Journal of Molecular Structure 1006 (2011) 375–378

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

A tri-nuclear oxygen centred (salicylaldoximato)copper(II) compound: The preparation and structure of $[\{\{Cu(saloxH)\}_3O\}_3H_{1.5}]\cdot Cl_{4.5}\cdot 12DMSO\cdot 1.83H_2O$ ☆

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ARTICLE INFO

Article history:
Received 29 July 2011
Received in revised form 15 September 2011
Accepted 16 September 2011
Available online 29 September 2011

Keywords:
Copper(II) compound
2-Hydroxy benzaldehyde oxime
Salicylaldoxime
Salicylaldoximato
Trinuclear compound
Crystal structure

ABSTRACT

Reaction of salycilaldoxime ($saloxH_2$) with copper(II) chloride in strongly alkaline methanol yields a sparingly soluble green product which recrystallised from DMSO as a solvate of composition $[\{\{Cu(saloxH)\}_3O\}_3H_{1.5}]\cdot Cl_{4.5}\cdot 12DMSO\cdot 1.83H_2O$. This has three independent planar, oxygen-centred, triangular cations, $[\{Cu(saloxH)\}_3O]$, in the asymmetric unit. The central oxygen atom is surrounded by three square-planar coordinated copper(II) ions, which are bonded to the central O-atom, the O_{phenol} and $N_{oximato}$ atoms of one $saloxH^-$ chelate and to the $O_{oximato}$ atom of the adjacent $saloxH^-$ ligand. These triangular cations are stacked, with alternating short {2.46(1) or 2.53(1) Å} and long {7.31(1) or 7.05(1) Å} central oxygen separations, with the closer pairs linked by a hydrogen bond. The 4.5 positive charges of the three cations of the asymmetric unit, $[\{Cu_3(saloxH)_3(O)_{1.5}(OH)_{1.5}\}_3)]^{4.5+}$ are balanced by 4.5 chloride ions. Two DMSO molecules lie between the wider spaced pairs of triangles, with their oxygen atoms weakly coordinated to copper(II) ions, with 10 further DMSO molecules and water molecules packed around and between the triangular cations.

1. Introduction

Salycilaldoxime (2-hydroxy benzaldehyde oxime, salicylaldehyde oxime, $saloxH_2$) is a classical reagent for the gravimetric determination of copper(II) and nickel(II). The sparingly water-soluble compound $[Cu(saloxH)_2]$ crystallizes as two polymorphs [1] which both have the *trans*-configuration with near co-planar square-planar $[Cu(saloxH)_2]$ molecules. For the β-polymorph these are stacked to produce chains with two weak axial contacts, with $Cu\cdots O_{phenol}$ = 2.66 Å [2,3]. For the α-polymorph they occur as pairs with one $Cu\cdots O$ = 2.66 Å contact [3,4]. Compounds with substituted salox ligands have related structures with a variety $Cu\cdots O_{phenol}$ interactions, which are often solvate dependent [5–8]. These all have mono-deprotonated salicylaldoximato moieties ($saloxH^-$), and it is generally assumed that the oxime, rather than the phenol function, is deprotonated. The separations between the phenol-O and oximato-O atoms of these compounds are generally indicative of hydrogen bonding.

It has been reported that water-insoluble $[Cu(saloxH)_2]$ is formed between pH 3 and 10, but for pH > 11 "the soluble cupric disalicylaldoxime anion forms, with $K_{diss.} = 1.7 \times 10^{-4}$, where K_{diss} = $[Cu^{2+}][salox^{2-}]^2/[\{Cu(salox)_2\}^{2-}]$". Similarly $[Ni(saloxH)_2]$ "forms in the pH range 6–12 and at pH > 12 the soluble nickelous disalicylaldoxime anion forms, with $K_{diss} = 6.4 \times 10^{-5}$" [9]. If compounds with doubly-deprotonated $salox^{2-}$ can be formed, as these figures suggest, then there is the potential for the formation of compounds with novel and potentially interesting properties, such as polynuclear chain polymers.

2. Results

We now report the preparation, and structure, of a copper(II) $saloxH^-$ compound, formed under strongly alkaline conditions, in an attempt to isolate a compound with the coordinated doubly deprotonated $salox^{2-}$ moiety. When salycilaldoxime was added to a solution of copper chloride hydrate a light, olive green coloured, precipitate formed. When KOH was added, this changed to dark green and a sparingly soluble dark green, extremely finely divided, product formed. This recrystallised from methanol as finely divided material, with crystals far too small for a structural study. Recrystallisation from DMSO gave lustrous green crystals, see Scheme 1.

Similar reactions occurred when copper(II) perchlorate hydrate or copper(II) nitrate hydrate were substituted for the copper(II) chloride. The sparingly soluble, finely divided, dark green products which formed in methanol crystallised from DMSO as dark green solvates. Similar sparingly soluble dark green products which formed with nickel(II) salts in alkaline methanol dissolved in DMSO but crystalline solvates were not isolated.

☆ Index page: Copper chloride reacts with salicyladoxime ($saloxH_2$) in basic methanol to form a green product which crystallizes from DMSO with oxygen-centred triangular cations, $[O\{Cu(saloxH))\}_3]^+$, which are stacked, with H-bonds between alternate pairs of oxygen atoms.

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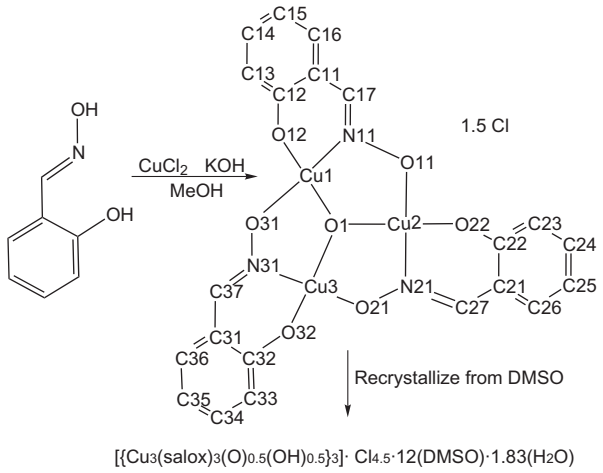
doi:10.1016/j.molstruc.2011.09.034



$[\{Cu_3(salox)_3(O)_{0.5}(OH)_{0.5}\}_3]\cdot Cl_{4.5}\cdot 12(DMSO)\cdot 1.83(H_2O)$

Scheme 1. Preparation of the saloxH$^-$ compound, showing atom labelling for cation 1.

The DMSO solvate of the saloxH$^-$ compound obtained from copper(II) chloride has been characterised by X-ray diffractometry, taking care to ensure no loss of the incorporated solvent. The asymmetric unit has an elementary composition of $C_{87}H_{125.17}Cl_{4.5}Cu_9N_9O_{34.83}S_9$, with eight asymmetric units in the unit cell. Each asymmetric unit contains three independent planar triangular cations. Each cation has a central oxygen atom, bonded to three copper(II) ions. Each copper(II) ion is in square-planar coordination by the central oxygen atom and by the oximato nitrogen and phenolic oxygen atoms of one salicylaldoximato chelate and by bridging coordination by the oximato oxygen atom of the adjacent salycilaldoximato chelate, see Scheme 1 and Fig. 1.

Each triangular cation has the overall composition $\{Cu_3(saloxH)_3O\}$; cation 1, includes central oxygen labelled O1 and Cu1, Cu2 and Cu3, cation 2 includes O2, Cu4, Cu5 and Cu6 and cation 3 includes O3, Cu7, Cu8 and Cu9. The atoms of the salicyaldoximato ligand bonded to Cu1 have labels: aromatic ring carbon C11–C16, aldehyde carbon C17, phenol oxygen O11, oxime nitrogen N12 and oximato oxygen O12 and similarly for the other salicylaldoximato ligands.

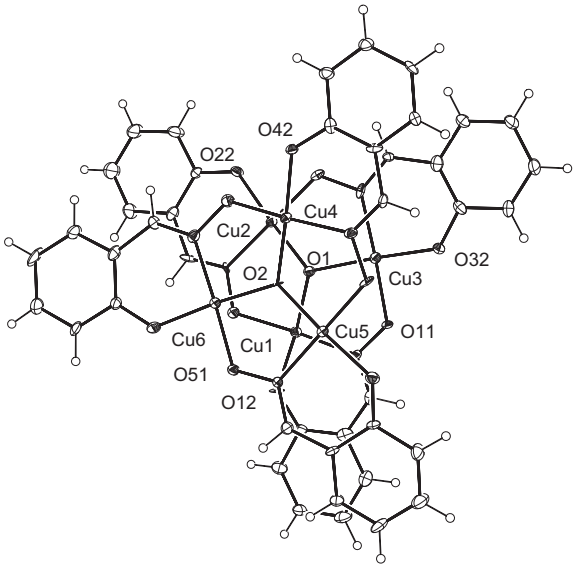


Fig. 1. Down-axial view of the cation pair including central atoms O1 and O2, with interleaved chloride ions, drawn [14] with displacement ellipsoids at 50% probability. Hydrogen atoms are shown as circles with arbitrary radius.

The planar triangular cations are "stacked like pancakes", with alternating sets of the three cations of the asymmetric unit reversed (symmetry operation A = $1-x, y, \frac{1}{2}-z$ relates cations 3 and 3^A and symmetry operation B = $\frac{1}{2}-x, 3/2-y, -z$ relates cations 1 and 1^B), see Fig. 3. Alternating short and long distances separate the central oxygen atoms of adjacent cations in the stacks {distances $O1\cdots O1^B = 7.31(1)$; $O1\cdots O2 = 2.532(9)$; $O2\cdots O3 = 7.047(9)$; $O3\cdots O3^A = 2.46(1)$ Å. The central oxygen atoms are approximately aligned, with angles $O1^B\cdots O1\cdots O2 = 170.6(3)°$; $O1\cdots O2\cdots O3 = 168.9(2)°$ and $O2\cdots O3\cdots O3^A = 171.6(1)°$.

The oxygen atoms of the closer pairs $O1\cdots O2$ and $O3\cdots O3^A$ are displaced from their respective Cu_3 planes towards each other: O1 towards O2 by 0.391(7); O2 towards O1 by 0.200(6); and O3 towards $O3^A$ by 0.316(6) Å, see Figs. 2 and 3.

It is probable that the oxygen atoms of the closer cation pairs are linked by a hydrogen bond. i.e. alternate central oxygen atoms are formally present as OH^- and as O^{2-} ions. The hydrogen-bonded pairs of triangular cations including $O1\cdots O2$ and $O3\cdots O3^A$ could be regarded as forming hexa-nuclear clusters.

The close cation pair including O3 and $O3^A$ are related by symmetry operation A, but there is no imposed symmetry on the close cation pair including O1 and O2, or on the individual triangular cations. The close pairs of triangular cations have their orientations reversed, so the N–O oxime bonds are arranged clockwise (looking from O1 to O3) for cations 1 and 3, counterclockwise for cations 2 and 3^B. The groups Cu–O···O–Cu (e.g. Cu1–O1···O2–Cu4) oriented towards the aromatic rings have torsion angles ca. 65°; the groups oriented towards the bridging oximato groups have torsion angles ca. 55°, see Fig. 2. Hydrogen atoms on the phenol or oxime functions were not located but the phenol and oximato oxygen atoms on adjacent ligands of each triangle are separated by ca. 2.6 Å, which is indicative of hydrogen bonding.

The set of three aromatic rings of each triangular cation are close to coplanar, with increasing displacement from this plane by the oximato nitrogen atoms, oximato oxygen atoms, copper(II) ions and central oxygen atom. Displacements of atoms from the planes defined by the atom groups {Cu1, Cu2, Cu3}, {Cu4, Cu5, Cu6} and {Cu7, Cu8, Cu9} are listed in Supplementary data. Irregularities in these displacements are largely related to the axial coordination of DMSO oxygen atoms to Cu1, Cu3 and Cu8 (below).

The means of significant bond lengths are: $Cu–O_{central} = 1.914$; $Cu–O_{phenol} = 1.911$; $Cu–N_{oximato} = 1.958$ and $Cu–O_{oximato} = 1.916$ Å (with s.u. of individual values 0.007 Å). The mean of the Cu–O–Cu angles is 117.4° (individual s.u. 0.3°). Values of selected bond lengths and angles are listed in Supplementary data. The small displacements of donor atoms and Cu atoms from the r.m.s. plane of the donor atoms (e.g. the plane defined by O1, O11, N12, O22 for Cu1) are listed in Supplementary data.

The three cations of the asymmetric unit have 1.5 O^{2-} and 1.5 OH^- ions, with overall 4.5 positive charges as $[\{\{Cu_3(saloxH)_3(O)\}_3(H)_{1.5}\}_3]^{4.5+}$. There are five Cl^- sites within the asymmetric unit, with half occupancy Cl5 on the plane $x = 0.5$, $z = 0.25$, resulting in occupancy of 4.5 chloride ions for the asymmetric unit, which balances the 4.5 positive charge on the cations.

The chloride ions are arranged in columns parallel with the cation stacks, lying between the benzene rings on the periphery of the cation stacks. Each chloride ion is approximately centrally located with respect to the close-paired triangular cations, approximately 3.5 Å from each of four copper(II) ions and approximately 2.7 Å from two oximato and two phenolic oxygen atoms, plus in some cases, DMSO oxygen atoms.

There are 12 DMSO molecules in the asymmetric unit, though there are 13 DMSO sites, with sites including S10 and S11 having half-occupancies. DMSO molecules lie in the wider gaps between cations 1 and 1^B and cations 2 and 3, with oxygen atoms weakly axially coordinated to copper(II) ions. The DMSO molecule including