotropic displacement parameters in the refinement. Data collection, all calculations and graphics were carried out using *SHELXTL-Plus*.

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Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71057 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1022]

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Single-Crystal Structure Refinement of Spinel-Type $CuCr_2Se_4$

I. Okońska-Kozlowska and J. Kopyczok

Silesian University, Institute of Chemistry, Szkolna 9, 40-007 Katowice, Poland

H. D. Lutz and Th. Stingl

Universität-GH-Siegen, Anorganische Chemie I, D-57068 Siegen, Germany

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Abstract

Chromium copper selenide $CuCr_2Se_4$ crystallizes in the normal spinel structure (space group $Fd\bar{3}m$). Copper and chromium are tetrahedrally and octahedrally coordinated in the cubic close packing of selenium atoms, respectively.

Comment

Hitherto structure determinations of spinel-type copper chromium selenide $CuCr_2Se_4$ have been performed by neutron powder diffraction studies (Colominas, 1967; Robbins, Lehmann & White, 1967). The phase relationships of the system $CuSe$–Ga_2Se_3–Cr_2Se_3 were investigated by Okońska-Kozlowska (1989). The growth of single crystals of spinel-type $CuCr_2Se_4$ and $(Cu,Ga)Cr_2Se_4$ and their electrical properties have been described (Okońska-Kozlowska, Kopyczok, Wokulska & Kammel, 1992). In order to compare the cation distribution of this compound with that of spinel-type copper gallium chromium selenide solid solutions we redetermined the crystal structure of $CuCr_2Se_4$ on the basis of single-crystal X-ray measurements.

The structure determination of $CuCr_2Se_4$ confirms the literature data. The standard deviations of the atomic coordinates and bond lengths are improved by an order of magnitude. Deviation from normal spinel cation distribution has not been observed.

Experimental

Crystal data

Cr_2CuSe_4
$M_r = 483.38$
Cubic
$Fd\bar{3}m$
$a = 10.337\ (6)$ Å
$V = 1104.4$ Å^3
$Z = 8$
$D_x = 5.81$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7093$ Å

Cell parameters from 25 reflections
$\theta = 17.9$–$22.8°$
$\mu = 33.58$ mm^{-1}
$T = 293$ K
Pyramid-like
$0.20 \times 0.14 \times 0.14$ mm
Black
Crystal source: chemical vapor transport of the elements

Data collection

Enraf–Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{min} = 0.709$, $T_{max} = 0.979$
862 measured reflections
197 independent reflections
186 observed reflections [$I>3\sigma(I)$]

$R_{int} = 0.081$
$\theta_{max} = 39.75°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 18$
3 standard reflections monitored every 200 reflections
frequency: 300 min
intensity variation: <1%

Refinement

Refinement on F
Final $R = 0.027$
$wR = 0.033$
$S = 0.91$

$\Delta\rho_{min} = -1.60$ e Å^{-3}
Extinction correction: Zachariasen (1967); Larson (1969)

186 reflections
10 parameters
$w = 1/\sigma^2F$
$(\Delta/\sigma)_{\max} \leq 0.001$
$\Delta\rho_{\max} = 1.56$ e Å^{-3}

Extinction coefficient: 0.034 (2)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional coordinates* (x,x,x) *and anisotropic displacement parameters* ($\times 10^{-2}$ Å^2) *with data of Colominas* (1967) *in square brackets*

$$u_{11} = u_{22} = u_{33},\ u_{12} = u_{13} = u_{23},\ T = \exp(-2\pi^2\sum_{i=1}^{3}\sum_{j=1}^{3} u_{ij}h_ih_ja_i^*a_j^*).$$

	Site	x	u_{11}	u_{12}
Cu	8(*a*) ($\bar{4}3m$)	1/8	0.48 (4) [0.5 (2)]	0.0
Cr	16(*d*) (.$\bar{3}m$)	1/2	0.29 (4) [0.5 (2)]	0.02 (3)
Se	32(*e*) (.3*m*)	0.25739 (5) [0.2576 (3)]	0.32 (3) [0.5 (2)]	−0.05 (1)

Table 2. *Geometric parameters* (Å, °)

Se—Cu	2.3703 (8)	Se—Se	3.8706 (1)
Se—Cr	2.5100 (4)	Cr—Cr	3.6553 (1)
Se—Se	3.4384 (1)	Cu—Cu	4.4758 (0)
Se—Se	3.6577 (1)		
Se—Cu—Se	109.47 (3)	Se—Cr—Se	86.46 (1)
Se—Cr—Se	180.0	Cu—Se—Cr	122.79 (1)
Se—Cr—Se	93.54 (1)	Cr—Se—Cr	93.43 (2)

Single crystals of $CuCr_2Se_4$ [as well as those of $(Cu,Ga)Cr_2Se_4$ mixed crystals] were grown by the chemical vapor transport method using $CrCl_3$ as transporting agent. Silica ampoules of 20 mm inner diameter and 150-180 mm length containing powdered substrates (CuSe, Ga_2Se_3, $CrCl_3$, Cu, Ga and Se) were evacuated to about 10^{-3} Pa and sealed. A horizontal zone furnace with melting zone temperatures of 1053-1253 K and crystallization zone temperatures of 935-1101 K was used. The samples were slowly cooled after 6 d of heating. Pyramidal monocrystals 0.2-4.0 mm in diameter were obtained. Unit-cell parameters were obtained by least squares. Data were corrected for Lorentz and polarization effects using *NRCVAX* (Gabe, Lee & Le Page, 1985). Empirical absorption corrections were applied using nine reflections in the range $13.7 < 2\theta < 49.2°$. Standard reflections were 084, 804 and 10,2,2. The structure was refined by full-matrix least-squares techniques including the positional and anisotropic thermal parameters, the extinction coefficient, and the scale factor ($N_p = 10$). Initial parameters for the atomic positions were taken from the literature (Colominas, 1967).

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71104 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1039]

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Structure of Bis[(*S*)-prolinamidato]-copper(II) Dihydrate

Giovanna Gasparri Fava, Marisa Belicchi Ferrari and Giorgio Pelosi

Istituto di Chimica Generale ed Inorganica, Università degli Studi di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy

Eriberto De Munari, Roberto Corradini, Rosangela Marchelli and Arnaldo Dossena

Istituto di Chimica Organica, Università degli Studi di Parma, Viale delle Scienze 78, I-43100 Parma, Italy

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Abstract

Crystals of bis[(*S*)-prolinamidato]copper(II) have been prepared and their structure determined by X-ray crystallography. The Cu coordination is tetrahedrally distorted square planar. An O atom of a molecule related by a twofold screw axis interacts weakly with Cu^{II}, serving as a bridging element to form a polymeric structure. A new chiral centre of (*S*) configuration is produced at the amino N atom on coordination to Cu^{II}.

Comment

Chiral discrimination of amino acids and derivatives in HPLC has been obtained by using copper(II) complexes of amino acids, according to a mechanism of ligand exchange [ligand exchange chromatography, LEC (Davankov, Navratil & Walton, 1988)]. (*S*)-Proline, in particular, has been selected as the chiral ligand on account of its rigid cyclic structure, either bound to the stationary phase (Davankov & Zolotarev, 1978) or added to the eluent associated to an ion-exchange resin (Hare & Gil-Av, 1979) or to a reversed-phase column (Gil-Av, Tishbee & Hare, 1980). As part of a general project aimed at