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# The Crystal Structure and EPR g-Tensors of $[Cuterpy(ONO)OH_2]NO_2 \cdot H_2O$

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Recently we reported our structural and spectroscopical investigations of a series of compounds $CuterpyX_2 \cdot nH_2O$ [1]. In these complexes the five-fold coordinated $Cu^{2+}$-ions are bonded to three N-atoms of the nearly-planar terpyridine molecule. The two additional bonds which complete the approximately square pyramid are formed either by two $X^-$, as in $CuterpyCl_2 \cdot nH_2O$, or by one $X^-$ and one $H_2O$-molecule, as in $[Cuterpy(ONO)(OH_2)] \cdot H_2O$, whose structural details in connection with EPR g-tensors particularly are considered here.

## Experimental

The preparation of the compound has been described elsewhere [1]. The EPR spectra of the single crystals were taken with a VARIAN E15 spectrometer at 35 GHz with DPPH as internal standard. The coordinate transformation of laboratory axes to the main g-tensors and the molecular frame was performed by a computer program based on common procedures.

X-ray structure analysis of a well developed, columnar, dark-green single crystal of about 0.2 × 0.3 × 0.5 $mm^3$ (along *a*, *b*, and *c*) was made using a PHILIPS 4-circle diffractometer PW 1100 with MoKα radiation up to $\theta = 24°$ (graphite monochromator, $\omega/2\theta$ scan, scan width in $\theta = 1.2°$). Out of 2741 independent reflections 437 were unobserved, *i.e.* $F_o < F_{min} = \sigma(F)$. The following crystal data were determined: $CuC_{15}H_{15}N_5O_6$, space group $P\bar{1}$, $a = 13.508(6)$, $b = 8.761(4)$, $c = 8.177$ Å, $\alpha = 110.07(4)°$, $\beta = 86.06(4)°$, $\gamma = 105.31(4)°$, $Z = 2$, $V = 876.4$ Å$^3$, $D_x = 1.610$ g cm$^{-3}$.

The Cu position was determined by a Patterson synthesis, the other atoms (including H) by two Δ-Fourier syntheses. The isotropic refinement yielded R = 6.0%, by using anisotropic temperature factors (except for H) R dropped to 3.5% ($R_w$ = 4.3%) for the 2304 observed reflections. 123 out of the 437 unobserved reflections were calculated $F_c > F_{min}$ (but all $< 2F_{min}$). In the last cycles the parameters of the 11 H-atoms of the terpyridine group were held fixed at calculated positions (C–H = 1.00 Å). Individual weights and the atomic form factors of the International Tables (Vol. IV) were used. The final parameters are given in Table I, the resulting distances and angles in Fig. 1 and Table II.

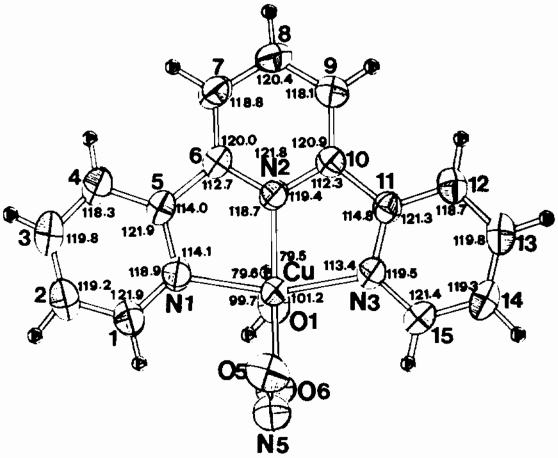

Fig. 1. Geometry of $Cuterpy(ONO)OH_2$ polyhedra in $[Cuterpy(ONO)OH_2]NO_2 \cdot H_2O$ (numbering of atoms as in Table I).

## Results and Discussion

The $Cu^{2+}$ ion is nearly planar-coordinated by the three N-atoms of the terpyridine molecule (Cu–N = 2.04, 1.94, and 2.05 Å) and one nitrite ligand (Cu–O6 = 1.97 Å). The approximately planar $CuN_3O$-entity is completed to square pyramid by an axial bond to one $H_2O$-molecule (Cu–O1 = 2.24 Å). This apical bond includes an angle of ≈6° with the normal of the $CuN_3O$-plane, and is significantly longer than the equatorial bonds.

As the angles N–Cu–N are found to amount to 79.5° only, the overall symmetry of the next nearest ligands deviates appreciably from point symmetry $C_{4v}$, but a pseudo mirror plane through Cu–N2–O6–O1 is obeyed. Thus, in agreement with $CuterpyCl_2$, we find two longer and one shorter Cu–N bond with the same average distance of 2.01 Å.

In contrast to $CuterpyCl_2$ with the Cu ion shifted by about 0.14 Å out of the $N_3Cl$-plane, we find the transition metal ion nearly in plane (deviations from best plane through $N_3O$: N1 0.12, N2 –0.13, N3 0.06, O6 –0.08, Cu –0.11 Å). The terpyridine molecule is folded by about 12° away from the O1 position (dihedral angle N1C1–5/N3C11–15 = 11.5°).

The terpy–Cu–O6 plane is nearly parallel to $(21\bar{2})$ (plane equation for the ring N2C6–10: $6.515x + 3.233y - 6.590z - 1.416 = 0$), only about 1.8 Å away from the center of symmetry in ½, 00, form-

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0020-1693/84/$3.00

TABLE I. Atomic Parameters of [Cuterpy(ONO)OH$_2$]·NO$_2$·H$_2$O, $C_{15}H_{15}CuN_5O_6$. $\sigma$ is the Averaged Absolute Standard Deviation of the Coordinates in $10^{-3}$ Å. The $B_{ik}$ (in Å$^2$) refer to the Expression $\exp(-\frac{1}{4}(B_{11}a^{*2}h^2 + \ldots + 2B_{23}b^*c^*kl))$.

| Atom | x | y | z | $\sigma$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ | $\sigma$(B) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 0.3238 | 0.1343 | 0.1965 | 0.4 | 3.13 | 2.76 | 3.21 | 0.62 | −0.75 | 0.64 | 0.02 |
| N1 | 0.4504 | 0.0754 | 0.2534 | 3 | 3.20 | 3.51 | 3.20 | 0.56 | −0.43 | 1.02 | 0.11 |
| C1 | 0.5281 | 0.1785 | 0.3652 | 4 | 3.52 | 3.81 | 3.29 | 0.22 | −0.60 | 0.95 | 0.15 |
| C2 | 0.6071 | 0.1220 | 0.4023 | 4 | 3.14 | 5.53 | 3.36 | 0.43 | −0.61 | 1.59 | 0.16 |
| C3 | 0.6055 | −0.0448 | 0.3264 | 4 | 3.19 | 5.94 | 4.01 | 1.42 | 0.00 | 2.22 | 0.17 |
| C4 | 0.5260 | −0.1534 | 0.2102 | 4 | 3.65 | 4.47 | 3.66 | 1.38 | 0.08 | 1.70 | 0.15 |
| C5 | 0.4499 | −0.0887 | 0.1761 | 3 | 3.06 | 3.19 | 2.85 | 0.70 | −0.06 | 1.19 | 0.13 |
| N2 | 0.3015 | −0.0952 | 0.0377 | 3 | 3.13 | 3.03 | 3.00 | 0.44 | −0.46 | 0.87 | 0.11 |
| C6 | 0.3631 | −0.1878 | 0.0518 | 3 | 3.15 | 3.10 | 3.12 | 0.66 | −0.06 | 1.08 | 0.13 |
| C7 | 0.3438 | −0.3563 | −0.0501 | 4 | 4.26 | 3.14 | 4.40 | 0.85 | −0.29 | 1.16 | 0.15 |
| C8 | 0.2607 | −0.4254 | −0.1655 | 4 | 4.99 | 2.91 | 4.50 | 0.34 | −0.90 | 0.43 | 0.17 |
| C9 | 0.1983 | −0.3274 | −0.1790 | 4 | 3.92 | 3.62 | 4.01 | −0.07 | −1.06 | 0.76 | 0.16 |
| C10 | 0.2220 | −0.1597 | −0.0749 | 3 | 3.02 | 3.53 | 3.05 | 0.37 | −0.39 | 1.05 | 0.13 |
| N3 | 0.2061 | 0.1221 | 0.0424 | 3 | 3.35 | 3.99 | 3.90 | 0.88 | −0.42 | 1.42 | 0.12 |
| C11 | 0.1698 | −0.0319 | −0.0770 | 3 | 3.00 | 3.78 | 3.34 | 0.44 | −0.44 | 1.28 | 0.14 |
| C12 | 0.0919 | −0.0623 | −0.1954 | 4 | 3.74 | 5.01 | 4.23 | 0.56 | −1.05 | 1.58 | 0.17 |
| C13 | 0.0513 | 0.0685 | −0.1892 | 4 | 3.91 | 6.34 | 5.33 | 1.37 | −0.88 | 2.56 | 0.19 |
| C14 | 0.0876 | 0.2238 | −0.0675 | 4 | 3.93 | 5.56 | 6.13 | 1.76 | −0.14 | 2.97 | 0.19 |
| C15 | 0.1659 | 0.2479 | 0.0479 | 4 | 3.88 | 4.09 | 4.84 | 1.30 | −0.32 | 1.72 | 0.16 |
| O1 | 0.2259 | 0.0729 | 0.4093 | 3 | 3.89 | 5.13 | 4.72 | 1.44 | 0.14 | 2.02 | 0.12 |
| H1a | 0.194 | −0.017 | 0.383 | 47 | 4.0 |  |  |  |  |  | 1.0 |
| H1b | 0.193 | 0.144 | 0.448 | 52 | 4.0 |  |  |  |  |  | 1.0 |
| O2 | 0.1028 | 0.2942 | 0.5040 | 3 | 5.09 | 5.26 | 6.27 | 1.74 | 0.18 | 1.26 | 0.14 |
| H2a | 0.116 | 0.354 | 0.447 | 47 | 5.0 |  |  |  |  |  | 1.0 |
| H2b | 0.054 | 0.302 | 0.569 | 61 | 6.0 |  |  |  |  |  | 1.0 |
| O3 | 0.0795 | −0.4653 | 0.3509 | 5 | 12.71 | 9.96 | 14.32 | 5.32 | 2.06 | 3.66 | 0.33 |
| N4 | 0.1411 | −0.3512 | 0.3341 | 5 | 10.87 | 6.04 | 10.20 | 2.40 | 1.56 | 1.95 | 0.29 |
| O4 | 0.0958 | −0.2419 | 0.3355 | 4 | 7.40 | 6.50 | 12.23 | 2.58 | 0.05 | 3.86 | 0.22 |
| O5 | 0.4264 | 0.4131 | 0.1442 | 3 | 6.73 | 4.92 | 6.01 | 1.78 | 0.90 | 1.87 | 0.15 |
| N5 | 0.4012 | 0.4720 | 0.2909 | 3 | 5.17 | 3.95 | 6.51 | 0.91 | −0.82 | 1.30 | 0.16 |
| O6 | 0.3483 | 0.3673 | 0.3582 | 3 | 5.84 | 4.06 | 4.68 | 0.97 | −0.21 | 0.75 | 0.13 |

TABLE II. a) Bond Lengths in [Cuterpy(ONO)OH$_2$]·NO$_2$·H$_2$O in Å. Distances Related by the Pseudo Mirror Plane are given in One Line of the First Two Columns.

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| Cu–N1 | 2.036(3) | Cu–N3 | 2.053(3) | O1–H1a | 0.75(3) | N4–O3 | 1.162(7) |
|  | Cu–N2 | 1.939(2) |  | O1)H1b | 0.82(4) | N4–O4 | 1.263(7) |
|  | Cu–O6 | 1.968(2) |  | H1a···O4 | 1.99(3) |  |  |
|  | Cu–O1 | 2.241(3) |  | H1b···O2 | 1.94(5) | N5–O5 | 1.197(4) |
| N1–C5 | 1.355(4) | N3–C11 | 1.352(4) | O1···O4 | 2.738(4) | N5–O6 | 1.265(4) |
| N1–C1 | 1.349(4) | N3–C15 | 1.338(5) | O1···O2 | 2.759(4) |  |  |
| C1–C2 | 1.379(6) | C15–C14 | 1.391(6) |  |  |  |  |
| C2–C3 | 1.373(6) | C14–C13 | 1.367(5) | O2–H2a | 0.79(5) |  |  |
| C3–C4 | 1.394(4) | C13–C12 | 1.380(7) | O2–H2b | 0.82(5) |  |  |
| C4–C5 | 1.384(6) | C12–C11 | 1.389(5) | H2a···O3″ | 2.17(5) |  |  |
| C5–C6 | 1.477(4) | C11–C10 | 1.477(6) | H2b···O4‴ | 2.12(5) |  |  |
|  |  |  |  | O2···O3″ | 2.885(7) |  |  |
| N2–C6 | 1.342(5) | N2–C10 | 1.333(4) | O2···O4‴ | 2.901(5) |  |  |
| C6–C7 | 1.387(4) | C9–C10 | 1.385(4) |  |  |  |  |
| C7–C8 | 1.382(5) | C8–C9 | 1.386(6) |  |  |  |  |

b) Some bond angles in °. For the angles within the Cu – terpy – ONO plane see Fig. 1.[a]

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| O1–Cu–N1 | 97.0(1) | Cu–O6–N5 | 112.1(2) | O1–H1a···O4 | 173(4) |

*(continued on facing page)*

TABLE II. *(continued)*

| | | | | | |
|---|---|---|---|---|---|
| O1–Cu–N3 | 96.7(1) | O5–N5–O6 | 115.6(3) | O1–H1b···O2 | 171(4) |
| O1–Cu–N2 | 96.3(1) | | | O2–H2a···O3″ | 151(4) |
| O1–Cu–O6 | 83.9(1) | O3–N4–O4 | 107.6(5) | O2–H2b···O4‴ | 159(4) |
| N1–Cu–N3 | 156.1(1) | | | H1a–O1–H1b | 114(3) |
| N2–Cu–O6 | 179.2(5) | | | H2a–O2–H2b | 117(5) |

[a] Numbering of atoms and bond angles (in °) in the Cu – terpy – ONO – $OH_2$ entity ($\sigma \approx 0.3–0.4°$). The thermal ellipsoids correspond to 50% probability (except for H).

ing double molecules with a distance of about 3.6 Å (*e.g.*, Cu···C4′ = 3.80, C1···C7′ = 3.57, C2···C10′ = 3.46, C2···C9′ = 3.55, C3···C10′ = 3.54, and C3···C11′ = 3.58 Å). By this packing the sixth site of the Cu-coordination is shielded within the crystal.

All four water protons are involved in hydrogen bonds. The first $H_2O$ molecule, directly bound to Cu, forms two almost linear H-bonds to $H_2$O2 (O1···O2 = 2.76 Å, angle at H1b = 171°) and to O4 of the non-complexed nitrite group (O1···O4 = 2.74 Å, ∢ at H1a = 171°), whereas $H_2$O2 forms weaker bonds to symmetry related nitrite groups (O2···O3″ = 2.89 Å, ∢ at H2a = 151°; O2···O4‴ = 2.90 Å, ∢ at H2b = 159°). There may exist rather weak C–H···O hydrogen bonds (5H···O and one H···N distances are shorter than 2.6 Å, the sum of the van der Waals' radii). The temperature factors of the 'free' $H_2O$ and $NO_2$ group are appreciably greater than those of the complexed groups.

Both $NO_2$ groups show different N–O distances. This agrees with the observation of two split vibrations $\gamma_{NO}$(as) = 1380, 1400 cm$^{-1}$ and $\gamma_{NO}$(sy) = 1125, 1185 cm$^{-1}$ in the IR-spectra.

As the two $CuN_3O_2$-polyhedra within one unit cell are anti-parallel, the single-crystal EPR-spectra can yield only one signal in all directions of the external magnetic field.

As we have two magnetically similar ions no exchange coupling can be detected from this experiment. The g-values at 300 and 77 K are found with $g_1$ = 2.237, $g_2$ = 2.079 and $g_3$ = 2.035(2) as orthorhombic. The direction cosines of main g-tensors are given in Table III in the molecular frame centered on the metal atom, with the y-axes in the Cu–N2 bond direction, the z-axes including an angle of ≈6° with the Cu–O1 distance, and the terpyridine molecule in the xy-plane. As expected, the maximal g-tensor points in the limit of experimental error (±5°) in direction of the longest distance Cu–$OH_2$ (2.24 Å) corresponding to the elongated square pyramidal geometry of the complex.

The others include angles of 30 and 60°, with the Cu–N2 direction. Thus the difference in the Cu–N1- and Cu–N3-directions is reflected in the shift of g-tensors in the xy-plane. The g-tensors as a physical entity establish the structurally determined different Cu–N1(3)-distances as bond strength differences, because otherwise a g-tensor should lie in the Cu–N2 direction. This is in contrast to Cuterpy-$Cl_2 \cdot H_2O$ where these distances are found equal with only one $g_\perp$-value (molecular oreintations not established).

TABLE III. Principal g Tensors and Directions for [Cuterpy-(ONO)$OH_2$]$NO_2 \cdot H_2O$ (Molecular Frame with Terpyridine in the xy-Plane and N2 in the y-Direction).

| g | direction cosines | | |
|---|---|---|---|
| | x | y | z |
| 2.237 | −0.020 | −0.050 | 0.999 |
| 2.079 | 0.861 | 0.506 | −0.041 |
| 2.035 | −0.508 | 0.859 | −0.028 |

The crystal structure of [Cuterpy(ONO)$OH_2$]$NO_2 \cdot H_2O$ results in a geometry of the $CuN_3O_2$-entity near to a squared pyramid. As the terpyridine ligand is very rigid if coordinated, deviations from this symmetry should have origins in special-bonding properties of the two additional ligands in the complex. A trend to more distortion in direction of the alternative symmetry for five-fold coordination (*i.e.* the trigonal bipyramid with the two x-atoms in the equatorial plane) should be expected for weaker bonded ligands X. This can be illustrated on the basis of the AO-model parametrization scheme where the energy difference between the $d^9$ configuration ground states of the two symmetries results in $E_0(D_{3h}) - E_0(C_{4v})$ – ¼ $e\sigma(X)$ with equal terpyridine- and X-atom $\sigma$-bonds. Thus, if $\sigma$-bond strength decreases the trigonal bipyramid should be the prefered configuration. This analysis should be established by consideration of complexes with weaker $\sigma$-bonded $Br^-$- and $I^-$-ligands where crystallographic data are not yet available.

## References

1 W. Henke, S. Kremer and D. Reinen, *Inorg. Chem., 22,* 2858 (1983).