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ORIGINAL PAPER

Single Crystal XRD Structure Determination and Analysis of Bis(2,9-Dimethyl-1,10-Phenanthroline-κ^2N,N') (Sulfato-κ^2O,O')Nickel(II), Hydrate ($NiNeo_2SO_4 \cdot H_2O$; Neo: 2,9-Dimethyl-1,10-Phenanthroline)

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Abstract The title compound is monomeric with a Ni(II) hexacoordinated center. The coordination sphere is formed with four nitrogens from two neocuproine molecules and two oxygens from a sulfate ion that acts as a bidentate ligand. A water molecule completes the formula with an important role in the stabilization of the structure through the formation of O_W–H···O_S bridges, in which it acts as a donor and interactions of the type C_{ar}–H···O_W and C_{Met}–H···O_W, where it is an acceptor group (W: water; S: sulfate; ar: arene; Met: methyl). The compound is monoclinic, space group $P2_1/c$ with $a = 14.4829(4)$ Å, $b = 14.4563(4)$ Å, $c = 12.1559(3)$ Å, $\beta = 94.407(1)°$, $V = 2{,}537.55(12)$ Å^3 and $Z = 4$. The structure was solved by direct methods with a conventional R (on F) = 0.0359 for 4841 reflexions with Fo $> 4\sigma$(Fo). Three levels of super-structural hierarchy can be identified in the crystal construction: (1) the primary structure corresponding to the molecular skeletons of their building blocks, the isolated complex itself and the water molecule, (2) an 1D supramolecular array that form chains through a non-covalent polymerization via interactions O_W–H···O_S, C_{ar}–H···O_W, C_{ar}–H···O_S and C_{Met}–H···O_W and (3) finally the 3D macroscopic conglomerate formed through inter-chains interactions C_{ar}–H···O_W, C_{ar}–H···O_S, C_{Met}–H···ar and offset stacked arene–arene.

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Experimental

Synthesis

The compound was obtained by direct mixing of a methanolic solution of neocuproine with an aqueous solution of nickel(II) sulfate hexahydrate in a 1:1 M ratio. After 2 weeks of slow evaporation blue blocks appeared suitable for diffraction measurements. All starting materials were reagent quality and used without further purification.

Elemental Analysis

The formulation of the compound was supported by elemental analysis (C, H, N) performed on a Carlo Erba EA 1108 instrument and, ultimately, by the structure resolution by single crystal X-ray diffraction.

Required (%): C 57.1; H 4.5; N 9.5.

Measured (%): C 57.4, H 4.4, N 9.1.

Structure Determination

A highly redundant data set was collected at 150 K on a Bruker Smart Apex diffractometer using a graphite monochromated Mo Kα source ($\lambda = 0.71073$ Å). Measurements yielded 5,569 independent reflections of which 4,841 were considered observed [$I > 2\sigma(I)$], with an internal consistency $R_{int} = 0.0253$. The structure resolution was achieved routinely by direct methods and difference Fourier. The structure was refined by least squares on

F^2, with anisotropic displacement parameters for non-H atoms. Hydrogen atoms unambiguously defined by the stereochemistry (C–H's) were placed at their calculated positions and allowed to ride into their host carbons both in coordinates as well as in thermal parameters. Those corresponding to aqua were located in a late Fourier map and refined without restrains. All calculations to solve and refine the structure and to obtain some derived results were carried out with the computer programs SHELXS97 [1], SHELXL97 [1] and SHELXTL/PC [1]. MERCURY [2] was used to draw molecular drawings and further derived results. Full use of the CCDC package was also made for searching in the CSD Database [3]. Pertinent results are given in Table 1.

CCDC 771683 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK, Fax: +44(0)1223-336033.

Results and Discussion

Note: since there is no general agreement on the limiting values of the geometric parameters that characterize C–H···A non-covalent bonding interactions, in which the electrostatic component predominates, it is convenient to consider values that lie among the most accepted ranges (see for example ref. [5–10]). In accordance with this, we use the following conditions while accepting a C–H···O/N geometry as a hydrogen bridge: C–H···A ≥ 110° and H···A ≤ vdW sum + 0.3 Å; intramolecular: donor and acceptor separated by >3 bonds.

$NiNeo_2SO_4{\cdot}H_2O$ is monomeric with a Ni(II) hexacoordinated center (Fig. 1). The coordination sphere is formed with four nitrogens from two neocuproine molecules and two oxygens from a sulfate ion that acts as a bidentate ligand, with metal–N/O distances between 2.080(2) Å (Ni1–N12) and 2.130(2) Å (Ni1–O1). The intramolecular non-covalent bonding interactions C(15)–H(15B)···O4, C(15)–H(15C)···O2 and C(31)–H(31A)···O3 help in the stabilization of the complex structure. A water molecule completes the formula with an important role in the stabilization of the structure through the formation of O_W–H···O_S bridges (in the sense of ref. [10]) (Table 2 and Fig. 2), in which it acts as a donor and interactions of the C_{ar}–H···O_W and C_{Met}–H···O_W types, where it is an acceptor group.

The coordination polyhedra is distorted because of the steric restrictions imposed by the three chelate ligands, with angles between 67.82(5)° (O1Ni1O2) and 104.34(6)° (N1Ni1N28) for those corresponding to the ideal value of

Table 1 Crystal and structure refinement data

Crystal data	
$C_{28}H_{30}N_4O_4S{\cdot}H_2O$	$V = 2537.55(12)$ Å
$M_r = 589.30$	$Z = 4$
Monoclinic, $P2_1/c$	Mo Kα radiation
$a = 14.4829(4)$ Å	$\mu = 0.896$ mm^{-1}
$b = 14.4563(4)$ Å	$T = 150(2)$ K
$c = 12.1559(3)$ Å	Blocks, blue
$\beta = 94.41(1)°$	0.20 × 0.14 × 0.12 mm^{-3}
Data collection	
Bruker SMART CCD area-detector diffractometer	
Absorption correction: multi-scan [4]	$R_{int} = 0.0253$
$T_{min} = 0.84$, $T_{max} = 0.90$	$\theta_{max} = 27.8°$
20,766 measured reflections	$h = -18$ to 18
5,569 independent reflections	$k = -17$ to 18
4841 reflections with $I > 2\sigma(I)$	$l = -15$ to 15
Refinement	
$R[F^2 > 2\sigma(F^2)] = 0.0359$	
$wR(F^2) = 0.1061$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.81$	
5,569 reflections	
376 parameters	$\Delta\rho_{max} = 1.04$ eÅ^{-3}
0 restraints	$\Delta\rho_{min} = -0.27$ eÅ^{-3}

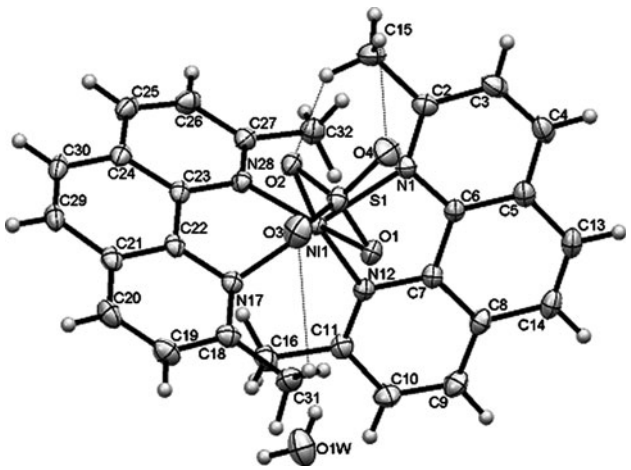

Fig. 1 ORTEP diagram of $NiNeo_2SO_4{\cdot}W$ with labelling except for H atoms for clarity. Thermal ellipsoids are drawn at the 50% probability level. Intramolecular H-bridge in *dotted line*

Table 2 Hydrogen-bridge and short-contact geometry (Å, °)

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1W···O3^{i}	0.85(3)	1.99(4)	2.837(2)	174(3)
O1–H2W···O4^{ii}	0.88(4)	1.89(4)	2.768(2)	175(3)

Symmetry codes: ^{i} x, −y + 1/2, z + 1/2; ^{ii} x, y + 1, z

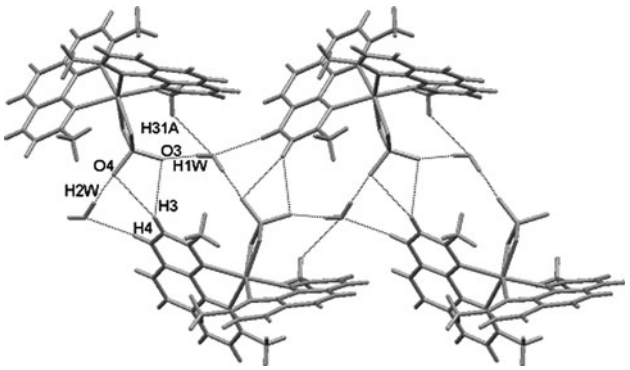

Fig. 2 Polymerization of the tectons $\cdots(\mathrm{Cplx}\cdots\mathrm{W^{i}})_n\cdots$ (i: x, y − 1, z) in the direction of **c** via interactions O_W–H···O_S, C_{ar}–H···O_W, C_{ar}–H···O_S and C_{Met}–H···O_W, viewed in the direction of **a**

90° and between 159.51(6) (O1Ni1N28) and 175.15(6) (N1Ni1N17) for those corresponding to the ideal value of 180°. However it fullfills the Valence Sum Rule of the Bond Valence model [11] with $\Sigma s_i = 1.94$ v.u. (*s*: bond valence; *i*: *i*th donor atom; ideal 2.00 v.u.) and the Vector Sum Postulate of the Vector Bond Valence model (VBV) [12] with $|\Sigma \mathbf{s_i}| = 0.07$ v.u. (bold type refer to a vector; ideal 0.00 v.u.). Also in accordance with the VBV model the sum of the angles between the three ligand resultant vectors equals 360.0°, the ideal value. Consequently, the coordination sphere is stable.

The complex molecule has a pseudo twofold axis passing through the sulfur atom and the metal centre. In order to establish how many similar complexes have a real twofold axis, we perform a search in the CSD v5.3 updated to February 2010 [3] of structures having: (1) a transition metal cation; (2) a bidentate sulfato; (3) two molecules of *N*,*N*′-bidentate bases (*N* and *N*′ being cyclic and bonded to three atoms) having the fragment N(sp^2)–C(sp^2)–C(sp^2)′–N(sp^2)′ in the chelate ring. Seven compounds out of eight retrieved [13], having very different organic ligands, metal centres and solvates, possess a twofold axis passing through the S atom and the metal centre, absent in our complex molecule.

Neocuproine molecules are not planar, with dihedral angles between neighbouring rings 1.6° and 3.7° in one molecule and 4.1° and 5.8° in the other. Both molecules exhibit a pronounced slant as measured by the angle between the coordination plane (N–Ni1–N′) and the mean plane subtended by N–$C_{central}$–$C_{central}$′–N′: 24.0° in one molecule and 25.7° in the other.

The anion shows some departures from a regular geometry, as expected since two oxygen are coordinated to the metal centre while the other two are not, but participate of strong H-bridges (Table 2). The coordination mode of the anion to $Ni^{(II)}$ is not a common one. In fact, a search in the CSD mentioned above of structures containing a $Ni^{(II)}$ centre and the SO_4^{2-} group, gave as result 84 structures of which only 3 contain the anion as a bidentate chelate: FOWDUR, TIYQUN and XIRKOZ.

Three levels of the super-structural hierarchy described by Fyfe and Stoddart [14] can be identified in the crystal construction. At a fundamental level is the primary structure corresponding to the molecular skeletons of its building blocks, the isolated complex itself and the water molecule. In a higher order there is a 1D supramolecular array in the form of a chain, formed through a non-covalent polymerization $\cdots(\mathrm{Cplx}\cdots\mathrm{W^{iii}})_n\cdots$ (Cplx: complex; iii: x, y − 1, z) in the direction of **c** of the tectons related by a glide plane via interactions O_W–H···O_S, C_{ar}–H···O_W, C_{ar}–H···O_S and C_{Met}–H···O_W (Fig. 2). In this supramolecular array, in which neighbouring tectons align in zig–zag, it is possible to differentiate a high-polarity region containing the water molecules, the anions and the metal nuclei, sandwiched by two identical low-polarity regions composed of molecules of neocuproine. Finally the 3D macroscopic conglomerate, the crystal, which is built through inter-chains non-covalent bonding interactions C_{ar}–H···O_W, C_{ar}–H···O_S, C_{Met}–H···ar and offset stacked arene–arene, in such a manner that the high-polarity region of a chain is entirely surrounded and H-bridged by the low-polarity regions of four neighbouring chains (Fig. 3).

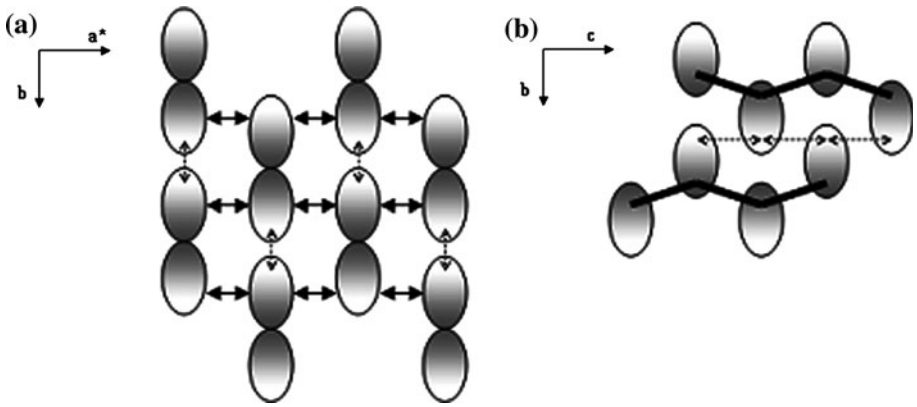

Fig. 3 Scheme showing the arrangement of the non-covalent polymer chains (not to scale). Each ellipse symbolizes a molecule, with the high-polarity region in *dark* and the low-polarity one in *light*. *Filled arrows* symbolize C_{ar}–H···O plus arene–arene interactions, *dotted ones* symbolize C_{Met}–H···arene interactions. **a** Chains viewed along them (in the direction of **c**). **b** Two chains fragments viewed in the direction of –**a***

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