

In a separate experiment cedrol (0.6 g) was oxidised with lead tetraacetate according to the procedure described above. The reaction mixture was hydrolysed in a mixture of acetic acid and water followed by a further oxidation in acetone solution with 8 N chromic acid in sulphuric acid (Jones reagent) as described for similar oxidations by Heusler *et al.*⁵ The product thus obtained was adsorbed from light petroleum on to a silica gel column (40 g). Ether (4 %) in light petroleum eluted 8,14-cedranoxide (0.3 g). Further elution with increasing concentrations of ether gave more polar fractions of which one (0.05 g, eluted by 15 % ether in light petroleum) was identified as 14,8-cedranolide III (TLC, IR, and GLC). This oily compound was further characterised by a lithium aluminium hydride reduction which yielded the crystalline 8S, 14-cedrandiol.³

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Crystal Structure of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$

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In connection with the problem of bonding of the nitrate group in copper(II) complexes, the structure of one of the hydrates, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ has been established. Some preliminary structural data

for this material have been published¹ and now the results of a complete X-ray analysis are reported briefly.

Crystals from two different sources were used for the X-ray studies: a) commercially available copper(II) nitrate with the formula $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, pro analysi (product of Lachema, Czechoslovakia), b) material obtained by crystallisation from nitric acid solution according to the reported preparation of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$.² (Found for a: Cu 27.10, 27.14; N 11.32, 11.47; H 2.28, 2.36. Calc. for $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$: Cu 26.30; N 11.60; H 2.50. Found for b: Cu 27.46, 27.56; N 11.09, 11.38; H 2.30, 2.30. Calc. for $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$: Cu 27.32; N 12.04; H 2.50).

Both kinds of crystals are hygroscopic or efflorescent, depending on the temperature and humidity of the air. Single crystals were coated with nitrocellulose to prevent decomposition during the X-ray investigation.

Crystal data for $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$: The crystals are monoclinic, with $a = 16.455 \pm 0.003$; $b = 4.941 \pm 0.001$; $c = 15.962 \pm 0.003$ Å, $\beta = 93.75 \pm 0.01^\circ$. The measured density at 23°C (by flotation) is 2.28 g/cm³. The calculated density, corresponding to 8 formula units per cell, is 2.37 g/cm³. Weissenberg photographs showed the following reflection conditions:

$$F_{hkl} \text{ were present only for } h+k+l=2n,$$

$$F_{hol} \text{ were present only for } h=2n, l=2n.$$

This leads to the space groups $I2/c$ or Ic . A transformation of the axes: $X=x$, $Y=y$, $Z=x-z$, leads to the International Tables space groups No. 15, $C2/c$ and No. 9, Cc , respectively.³ The solution of the structure of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ was based on the centrosymmetric $I2/c$ space group symmetry.

The three-dimensional intensities were recorded by equi-inclination Weissenberg photography with $\text{CuK}\alpha$ radiation and estimated photometrically. The hnl ($n=0-4$) data were collected. The structure has been solved by the heavy atom method on the basis of a three dimensional Patterson synthesis. The atomic positions, isotropic temperature parameters, and scale factors have been refined by the least squares full matrix method using the programs of Gantzel *et al.*⁴ The weighting scheme of Cruickshank⁵ was used. The R value, based on observed structure factors only, is 0.109. Differential Fourier synthesis did not show larger maxima of electron

density. The refined atomic positions and temperature coefficients are given in Table 1.

Table 1. Atomic parameters and temperature factors in the structure of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$. All atoms occupy the general positions (8) in space group $I2/c$, oxygen O_3 only is in a special position on the rotation axis (4).

Atoms	x	y	z	B (in \AA^2)
Cu	0.1261	0.0084	0.1139	0.74
O_1 (H_2O)	0.2415	0.0043	0.0893	1.38
O_2 (H_2O)	0.0108	0.0370	0.1406	1.60
O_3 (H_2O)	0.5000	0.0511	0.2500	1.32
O_4	0.1567	0.7485	0.2573	0.91
O_5	0.3707	0.0034	0.4208	0.91
O_6	0.4091	0.3382	-0.0045	1.11
O_7	0.1584	0.1784	0.2271	0.75
O_8	0.1916	-0.0118	0.3548	1.57
O_9	0.4227	-0.0520	0.0508	1.93
N_1	0.1690	-0.0104	0.2803	0.26
N_2	0.0984	0.5792	0.0140	0.29

The results of the crystal structure determinations can be summarised as follows:

1) The commercial product, formulated as $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and the hydrate $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, prepared according to Schreinemakers *et al.*,² yield the same diffraction pattern not only as far as the symmetry of the spots is concerned, but also with the visual appreciation of intensities, despite the fact that chemical analysis had revealed a slight difference in the composition of the two kinds of crystals.

2) The results of the structural analysis show the correct formula to be $\text{Cu}(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot 0.5\text{H}_2\text{O}$.

3) The copper atom in this substance has an unusual coordination (see Fig. 1). In one plane it is covalently coordinated by two water molecules (1.963 and 1.977 \AA) and two oxygen atoms of the nitrate groups (1.989 and 2.032 \AA). Three more oxygen atoms (from nitrate groups) are at slightly greater distances from the copper atom. Two (at 2.590 and 2.644 \AA) are on one side of the plane, while the third (2.590 \AA) is on the opposite side.

4) The nitrate groups in the structure of $\text{Cu}(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot 0.5\text{H}_2\text{O}$ are not equivalent. Both are bound by one stronger and one weaker bond to the copper atom, but one of them simultaneously creates a bridge to the next copper atom.

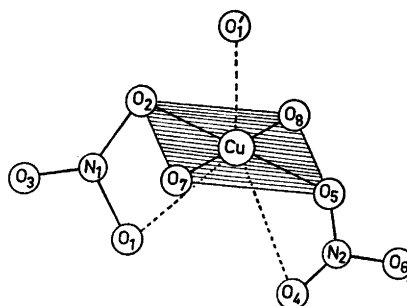


Fig. 1. A schematic representation of the atomic arrangement around the copper(II) atom in the crystal structure of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$.

5) Hydrogen bonding occurs between the nitrate groups and both types of water molecules, and between the ligand water molecules and the water of crystallisation.

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