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Preparation and Molecular Structure of Diaquabis-(2,6-dihydroxybenzoato)dioxouranium(VI) Octahydrate

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Metal complexes formed by dihydroxybenzoic acids could be of help in elucidating the metal binding properties of humic-like substances, which are of major importance in the environmental behavior of metals. In this connection, compounds obtained by reaction of 2,6-dihydroxybenzoic acid with some divalent metal ions have been isolated and fully characterised [1, 2]. Interestingly, the role of hydrogen bonding in favouring the formation of outer-sphere arrangements in the solid state has been shown by X-ray analysis.

Here we report preliminary structural data for the title compound which was obtained by reaction of 2,6-dihydroxybenzoic acid with uranyl acetate in aqueous solution.

Crystal data: monoclinic, space group $C2/m$, a = 6.704(3), b = 20.171(6), c = 9.454(4) Å, β = 99.57(3)°, V = 1260.6 Å^3, D_c = 1.99 g cm^{-3}, D_m = 2.03 g cm^{-3}, Z = 2, MoKα radiation, λ = 0.7107 Å. 1627 independent reflections were used for the structure determination and refinement (usual R = 0.033).

A view of the complex is reported in Fig. 1, together with the more significant bond distances and angles. The molecule consists of uranyl groups equatorially surrounded by two *trans* bidentate carboxylate groups and two oxygen atoms from water molecules. The remaining eight water molecules are hydrogen bonded to the rest of the structure to give intermolecular contacts between neighbouring units.

Also in this case, hydrogen bonding appears to be responsible for uncommon structural features of the complex. In fact, coordination of dioxouranium-(VI) by only two carboxylate groups is rather unusual [3] and is probably accounted for by the favourable involvement of an extended network of hydrogen bonds.

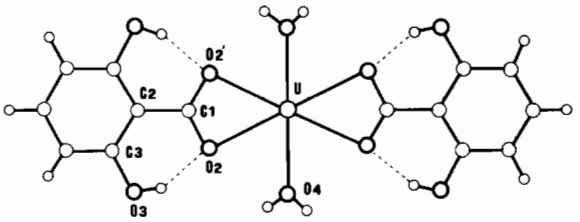

Fig. 1. View of the molecule along the O–U–O axis. The oxygen atoms of the uranyl group, O(1) and O(1)', are not shown. Important bond lengths and angles: U–O(1) 1.760 (0.006), U–O(2) 2.485 (0.003), U–O(4) 2.462 (0.006), C(1)–O(2) 1.275 (0.005), C(3)–O(3) 1.361 (0.006) Å; O(2)–U–O(2)' 51.8 (0.2), O(2)–C(1)–O(2)' 116.6 (0.7) deg.

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Structures and Reactivities of Copper(I) and Silver(I) Complexes of Potentially Quadridentate N_4 and N_2S_2 Donor Ligands

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In designing model complexes for the active sites in copper proteins it is important to know the influence of different hetero-atoms and conformational changes of the carbon skeleton on the chemical and physical properties of the metal centre.

We have investigated the structural properties of copper(I) and silver(I) complexes with potentially quadridentate N_4 and N_2S_2 donor ligand systems, schematically represented in Fig. 1, which have the connecting *(R)(S)*-1,2-diiminocyclohexane group in common.

From the reaction of the N_4 donor ligand with $M(O_3SCF_3)$ (M = Cu^I or Ag^I) we obtained dimeric

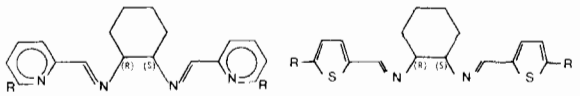

Fig. 1. The N_4 and N_2S_2 ligand system (R = H or Me).

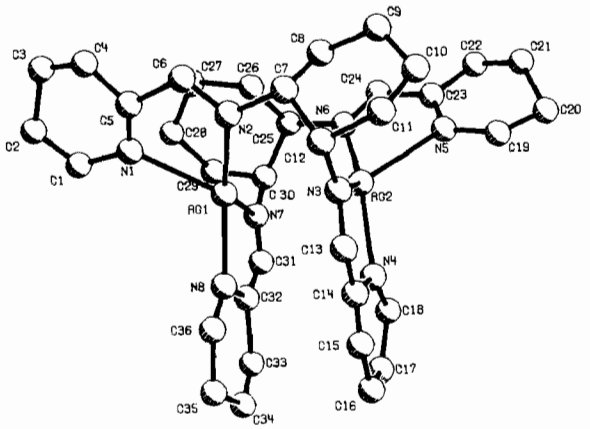

Fig. 2. PLUTO drawing of the $[Ag_2(N_4)_2]^{2+}$ unit.

$[M_2(N_4)_2]^{2+}$ $2O_3SCF_3^-$ complexes. The X-ray structure of the silver(I) complex showed that each ligand acts in a di-bidentate manner bridging the two metal centres (see Fig. 2). The silver ions have distorted tetrahedral geometries with each Ag^I centre taking part in two short Ag–N (2.25 Å) and two long Ag–N (2.43 Å) interactions. The N–Ag–N bond angle between the two short Ag–N bonds is *circa* 150° [1].

The copper(I) and silver(I) complexes are very stable and do not react further either with excess N_4 ligand or with H_2O, O_2 and CO. However, detailed ^1H studies have shown that inter- and intramolecular exchange (*e.g.* metal-ion or ligand exchange) occurs. These will be discussed. In contrast to these results reactions of the N_2S_2 ligand system with $M(O_3SCF_3)$ (M = Cu^I or Ag^I) give rise to two different types of complexes, *i.e.* a dimeric $[M_2(N_2S_2)_2]^{2+}2O_3SCF_3^-$ and a monomeric $[M(N_2S_2)_2]^+O_3SCF_3^-$ complex. According to ^1H and ^{109}Ag NMR data the dimeric complex has a structure similar to that found for the $[M_2(N_4)_2]^{2+}$ $2O_3SCF^{3-}$ complex. However, in the $[M_2(N_2S_2)_2]^{2+}$ dication the imine-N atoms of the N_2S_2 ligands have strong interactions with the metal centres, while the thiophene-S atoms coordinate only weakly with the metal-IB centre. This coordination behaviour is reflected by the reactivity of the copper(I) complex, which reacts rapidly with CO (ν_{CO} = 2092 cm^{-1}). An X-ray study is underway.

The X-ray structures of the mononuclear $[M(N_2S_2)_2]^+$ $O_3SCF_3^-$ complexes have been resolved for M = Cu^I and M = Ag^I to establish the exact molecular conformations and to test the validity of the assumption that copper(I) can be replaced by silver(I) with retention of the structural features [2]. As a result of the constraint of the N_2S_2 system, each ligand is primarily bonded to the metal centre (M = Cu or Ag) by one imine-N atom [N(1) and N(3)] with the remaining three hetero-atoms being held in close proximity to the metal centre (see Fig. 3: M = Cu). These complexes do not react with H_2O, O_2 and CO.

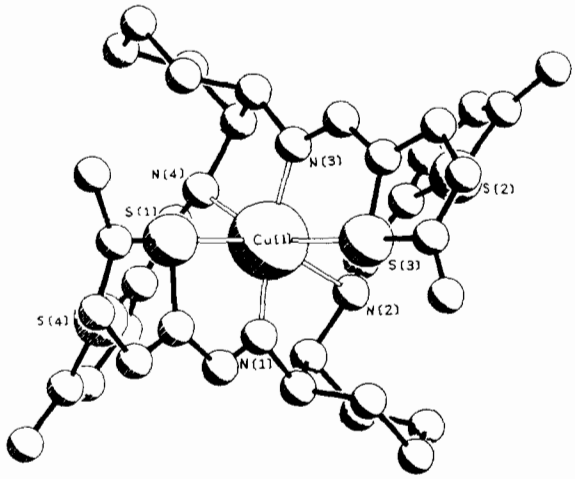

Fig. 3. PLUTO drawing of the $[Cu^I(N_2S_2)_2]^+$ cation. The $[Ag^I(N_2S_2)_2]^+O_3SF_3^-$ complex has a similar geometry.

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R14

Application of INEPT ^{109}Ag and ^{15}N NMR Spectroscopy for the Study of Metal–Ligand Interactions of Silver Analogues of Copper(I) Model Compounds

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Because of the presence of copper (in its reduced state) at active sites in proteins it has become very