

- International Tables for X-ray Crystallography* (1959). Vol. II. Birmingham: Kynoch Press.
- KLESSINGER, M. (1966). *Theoretica Chim. Acta, Berlin*, **5**, 251.
- KÖNIG, W. (1922). *Ber. dtsh. chem. Ges.* **55**, 3297.
- KÖNIG, W. (1926). *J. prakt. Chem.* **112**, 1.
- KULPE, S., LEUPOLD, D. & DÄHNE, S. (1966a). *Angew. Chem.* **78**, 639.
- KULPE, S., LEUPOLD, D. & DÄHNE, S. (1966b). *Angew. Chem. Intern. Edit.* **5**, 599.
- KUTSCHABSKY, L. (1965). *Mber. dtsh. Akad. Wiss. Berlin*, **7**, 511.
- LEUPOLD, D. & DÄHNE, S. (1965). *Theoretica Chim. Acta, Berlin*, **3**, 1.
- TROTTER, J. (1960). *Acta Cryst.* **13**, 86.
- WALLENFELS, K. & DRABER, W. (1964). *Tetrahedron*, **20**, 1889.

Short Communications

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Acta Cryst. (1969). **B25**, 1417

The crystal structures of copper tetrammine complexes.* **B. Na₄[Cu(NH₃)₄][Cu(S₂O₃)₂].NH.** By B. MOROSIN, *Sandia Laboratories, Albuquerque, New Mexico 87115, U.S.A.* and ALLEN C. LARSON, *University Chemical Laboratory, Cambridge, England* and *Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544, U.S.A.*

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The room temperature crystal structure of tetrasodium tetramminecopper(II) di-catena-di- μ -thiosulphato-cuprate(I) monoammoniate has been re-examined with the use of previously published data. The large hole in the published structure has been shown to contain a molecule of ammonia. Additional refinement by the full-matrix least-squares method, which included an extinction correction, reduced R from 0.115 to 0.056.

This redetermination shows that the coordination about copper(II) is a tetragonally distorted octahedral arrangement with four ammonia molecules (1.99 Å) in a square planar arrangement and two more distant ammonia molecules (2.88 Å) in the remaining positions; however, there are no other significant positional differences with respect to the previously determined structure.

Introduction

Recently the crystal structures of $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{NH}_3)_4\text{SeO}_4$ (Morosin, 1969) have been determined. During discussion of the coordination about copper in those compounds, one of the authors suggested that the rather large hole in the $\text{Na}_4\{\text{Cu}(\text{NH}_3)_4\}\{\text{Cu}(\text{S}_2\text{O}_3)_2\}_2$ structure (Ferrari, Braibanti & Tiripicchio, 1966; hereafter FBT) might really be filled by a water molecule. This was consistent with the measured density ($d_m = 2.45 \text{ g.cm}^{-3}$; FBT) being larger than the calculated density ($d_x = 2.41 \text{ g.cm}^{-3}$ by FBT; d_x for hydrate is 2.46 g.cm^{-3}) and with an R value of 0.115 for intensity data measured by a microdensitometer. A three-dimensional difference synthesis using FBT's observed structure factors and positional and thermal parameters revealed a large nonspherical peak at the predicted position. The subsequent difference synthesis and full-matrix least-squares refinement confirmed the presence of an extra molecule in FBT's structural data; this extra entity is believed to be an ammonia rather than a water molecule.

Results

Full-matrix least-squares refinements were carried out on several models. These refinements used FBT's intensity data,

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their positional and thermal parameters (together with the initial oxygen (water) or nitrogen (ammonia) atom coordinates from the Fourier synthesis), neutral scattering factors (Cromer & Waber, 1965; spherical NH_3 scattering factors were kindly provided by Dr D. T. Cromer) and dispersion corrections (Cromer, 1965). An extinction correction was also included as a least-squares parameter (Larson, 1967). The function $\sum w(F_o - F_c)^2$ was minimized with unit weights for observed and zero weight for unobserved reflections.

Initially we suspected water to be the extra molecular entity which was responsible for the peak in our difference synthesis. Subsequently we found the initial crystallographic work on this compound (Ferrari, Cavalca & Coghi, 1952; hereafter FCC) yielded crystals for which chemical analysis indicated an extra molecule of ammonia. We believe such a crystal was accidentally selected for data collection by FBT. Hence Table 1, which summarizes our different refinements, includes models B , C and D in which an oxygen atom (water) as well as models E , F and G in which a nitrogen atom (spherical ammonia in E and F) are considered as the extra entity. In all cases in which an extinction correction was included, the thermal parameters on all atoms remain real; in agreement with FBT these values are rather large along the z axis and small in the xy plane. A similar ratio between B_{11} and B_{33} for the ammonia (or water) molecule is also found.

Table 1. Models used with FBT's intensity data*

A. FBT's composition with no water [O(3)] or ammonia (NH ₃) molecule	0.070
B. Including O(3) at (0,0, $\frac{1}{2}$) with anisotropic thermal parameters; for O(3), $B_{11}=6.91$ and $B_{33}=10.8 \text{ \AA}^2$	0.057
C. Including O(3) disordered at (0,0, z) with isotropic thermal parameter; for O(3), $z=0.463$ (13) and $B=6.97 \text{ \AA}^2$	0.057
D. Refinement with space group $I4$; $z=0.538$ and $B=6.58 \text{ \AA}^2$ for O(3) [†]	0.052
E. Including NH ₃ at (0,0, $\frac{1}{2}$) with anisotropic thermal parameters	0.056
F. Same as E, but with 'occupational' parameter, p , for NH ₃ ; for NH ₃ , $p=1.11$ (9), $B_{11}=5.29$ and $B_{33}=12.55 \text{ \AA}^2$	0.056
G. Same as F, but with nitrogen scattering factors; $p=1.37$ (11), $B_{11}=7.27$ and $B_{33}=14.71 \text{ \AA}^2$	0.056

* When no extinction correction was included, R values for A, B and C models are 0.105, 0.079 and 0.078 respectively; for several atoms thermal parameters converge to nonpositive definite values, though never exceeding 1σ below positive values.

[†] Values of positional parameters which differ from those for model C by more than 2σ (σ of model D) are S(2) with $z=0.5103$ (21) and O(2) with $z=0.4878$ (45).

Initially models C, in which a disordered oxygen atom is located off the mirror plane, and D, in which the space group is noncentrosymmetric, were considered for two reasons: (a) the high ratio B_{11}/B_{33} for most atoms in models A or B and (b) the frequent occurrence of unequal copper-ligand separations in the longer separations of octahedrally coordinated copper atoms such as found in Cu(NH₃)₄SO₄·H₂O, Cu(NH₃)₄SeO₄ (Morosin, 1969) and Cu(NO₃)₂·CH₃NO₂ (Duffin & Wallwork, 1966). However,

a choice based on significance tests suggested by Hamilton (1965) could not be made between models B or C since identical values of R were obtained. Interestingly, the non-centric refinement (model D) yielded a lower R value and, even with the larger number of unknown parameters (74 vs. 47) by Hamilton's criteria at a 99.5% confidence level, indicated that model D is to be preferred over B or C (though not with respect to E, F or G). However, the ratios B_{11}/B_{33} remained as large as before and the crystals were found by FBT not to exhibit piezoelectricity. When we eventually suspected the presence of ammonia rather than water, models E, F and G were considered. In models F and G we attempted to see if the data indicated only a partial occupation of an ammonia group by refining an additional parameter for that site. Our refinements indicate that an entire molecule is present. The positional and thermal parameters given in Table 2 are for model E, which appears to be the most reasonable choice based on the data available to us.

In order to determine if the peak at 0,0, $\frac{1}{2}$ might be spurious and really result from, in part, a mathematical artifact, we performed three-dimensional Fourier syntheses with a variety of coefficients as our input data. With a secondary extinction correction applied, the syntheses employed the following coefficients: F_o and $(F_o - F_c)$ on models A and B, $F_o^2 - F_c^2$ on models A and E, and $(F_o - F_c)^2$ on model A. All indicate the presence of the extra molecular entity at 0,0, $\frac{1}{2}$.

Fig. 1 shows the stereoscopic view of the structure of this compound. The ammonia molecule is easily accommodated in the large hole at 0,0, $\frac{1}{2}$. The only interatomic separations significantly different from FBT are those involving this ammonia molecule; these consist of Cu-NH₃ separations of 2.88 Å and of O(2)-NH₃ separations of 3.38 Å.

Table 2. Final positional and thermal coordinates

	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu ^{II}	0	0	0	0.61	B_{11}	3.68	0	0	0
Cu ^I	0	$\frac{1}{2}$	$\frac{1}{2}$	1.38	B_{11}	3.04	0	0	0
S(1)	0.1074 (2)	0.4182 (2)	$\frac{1}{2}$	0.77	0.69	2.45	-0.18	0	0
S(2)	0.0893 (2)	0.2709 (2)	$\frac{1}{2}$	0.54	0.62	1.94	0.03	0	0
O(1)	0.1379 (4)	0.2352 (4)	0.2894 (12)	1.88	1.45	3.31	-0.06	2.41	-1.30
O(2)	-0.0130 (5)	0.2444 (5)	$\frac{1}{2}$	0.77	0.67	2.75	-0.67	0	0
Na	0.2065 (3)	0.3314 (3)	0	1.92	1.18	3.01	-0.15	0	0
N	0.1391 (6)	0.0427 (6)	0	0.04	0.11	3.80	-0.13	0	0
NH ₃	0	0	$\frac{1}{2}$	4.58	B_{11}	10.76			

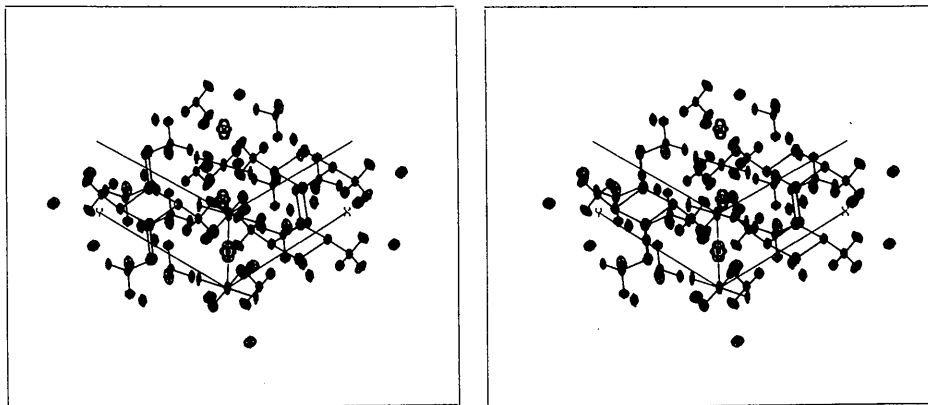


Fig. 1. Stereogram showing environment about the ammonia molecule in Na₄[Cu(NH₃)₄][Cu(S₂O₃)₂]₂.NH₃. The view is along the vector $[111]$; atoms included are those contained within $x = -0.35$ and 0.85 , $y = -0.35$ and 0.85 and $z = -0.25$ and 1.25 .

It should be emphasized that we have shown that an extra molecular entity is present only in the crystal data FBT's data arrived at the same conclusion as we (that there is present a molecular entity). In addition, their results (on crystals prepared by the method of FCC; Tomlinson, Hathaway, Billing & Nichols, 1969) are supported by polarized single-crystal electronic spectra and electron spin resonance spectra.

References

BRAIBANTI, A. (1968). Private communication.
CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 704.
DUFFIN, B. & WALLWORK, S. C. (1966). *Acta Cryst.* **20**, 210
FERRARI, A., BRAIBANTI, A. & TIRIPICCHIO, A. (1966). *Acta Cryst.* **21**, 605.
FERRARI, A., CAVALCA, L. & COGHI, L. (1952). *Gazz. Chim. Ital.* **82**, 385.
HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
HATHAWAY, B. J. & STEPHENS, F. (1968). Private communication.
LARSON, A. C. (1967). *Acta Cryst.* **23**, 664.
MOROSIN, B. (1969). *Acta Cryst.* **B25**, 19.
TOMLINSON, A. A. G., HATHAWAY, B. J., BILLING, D. E. & NICHOLS, P. (1969). *J. Chem. Soc.* In the press.

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Refinement of crystal structure of CoMo_2S_4 By K. ANZENHOFER and J. J. DE BOER, *Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N. V.), The Netherlands.*

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In continuation of a structure analysis of CoMo_2S_4 based on powder diffraction data, the authors have refined the structure from single-crystal data. The space group was determined as $C2/m$; the final R index was 8.7%. The distorted S-octahedra about the Co and Mo atoms are discussed in detail.

A structure analysis of CoMo_2S_4 based on powder data (van den Berg, 1968) revealed that the compound crystallizes in the monoclinic system with the space group assumed to be $C2/m$. Fig. 1 shows a projection of the structure along the b axis with the unshaded atoms at $y=0$ and the shaded atoms at $y=\frac{1}{2}$. In order to determine the space group, and to determine the positional parameters and the individual anisotropic temperature parameters accurately, we have carried out a complete refinement of the structure by use of single-crystal data.

Single crystals were prepared (by J. N. Helle of this laboratory) in a gas transport reaction with iodine as the carrier gas. The cell constants obtained from diffractometer measurements were:

$$\begin{aligned} a &= 13.091 \pm 0.002 \text{ \AA} \\ b &= 3.277 \pm 0.001 \\ c &= 5.897 \pm 0.001 \\ \beta &= 118.91 \pm 0.02^\circ. \end{aligned}$$

There are two structure units in a cell. The integrated intensities were measured on a Nonius automatic three-circle

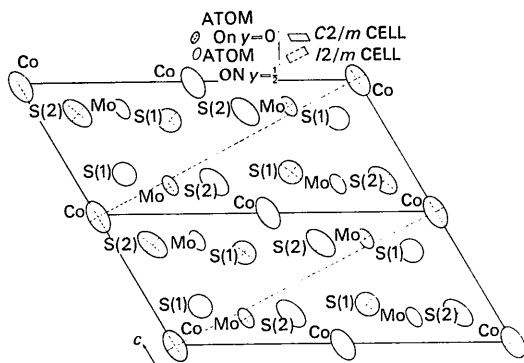


Fig. 1. CoMo_2S_4 projection along the b axis. The estimated vibration ellipsoids are shown.

diffractometer with Zr-filtered Mo $K\alpha$ radiation and the $\theta-2\theta$ scan method. The measurements were extended to $d_{\max} = 1.6 \text{ \AA}^{-1}$. A total of 594 reflexions proved to be of significant intensity.

The crystal used for diffractometry was plate-like with dimensions of $0.2 \times 0.15 \times 0.07 \text{ mm}$; it was rotated about the b axis, pointing in the direction of the 0.2 mm edge. An azimuthal scan of the 020 and 040 reflexion was carried

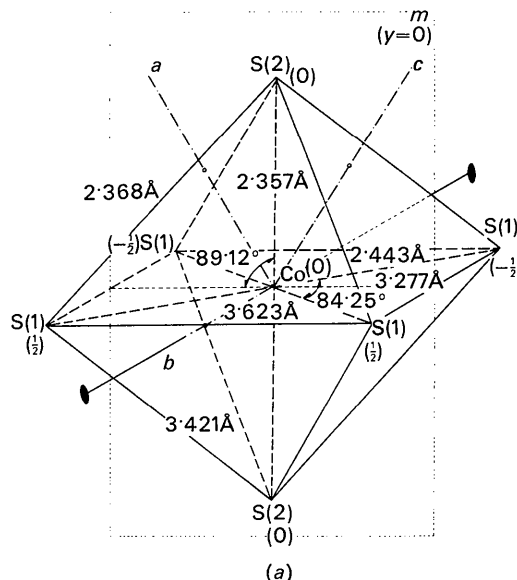


Fig. 2. (a) Octahedral environment of the Co atom at $(0,0,0)$. Local symmetry $2/m$, y coordinates are given in brackets. Mirror planes at $y=0$ (drawn) and at $y=+\frac{1}{2}$, $y=-\frac{1}{2}$. (b) Octahedral environment of the Mo atom at $(0.2569, 0, 0.2043)$. Mirror plane through the Mo, S(1c) and S(2c) atoms ($y=0$) and parallel to it at $y=+\frac{1}{2}$, $y=-\frac{1}{2}$. Local symmetry m , y coordinates are given in brackets.