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The Preparation of Sterically-crowded Macrocyclic Copper(II) Complexes from N,N′-di(*o*-benzoylphenyl)oxalodiamide: the X-ray Structure Determination of {5,12-diphenyl-18,19-dioxo-17,18,19,20-tetrahydrotribenzo[*e,i,m*][1,4,8,11]tetra-azacyclotetradecinato(2–)}dimethylformamidocopper(II)

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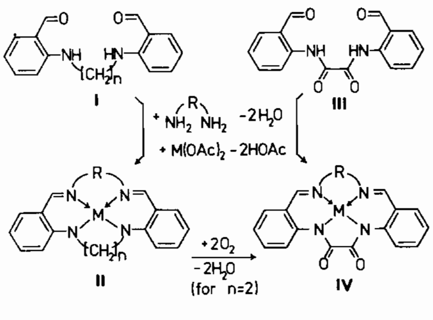
The use of N,N′-bis(2-aminobenzaldehyde) compounds I as precursors in the synthesis of metal complexes II of macrocyclic quadridentate imine ligands has been well documented [1, 2]. Recently [3] this approach was extended by using 2,2′-(oxalyldiimino)-bisbenzaldehyde III in condensation reactions with di-primary amines in the presence of metal(II) acetates. These gave (see Scheme) the neutral complexes IV, in which the deprotonated amide nitrogen atoms are co-ordinated to the metal ions. In certain cases the same oxamido complexes IV can be also obtained [4] by oxygenation of an ethane bridge between the anilino nitrogen atoms in the complexes II (see Scheme).



We report here the preparation of complexes related to IV which carry a phenyl substituent at the azomethine carbon atom, and are thus subject to severe steric constraints which are likely to reduce the planarity of the macrocycles and possibly force them to present non-regular geometries of their 'N_4^{2-}' donor sets to any complexed metal ion. The complexes V and VI were obtained by refluxing a solution of N,N′-di(*o*-benzoylphenyl)oxalodiamide [5], copper(II) acetate and 1,2-diaminoethane or 1,2-diaminobenzene in dimethylformamide under conditions similar to those described [3] for the preparation of the related aldimine complexes IV. After 48 hours the solutions were filtered, and crystals separated on cooling after addition of a small volume of methanol, giving V as its dihydrate and VI as a dimethylformamide adduct, as judged by infrared spectra and analytical data.

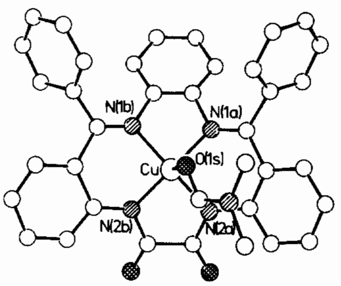
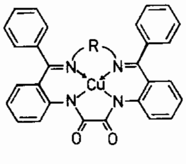


Fig. 1. The molecular structure of the dimethylformamide complex VI. Bond lengths to the Cu atom (Å) are: N(1a), 1.925(9); N(2a), 1.925(8); N(1b), 1.987(8); N(2b), 1.900(8); O(1s), 2.537(10); and angles subtended at the Cu atom by pairs of donor atoms are: N(1a), N(2a) 91.2(3); N(1a), N(1b) 86.8(4); N(1a), N(2b) 168.7(4); N(1a), O(1s) 86.0(4); N(2a), N(1b) 167.8(4); N(2a), N(2b) 88.1(3); N(2a), O(1s) 90.3(3); N(1b), N(2b) 91.6(3); N(1b), O(1s) 101.4(3); N(2b), O(1s) 105.3(4)°.



V R = -(CH$_2$)$_2$-
VI R = -(C$_6$H$_4$-o)-

Crystal data for VI: $C_{34}H_{22}N_4O_2Cu \cdot C_3H_7NO$, dark brown prisms from dmf, $M = 655.2$, triclinic, space group $P\bar{1}$, $a = 9.072(2)$, $b = 11.049(4)$, $c = 16.873(5)$ Å, $\alpha = 78.82(3)$, $\beta = 102.77(3)$, $\gamma = 107.78°$, $Z = 2$, $I/\sigma(I) > 3.0$, θ-range 3–25°, $R = 0.082$ for 2283 data obtained on a Philips PW1100 diffractometer with Mo-K_α radiation.

The structure determination shows that the copper atom in the complex VI has an approximately square-pyramidal coordination geometry (see Fig. 1). The apical donor atom is provided by the dimethylformamide oxygen atom, which is more weakly bonded than the basal nitrogen atoms.

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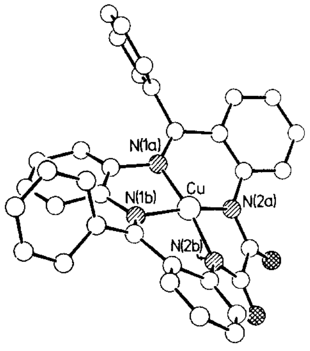

Fig. 2. The 'saddle-shaped' configuration of the chelate rings in VI. The co-ordinated dimethylformamide has been omitted for clarity.

The macrocyclic complex has an arrangement of its chelate rings which can be described as "saddle-shaped" [6]. The two 5-membered chelate rings containing the oxanilide nitrogens [N(2a) and N(2b)], and the *o*-phenylene nitrogen atoms [N(1a) and N(1b)], are tilted approximately equally (18° and 17° respectively) to the same side of the 'N_4' plane. The two *o*-anilino-imino six-membered chelate rings are bent to the other side of the 'N_4' plane by 13° and 9°. This conformation of the ligand increases the separation between the β-hydrogen atoms on the phenyl rings, and there are no particularly short intramolecular contacts between these hydrogen atoms (all > 2.5 Å).

Despite the "saddle-shape" of the macrocycle, its 'N_4^{2-}' donor set is very nearly planar (deviations of individual nitrogen atoms from the least squares plane are all less than 0.01 Å). It is therefore possible that other related phenylketimine macrocycles [7] may give complexes which have square planar, square pyramidal or *trans*-octahedral structures.

Acknowledgements

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