*Inorganica Chimica Acta,* 54 (1981) L17–L19
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# Properties and Structural Characterization of Mixed Complexes. The Copper(II) Complex with 2,2'-Bipyridyl and Oxydiacetate

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Received February 12, 1981

Structural investigations have been carried out on mixed ligand complexes of copper(II), due to their relevance as model compounds of metal-enzyme-substratum systems [1, 2].

Recently, we have considered of interest studying the way in which each ligand influences the formation of a typical structure, in solution [3] and in solid state [4], in the copper(II) ternary complexes. Now we report the structure of the mixed complex [Cu(bpy)(oda)$H_2O$]·$4H_2O$ (bpy = 2,2'-Bipyridyl; oda = oxydiacetate) and compare the coordination properties with those of analogous complex of ida (ida = iminodiacetate), previously investigated [4], in which the central donor atom of the tridentate ligand was a tetrahedral nitrogen atom.

## Experimental

Analytical grade oxydiacetic acid and 2,2'-Bypyridyl were employed to prepare the mixed complex [Cu(bpy)(oda)$H_2O$]·$4H_2O$. A stoichiometric amount of 2,2'-Bipyridyl in a water–ethanol mixture was added to the hot water solution containing the copper(II) oxydiacetate prepared by the procedure given by Whitlow and Davey [5]. The solution was then evaporated to obtain a microcrystalline powder the analytical results of which have been already reported [6]. This powder was dissolved in hot water and slowly evaporated at room temperature. After a week light blue crystals were obtained.

A Varian EPR-12 spectrometer equipped with a standard low temperature apparatus was used to obtain the e.p.r. spectra of the complex.

The crystals are triclinic with unit cell parameters $a$ = 14.069(9), $b$ = 8.898(5), $c$ = 11.078(7) Å, $\alpha$ = 114.1(1), $\beta$ = 52.0(2), $\gamma$ = 118.6(1)°, $D_{exp}$ = 1.54 g cm$^{-3}$, $D_{calc}$ = 1.55 g cm$^{-3}$ with $Z$ = 2 [Cu($C_{10}H_8N_2$)($C_4H_4O_5$)($H_2O$)]·$4H_2O$ units, space group $P1$. A total of 3091 independent reflexions, having

TABLE I. Bond Lengths (Å) and Angles (°) of Interest in [Cu(bpy)(oda)·$H_2O$]·$4H_2O$.

| | | | |
|---|---|---|---|
| a) Distances | | | |
| Cu–O(2) | 1.954(3) | O(4)–C(14) | 1.274(6) |
| Cu–O(3) | 2.458(4) | N(1)–C(1) | 1.347(4) |
| Cu–O(4) | 1.972(3) | C(1)–C(2) | 1.381(8) |
| Cu–(1) | 2.307(3) | C(2)–C(3) | 1.384(9) |
| Cu–N(1) | 2.024(4) | C(3)–C(4) | 1.382(5) |
| Cu–N(2) | 2.012(3) | C(4)–C(5) | 1.396(8) |
| O(2)–C(11) | 1.263(7) | C(5)–C(6) | 1.492(4) |
| O(1)–C(11) | 1.248(6) | C(6)–C(7) | 1.395(7) |
| C(11)–C(12) | 1.520(5) | C(7)–C(8) | 1.390(6) |
| C(12)–O(3) | 1.428(7) | C(8)–C(9) | 1.374(10) |
| O(3)–C(13) | 1.416(4) | C(9)–C(10) | 1.406(7) |
| C(13)–C(14) | 1.526(6) | N(2)–C(10) | 1.342(4) |
| O(5)–C(14) | 1.246(4) | N(2)–C(6) | 1.344(7) |
| b) Angles | | | |
| N(1)–Cu–O(2) | 174.8(1) | N(2)–Cu–W(1) | 92.7(1) |
| N(1)–Cu–O(3) | 105.2(1) | O(2)–Cu–O(3) | 76.2(1) |
| N(1)–Cu–O(4) | 92.2(1) | O(2)–Cu–O(4) | 93.0(1) |
| N(1)–Cu–N(2) | 80.7(1) | O(2)–Cu–W(1) | 86.5(1) |
| N(1)–Cu–W(1) | 93.1(2) | O(3)–Cu–O(4) | 75.8(1) |
| N(2)–Cu–O(2) | 94.2(7) | O(3)–Cu–W(1) | 159.1(1) |
| N(2)–Cu–O(3) | 100.0(1) | O(4)–Cu–W(1) | 93.9(1) |
| N(2)–Cu–O(4) | 170.6(1) | | |

TABLE II. E.P.R. Parameters.

| | $g_z$ | $g_y$ | $g_x$ | $A_z$ | $A_y$ | $A_x$ | $A_\parallel^N$ | $A_\perp^N$ |
|---|---|---|---|---|---|---|---|---|
| [Cu(bpy)(oda)][a] | 2.293(1) | 2.069(5) | 2.060(5) | 174(1) | 3(3) | 6(3) | 15(2) | 10(2) |
| | $g_\parallel$ | $g_\perp$ | | | | | | |
| [Cu(bpy)(oda)·$H_2O$]·$4H_2O$[b] | 2.29(1) | 2.08(1) | | | | | | |

[a]These values represent the best parameters obtained by a fitting procedure of the solution spectra [7]. [b]Values taken from the experimental spectra.

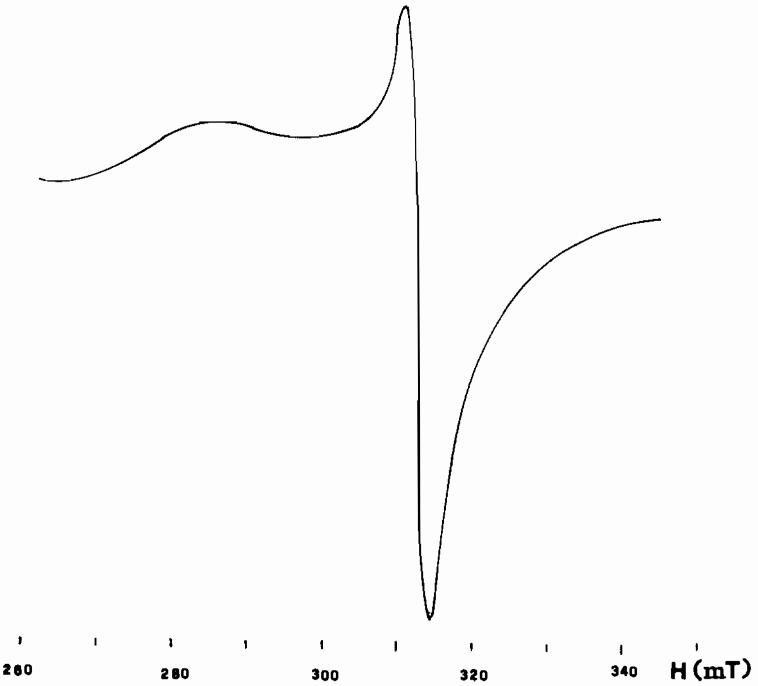

Fig. 1. X-band E.P.R. powder spectra of [Cu(bpy)(oda)$H_2O$]·$4H_2O$ at the temperature of 130 K.

$I > 3\sigma(I)$ and $\theta \leqslant 30°$, were collected on a SIEMENS AED diffractometer using Mo-K$\alpha$ radiation and corrected for Lorentz and polarization effects. No correction for absorption was applied ($\mu = 12.6\ \text{cl}^{-1}$, $0.01 < \mu\text{cryst} < 0.02$ cm). The structure was solved by Patterson and Fourier methods. The final anisotropic least-squares refinement including the contribution of hydrogen atoms, held constant, gave R = 0.041. Table I gives the important interatomic distances and angles.

## Results and Discussion

The powder of the [Cu(bpy)(oda)$H_2O$]·$4H_2O$ dissolved in a water–methanol mixture gave rise to spectra precisely identical to those obtained by mixing together the reagents in the same solvent mixture. The spectra have been already reported and discussed [7]. The powder spectrum of [Cu(bpy)(oda)$H_2O$]·$4H_2O$ is reported in Fig. 1 and the spin Hamiltonian parameters correlate fairly well with those obtained in solution as one can see by the values reported in Table II. These results suggest that the same particular arrangement of donor atoms is present both in solution and in solid state. The relatively small line-width ($\sigma < 40$ gauss) found in the solid state is probably due to a weak exchange interaction, however no half field lines could be detected in this study.

The crystals consist of [Cu(bpy)(oda)$H_2O$]·$4H_2O$ units, linked together with a complex set of hydrogen bonds involving the water molecules. The numbering scheme of the independent atoms is reported in Fig. 2.

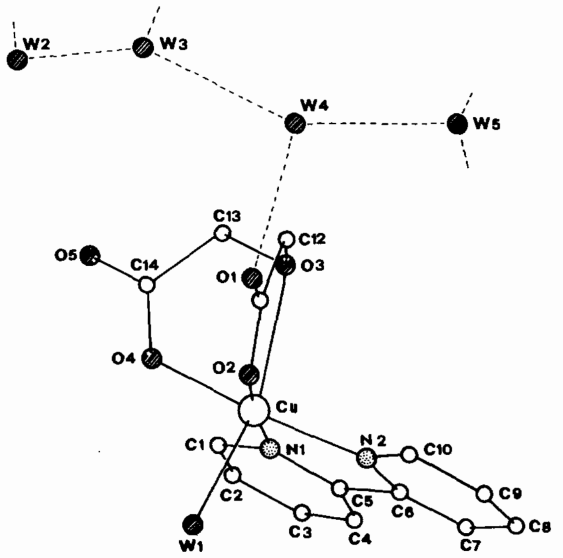

Fig. 2. A view of $[Cu(bpy)(oda)H_2O]\cdot 4H_2O$, together with the atom numbering scheme.

The coordination polyhedron around the copper atom may be described as a distorted octahedron, the two axial positions being occupied by the O(3) atom of the oda ligand [Cu–O(3), 2.458(4) Å] and by a water molecule [Cu–W(1), 2.307(3) Å]. The basal donors are coplanar within ±0.06 Å with a slight tetrahedral distortion. As expected the Cu–O equatorial bond distances are shorter [mean 1.963(3) Å] than the axial. The Cu–N bond lengths average to 2.018(4) Å. The large distortion of the O(3)–Cu–W(1) angle [159.1(1)°] appears to be a consequence of the coordination mode of the oda ligand.

The above results confirm the previous suggestion [6] that the title compound exhibits hexacoordination in the solid state, which is otherwise preserved in solution. In the analogous complex with the ida ligand, $[Cu(bpy)(ida)]\cdot 6H_2O$ [4], the metal atom has a distorted square-pyramidal stereochemistry both in solid state and in solution, although in the crystal the sixth position is occupied by an oxygen atom of a carboxylate group of another [Cu(bpy)(ida)] molecule [Cu···O, 3.008(4) Å]. Furthermore in the latter derivative the nitrogen atom of the ida ligand occupies a basal position, while in the oda analog the corresponding O(3) atom of the oda ligand, see Fig. 2, is in an axial position. In any case, as already observed in the ida derivative, the two chemically equivalent halves of the tridentate ligand (planar within ±0.05 and ±0.06 respectively) are bent along the Cu–O(3) direction making a dihedral angle of 108°, compared with that of 105° found in the ida analog.

## Acknowledgements

We wish to thank C.R.R.N.S.M. (Palermo) and University of Trieste for partial support.

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