Crystal Structure of the Copper Nitrate–Dinitrogen Tetroxide Adduct $Cu(NO_3)_2,N_2O_4$

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Summary The title compound consists of NO^+ ions and a polymeric anion composed of sheets of copper atoms linked by bridging nitrate ligands.

THE recent *X*-ray analysis of $Fe(NO_3)_3,1{\cdot}5N_2O_4$[1] has prompted renewed interest in dinitrogen tetroxide adducts of metal nitrates. It has been noted[2] that in some cases N_2O_4 forms strong adducts, of high thermal stability, which are most satisfactorily formulated as nitrosonium salts of nitrato-complexes, *e.g.* $NO^+[UO_2(NO_3)_3]^-$.[3] Other adducts show lower stability in that they release N_2O_4 readily on heating or *in vacuo*, *e.g.* $Co(NO_3)_2,2N_2O_4$[4] and have been thought to contain discrete molecules of N_2O_4 in the crystal lattice. The compound $Cu(NO_3)_2,N_2O_4$ is of particular interest since it is of intermediate stability,[5] and also the structure[6] and properties[7] of unsolvated copper(II) nitrate are well established.

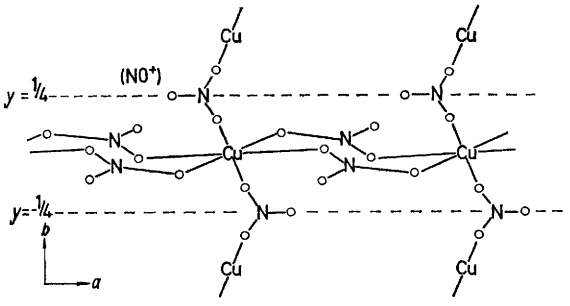

FIGURE. The structure of $Cu(NO_3)_2,N_2O_4$ projected onto the *ab* plane.

X-Ray data were obtained on a crystal grown in a sealed capillary tube and a small excess of liquid tetroxide ensured that no decomposition took place during the data collection. The crystals belong to the monoclinic space group $P2_1/m$, $Z = 2$, $a = 4{\cdot}690 \pm 0{\cdot}001$, $b = 11{\cdot}104 \pm 0{\cdot}002$, $c = 7{\cdot}127 \pm 0{\cdot}001$ Å, $\beta = 102{\cdot}13 \pm 0{\cdot}02°$. Intensity data on 856 independent reflections were collected on a four-circle diffractometer and the structure was solved by normal Patterson and Fourier methods. Refinement by full-matrix least-squares is proceeding; at present $R = 0{\cdot}063$ with all atoms varying anisotropically and all reflections at unit weight.

The essential features of the structure are shown in the Figure. The copper atoms lie on the centres of symmetry at (0,0,0) and $(0,\frac{1}{2},0)$ and one of the nitrate groups is bisected by the mirror plane at $y = \frac{1}{4}$ (see Figure). No molecular N_2O_4 is present in the lattice. Rather, copper atoms in the *a,b* plane are linked by bridging nitrate groups to form anionic polymeric sheets, charge balance being maintained by NO^+ ions which occupy available sites in the lattice at $y = \frac{1}{4}$. Chains of copper atoms along *a* are linked by bridging nitrate ligands in the *syn-anti*-mode.[8] These chains are linked sideways to copper atoms in adjacent chains, parallel to *a* and half way along *b*, by further bridging nitrate groups in the *anti-anti* conformation.[8] Thus each copper is co-ordinated to six oxygen atoms from six different nitrato-groups in a tetragonally distorted octahedral arrangement with four short (average 1·97 Å) and two long (2·61 Å) metal–oxygen bond distances.

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