Synthesis and *X*-Ray Crystal Structure of a Bis(2,2′-bipyridyl)-trithionatocopper(II) Complex

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Summary The compound obtained by treating bis(2,2′-bipyridyl)copper(II) chloride with potassium thiosulphate is shown to be a bis(2,2′-bipyridyl)trithionatocopper(II) complex; this is, to our knowledge, the only *X*-ray crystal structure of a trithionate complex to be determined.

During structural studies on the stabilization of the oxidation state two for copper in the presence of reducing agents, such as thiourea, iodide, *etc.*,[1–3] and in connection with an investigation on structural models involving the Cu^{I}–Cu^{II} redox couple in copper enzymes, $[Cu(bipy)_2Cl_2]$

(bipy = 2,2′-bipyridyl) was treated with potassium thiosulphate (molar ratio 1 : 1) in aqueous solution. A deep-blue crystalline compound, which showed analytical data and spectral properties inconsistent with the expected formula of a bipyridyl thiosulphate complex, was isolated. *X*-Ray analysis established the product to be bis(2,2′-bipyridyl)-trithionatocopper(II). As far as we know, the title compound is the only example known, from a structural point of view, of a metal complex containing a trithionate anion. The unexpected presence of the trithionate anion, instead of thiosulphate, could be attributed to a redox reaction involving Cu^{II} and the S^{-II} state of the thiosulphate.

Crystal data: $C_{20}H_{16}CuN_4S_3O_6$, orthorhombic, $a = 10{\cdot}29$ (2), $b = 13{\cdot}05(2)$, and $c = 16{\cdot}38(2)$ Å, $M = 568{\cdot}11$, $U = 2200{\cdot}5$ Å^3, $D_m = 1{\cdot}74$ g cm^{-3}, $D_c = 1{\cdot}71$ g cm^{-3}, $Z = 4$, μ (Cu-K_α) = 43·9 cm^{-1}, space group *Pbcn*. 2086 reflections were collected on an automated Siemens AED single-crystal diffractometer (Cu-K_α radiation, $\bar{\lambda} = 1{\cdot}5418$ Å). Excluding those with $I < 2\sigma(I)$, 1225 remained for the analysis and refinement, which were carried out by heavy-atom and least-squares methods, respectively. All the hydrogen atoms have been directly located from a final difference map which showed no relevant spurious peaks, indicating that the difference between D_m and D_c must be ascribed to experimental errors affecting the measured value. The present conventional *R* is 9·3%. The metal atom lies on a twofold symmetry axis, and the co-ordination around it is determined by the chelating behaviour of the two 2,2′-bipyridyl molecules which co-ordinate through their nitrogen atoms at the corners of a flattened tetrahedron. The two pyridine rings of the ligand are planar, but slightly twisted about the 2,2′ bond; the internal rotation angle is 7·5°. Bond distances and angles agree with the values usually found for these systems.[2,4] Also the trithionate anion is on a twofold axis. Its geometry is in agreement with those found for the pentathionate and hexathionate ions by Maroy.[5] The long interaction distance (2·82 Å) between the copper atom and two oxygen atoms of two trithionate groups (connected by the twofold axis) completes the metal co-ordination giving a distorted octahedral geometry. The trithionate anions are in bridging positions between adjacent metal atoms linking the co-ordination polyhedra in chains along [100].

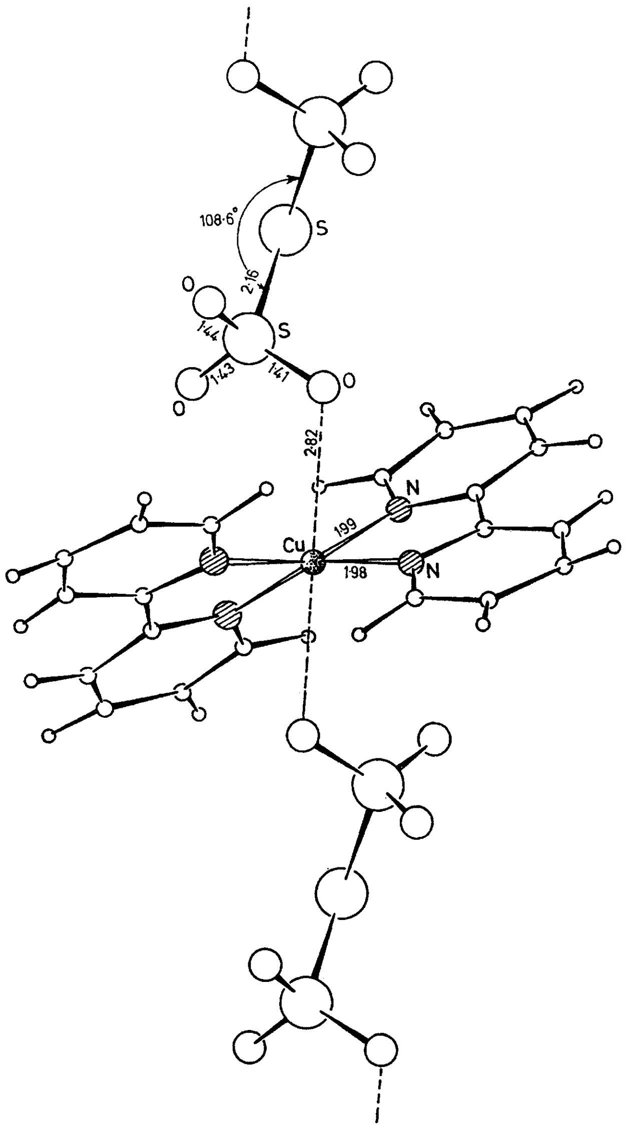

FIGURE. Projection of the structure of the bis(2,2′-bipyridyl)-trithionatocopper(II) on (010) showing the more important distances (Å). The mean e.s.d. is 0·01 Å.

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