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# Preparation and Crystal Structure of a Nickel(II)–Copper(II) Binuclear Chelate

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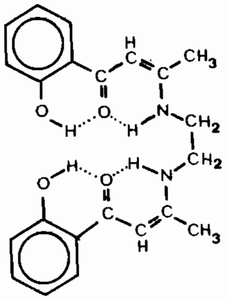
*The structure of the heterobinuclear complex NiCu(aapen)$H_2O$, where aapen is the tetranionic ligand derived from the condensation of 1,2-diaminoethane with* o*-acetoacetylphenol, has been determined from diffractometer data and refined to R = 6.3%. The crystals are monoclinic, $P2_1/c$, with a = 12.918(5), b = 8.481(4), c = 18.782(6) Å and β = 104.07(4)°; Z = 4. The ligand employed has two different coordination sets of atoms, $N_2O_2$ and $O_2O_2$, two oxygen atoms being common to both donor sets. In the complex the nickel atom is planarly retained in the inner $N_2O_2$ chamber (Ni–N = 1.84, 1.84 Å; Ni–O = 1.87, 1.88 Å) whilst the copper atom, incorporated in the outer $O_2O_2$ chamber, is five-coordinate, being axially bonded to a water molecule (Cu–O = 1.89, 1.89 Å; Cu–O (bridging) = 1.94, 1.96 Å; Cu–O($H_2O$) = 2.27 Å).*

## Introduction

Structurally interesting complexes can be obtained from 1,3,5-triketones or from their Schiff base derivatives, that is from ligands which can coordinate two metal ions through two sets of the same or of different donor atoms. The structure of $Cu_2$(aapen)$H_2O$ [1] and some studies [2–4] on mononuclear and binuclear complexes with parent ligands show that the organic moiety remains substantially planar when *d* metal ions of the first transition series are coordinated. However, as was found in mononuclear β-ketoamine uranyl complexes [5] and in the heterobinuclear $NiUO_2$(aapen)(dmso) [6] and $CuUO_2$(aapen)$(dmso)_2$ [7] introduction of very large ions such as $UO_2^{2+}$ in the $O_2O_2$ coordination chamber induces in the ligand and therefore in the $N_2O_2$ coordination set severe distortion from planarity which can cause unexpected coordination geometries for the metal ion bonded to these atoms.

This work reports the preparation and the crystal structure of the binuclear complex NiCu(aapen)$H_2O$. The Schiff base ligand $H_4$aapen (1) ($H_4$aapen = 3,8-dimethyl-1,10-di(*o*-hydroxyphenyl)-4,7-diazadeca-2,8-diene-1,10-dione) was obtained by condensation of 1,2-diaminoethane and *o*-acetoacetylphenol; it is a



$H_4$aapen (1)

potentially tetranionic ligand and contains two nitrogen and four oxygen donor atoms.

## Experimental

The ligand $H_4$aapen was obtained by condensation of *o*-acetoacetylphenol, prepared by the Wittig method [8], and ethylenediamine in MeOH. The mononuclear Ni($H_2$aapen) was prepared by reaction of stoichiometric amounts of $Ni(CH_3COO)_2 4H_2O$ and $H_4$aapen in hot 95% MeOH. The mononuclear complex was isolated by filtration and dried *in vacuo* (Found: C, 61.0; H, 5.3; N, 6.7; $C_{22}H_{22}N_2O_4Ni$ calcd.: C, 60.4; H, 5.0; N, 6.4%), In order to prepare the binuclear NiCu(aapen) complex Ni($H_2$aapen) (1 mmol) was dissolved in pyridine (30 ml). LiOH (2 mmol) in MeOH (10 ml) was added and, after 10 minutes, $Cu(CH_3COO)_2 4H_2O$ (1 mmol) in pyridine (5 ml) was added. The green solution was stirred under reflux for *ca.* 4 h. The pyridine was removed under reduced pressure and the residue treated with hot methanol; the hot suspension was filtered and the precipitate washed with methanol and dried over silica gel (Found C, 53.1; H, 4.2; N, 5.8; Ni, 11.6; Cu, 13.0. $C_{22}H_{20}N_2O_4NiCu$ calcd.: C, 53.0; H, 4.0; N, 5.6; Ni, 11.8; Cu, 12.7%). The binuclear complex was dissolved in hot chemical

TABLE I. Crystal Data for NiCu(aapen)$H_2O$.

| | |
|---|---|
| $C_{22}H_{22}O_5N_2NiCu$ | F.W. 516.2 |
| Crystal description | green prisms |
| Systematic absences | h0l  l ≠ 2n |
| | 0k0  k ≠ 2n |
| System | monoclinic |
| Space group | $P2_1/c\ (C_{2h}^5)$ |
| General positions | ±(x, y, z; x, ½ − y, ½ + z) |
| Cell dimensions | $a$ = 12.918(5) A |
| | $b$ = 8.481(4) A |
| | $c$ = 18.782(6) A |
| | $\beta$ = 104.07(4)° |
| Volume | 1996 $A^3$ |
| Density | observed 1.71 g $cm^{-3}$ (flotation) |
| | calculated 1.72 g $cm^{-3}$ |
| $\mu$(MoK$\alpha$) | 22 $cm^{-1}$ |

TABLE II. Final Coordinates ($\times 10^4$) for Atoms, with Estimated Standard Deviations.

| | | | |
|---|---|---|---|
| Cu | 4762(1) | 4449(2) | 3512(1) |
| Ni | 4574(1) | 2671(2) | 4813(1) |
| O(1) | 3694(6) | 5480(13) | 2796(5) |
| O(2) | 3677(8) | 3469(12) | 3941(5) |
| O(3) | 5627(7) | 3582(12) | 4417(5) |
| O(4) | 5915(7) | 5638(13) | 3344(5) |
| O(5) | 5013(7) | 2221(11) | 2909(5) |
| N(1) | 5513(10) | 1892(14) | 5638(6) |
| N(2) | 3488(10) | 1759(13) | 5142(6) |
| C(1) | 6526(13) | 2033(18) | 5804(7) |
| C(2) | 7204(13) | 1259(20) | 6490(8) |
| C(3) | 7110(14) | 2936(17) | 5376(8) |
| C(4) | 6674(10) | 3572(17) | 4704(7) |
| C(5) | 7334(11) | 4334(17) | 4263(7) |
| C(6) | 6924(10) | 5271(16) | 3628(7) |
| C(7) | 7665(12) | 5965(23) | 3236(8) |
| C(8) | 8787(12) | 5742(21) | 3495(9) |
| C(9) | 9150(13) | 4776(19) | 4092(9) |
| C(10) | 8411(10) | 4083(17) | 4464(8) |
| C(11) | 2475(13) | 1912(17) | 4820(8) |
| C(12) | 1625(13) | 1106(19) | 5155(8) |
| C(13) | 2023(12) | 2745(17) | 4154(8) |
| C(14) | 2638(12) | 3474(16) | 3738(7) |
| C(15) | 2144(10) | 4262(16) | 3049(6) |
| C(16) | 2709(10) | 5237(16) | 2658(7) |
| C(17) | 2094(11) | 5966(17) | 1985(7) |
| C(18) | 1015(11) | 5823(19) | 1745(7) |
| C(19) | 423(13) | 4849(23) | 2133(9) |
| C(20) | 1004(11) | 4028(22) | 2757(8) |
| C(21) | 5035(13) | 954(20) | 6137(8) |
| C(22) | 3826(12) | 849(15) | 5827(7) |

Anisotropic Thermal Parameters ($\times 10^3$) in the form: exp$[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

TABLE II. *(continued)*

| | | | | | | |
|---|---|---|---|---|---|---|
| Cu | 38 | 38 | 43 | 2 | 7 | 9 |
| Ni | 46 | 31 | 26 | 1 | 8 | 2 |
| O(1) | 35 | 60 | 38 | –1 | 2 | 25 |
| O(2) | 32 | 52 | 43 | –3 | 13 | 7 |
| O(3) | 35 | 54 | 37 | 13 | 6 | 11 |
| O(4) | 36 | 52 | 50 | –10 | 4 | 16 |
| O(5) | 47 | 59 | 40 | –4 | 13 | –14 |
| N(1) | 45 | 40 | 37 | 12 | 0 | –5 |
| N(2) | 54 | 35 | 22 | 13 | 5 | 6 |
| C(1) | 69 | 37 | 21 | 13 | –1 | –7 |
| C(2) | 73 | 49 | 35 | 21 | –16 | 5 |
| C(3) | 82 | 32 | 43 | 14 | 20 | 2 |
| C(4) | 31 | 32 | 29 | –1 | 0 | –9 |
| C(5) | 50 | 30 | 36 | 5 | –6 | –18 |
| C(6) | 38 | 26 | 42 | –24 | 6 | –11 |
| C(7) | 50 | 96 | 46 | –22 | 8 | –14 |
| C(8) | 50 | 58 | 77 | –5 | 14 | –24 |
| C(9) | 64 | 44 | 68 | –7 | 15 | –9 |
| C(10) | 30 | 45 | 56 | 4 | 9 | –15 |
| C(11) | 73 | 36 | 37 | –15 | 24 | 2 |
| C(12) | 69 | 57 | 55 | –24 | 33 | 3 |
| C(13) | 59 | 35 | 49 | 6 | 32 | 6 |
| C(14) | 59 | 24 | 30 | –2 | 27 | 2 |
| C(15) | 39 | 27 | 30 | 0 | 18 | –11 |
| C(16) | 36 | 36 | 34 | 17 | 0 | –8 |
| C(17) | 42 | 44 | 36 | 18 | –8 | –12 |
| C(18) | 51 | 66 | 20 | 22 | –7 | 1 |
| C(19) | 61 | 87 | 46 | 2 | –6 | 1 |
| C(20) | 43 | 91 | 47 | 8 | 8 | 15 |
| C(21) | 77 | 62 | 42 | –7 | 42 | 18 |
| C(22) | 60 | 25 | 51 | 9 | 21 | 24 |

grade dimethylsulphoxide and after three weeks crystals suitable for X-ray work were obtained. The compound could be formulated as NiCu(aapen)$H_2O$.

A well formed prismatic single crystal of approximate dimensions 0.10 × 0.10 × 0.15 mm was mounted on a glass fiber with epoxy adhesive. All the X-ray experimental work was performed using a Philips PW 1100 single crystal diffractometer with graphite monochromated MoK$\alpha$ radiation ($\lambda$ = 0.7107 Å). The unit cell parameters were obtained by a least-squares refinement of 25 angular settings carefully determined. Crystal data are summarized in Table I. A total of 3264 reflections were scanned within $2° < \theta < 25°$ with a scan rate of 2° in $2\theta$ $min^{-1}$. Of these, only 1627 unique reflections which obeyed the condition $F^2 > 3\sigma(F^2)$ were used in subsequent calculations. Two standard reflections, measured at intervals of 100, were constant within counting statistics. All data were corrected for Lp but not for absorption. The asymmetric unit comprises one binuclear molecule. Apart from small differences in the cell parameters, crystal data show that the compound is isomorphous with $Cu_2$(aapen)-$H_2O$. Therefore the coordinates of this were assumed as starting coordinates for NiCu(aapen)$H_2O$. Struc-

TABLE III. Bond Distances (A) with Estimated Standard Deviations.

| | | | |
|---|---|---|---|
| *Coordination* | | | |
| Cu–O(1) | 1.89(1) | Ni–O(2) | 1.88(1) |
| Cu–O(2) | 1.96(1) | Ni–O(3) | 1.87(1) |
| Cu–O(3) | 1.94(1) | Ni–N(1) | 1.84(1) |
| Cu–O(4) | 1.89(1) | Ni–N(2) | 1.84(1) |
| Cu–O(5) | 2.27(1) | | |
| *Ligand* | | | |
| C(1)–N(1) | 1.27(1) | C(11)–N(2) | 1.31(1) |
| C(1)–C(2) | 1.52(2) | C(11)–C(12) | 1.55(2) |
| C(1)–C(3) | 1.45(2) | C(11)–C(13) | 1.43(2) |
| C(3)–C(4) | 1.38(2) | C(13)–C(14) | 1.39(2) |
| C(4)–O(3) | 1.28(1) | C(14)–O(2) | 1.30(1) |
| C(4)–C(5) | 1.51(2) | C(14)–C(15) | 1.46(2) |
| C(5)–C(6) | 1.42(2) | C(15)–C(16) | 1.42(2) |
| C(6)–O(4) | 1.32(1) | C(16)–O(1) | 1.25(2) |
| C(6)–C(7) | 1.46(2) | C(16)–C(17) | 1.46(1) |
| C(7)–C(8) | 1.42(2) | C(17)–C(18) | 1.36(2) |
| C(8)–C(9) | 1.38(2) | C(18)–C(19) | 1.44(2) |
| C(9)–C(10) | 1.44(2) | C(19)–C(20) | 1.41(2) |
| C(10)–C(5) | 1.37(1) | C(20)–C(15) | 1.45(2) |
| C(21)–N(1) | 1.48(2) | C(22)–N(2) | 1.47(2) |
| | | C(21)–C(22) | 1.53(2) |

ture factors were calculated using scattering factors for neutral atoms taken from Cromer and Waber [9]. The metal scattering factors were corrected for the real and imaginary anomalous dispersion with constant average values $\Delta f' = -0.36$ and $\Delta f'' = 1.36$ for Cu and $\Delta f' = -0.37$ and $\Delta f'' = 1.20$ for Ni. Several cycles of full-matrix least squares refinement of the atom coordinates, anisotropic temperature factors and scale factor reduced the conventional R factor to 6.3% when the maximum shift of the positional variable parameters was $0.2\sigma$. A final three-dimensional difference synthesis showed no significant anomaly and revealed the positions of some but not all hydrogen atoms which were not taken into account considering the low interest of these atoms in the molecule. All calculations were performed using the X-ray '73 program system.

Final atomic positional parameters are listed in Table II. Intramolecular bond distances and angles are tabulated in Tables III and IV. Information concerning selected molecular planes and dihedral angles is given in Table V. Some intra- and intermolecular contact distances are given in Table VI.

## Description of the Structure

The crystal consists of binuclear NiCu(aapen)$H_2O$ molecules as illustrated in Fig. 1, in which the molecular structure is shown together with the numbering scheme used, and in Fig. 2 in which two molecules

TABLE IV. Bond Angles (°) with Estimated Standard Deviations.

| | | | |
|---|---|---|---|
| *Coordination* | | | |
| O(1)–Cu–O(2) | 91.0(4) | O(2)–Ni–O(3) | 81.9(4) |
| O(1)–Cu–O(4) | 95.9(4) | O(2)–Ni–N(2) | 94.9(4) |
| O(2)–Cu–O(3) | 78.2(4) | O(3)–Ni–N(1) | 95.1(5) |
| O(3)–Cu–O(4) | 92.2(4) | N(1)–Ni–N(2) | 88.1(5) |
| O(1)–Cu–O(3) | 164.8(4) | O(2)–Ni–N(1) | 176.7(5) |
| O(2)–Cu–O(4) | 164.9(4) | O(3)–Ni–N(2) | 176.4(4) |
| O(5)–Cu–O(1) | 101.5(4) | Cu–O(2)–Ni | 99.2(4) |
| O(5)–Cu–O(2) | 93.2(5) | Cu–O(3)–Ni | 100.7(4) |
| O(5)–Cu–O(3) | 90.0(4) | | |
| O(5)–Cu–O(4) | 98.5(5) | | |
| *Ligand*[a] | | | |
| Cu–O(1)–C(16) | 126(1) | Cu–O(4)–C(6) | 123(1) |
| Cu–O(2)–C(14) | 132(1) | Cu–O(3)–C(4) | 133(1) |
| Ni–O(2)–C(14) | 129(1) | Ni–O(3)–C(4) | 126(1) |
| Ni–N(2)–C(11) | 124(1) | Ni–N(1)–C(1) | 127(1) |
| C(11)–N(2)–C(22) | 120(1) | C(1)–N(1)–C(21) | 117(1) |
| N(2)–C(22)–C(21) | 111(1) | N(1)–C(21)–C(22) | 110(1) |
| N(2)–C(11)–C(12) | 120(1) | N(1)–C(1)–C(2) | 121(1) |
| C(12)–C(11)–C(13) | 113(1) | C(2)–C(1)–C(3) | 115(1) |
| N(2)–C(11)–C(13) | 127(1) | N(1)–C(1)–C(3) | 124(1) |
| C(11)–C(13)–C(14) | 123(1) | C(1)–C(3)–C(4) | 122(1) |
| C(13)–C(14)–O(2) | 122(1) | C(3)–C(4)–O(3) | 125(1) |
| O(2)–C(14)–C(15) | 117(1) | O(3)–C(4)–C(5) | 117(1) |
| C(13)–C(14)–C(15) | 121(1) | C(3)–C(4)–C(5) | 118(1) |
| C(14)–C(15)–C(16) | 124(1) | C(4)–C(5)–C(6) | 123(1) |
| C(14)–C(15)–C(20) | 117(1) | C(4)–C(5)–C(10) | 119(1) |
| C(15)–C(16)–O(1) | 128(1) | C(5)–C(6)–O(4) | 127(1) |
| C(17)–C(16)–O(1) | 115(1) | C(7)–C(6)–O(4) | 114(1) |

[a] Bond angles of the phenylene rings are between 117 and 123 degrees with a mean of 120 degrees.

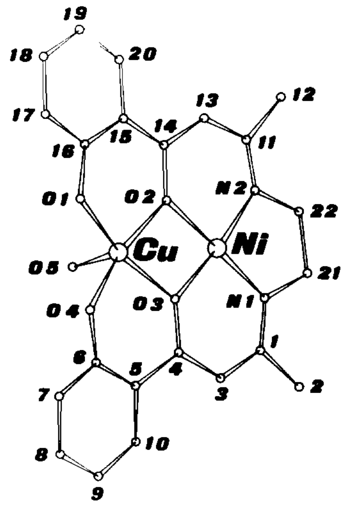


Fig. 1. A perspective view of the molecule.

TABLE V. Least-squares Planes and Distances (A) of Atoms from the Planes. The equation of a plane is PX + QY + RZ = S with coordinates referred to the crystallographic axes.$^a$

| | |
|---|---|
| *Plane I* | O(1), O(2), O(3), O(4).<br>−3.30X + 6.59Y + 11.60Z = 5.66 A<br>[O(1) −0.01, O(2) 0.01, O(3) −0.01, O(4) 0.01, Cu* − 0.20, Ni* 0.20] |
| *Plane II* | Ni, O(2), O(3), N(1), N(2).<br>−2.83X + 7.21Y + 9.73Z = 5.30 A<br>[Ni 0.02, O(2) 0.00, O(3) −0.01, N(1) 0.00, N(2) −0.01, C(1)* −0.03, C(2)* − 0.11, C(3)* 0.01, C(4)* −0.02, C(5)* −0.10, C(11)* 0.07, C(12)* 0.06, C(13)* 0.15, C(14)* 0.10, C(15)* 0.14] |
| *Plane III* | Cu, O(2), O(3).<br>−2.76X + 7.25Y + 9.59Z = 5.28 A |
| *Plane IV* | Cu, O(1), O(2).<br>−1.39X + 6.64Y + 11.65Z = 6.38 A |
| *Plane V* | Cu, O(3), O(4).<br>−5.09X + 6.48Y + 11.10Z = 4.35 A |
| *Plane VI* | O(1), O(2), C(14), C(15), C(16).<br>−3.07X + 6.72Y + 11.30Z = 5.69 A<br>[O(1) 0.02, O(2) −0.04, C(14) 0.06, C(15) −0.04, C(16) 0.00] |
| *Plane VII* | O(3), O(4), C(4), C(5), C(6).<br>−1.70X + 6.79Y + 11.38Z = 6.55 A<br>[O(3) −0.07, O(4) 0.05, C(4) 0.08, C(5) −0.02, C(6) −0.04] |

*Angles between the planes*

| Planes | Angle (°) | Planes | Angle (°) |
|---|---|---|---|
| I–II | 7 | III–IV | 11 |
| I–III | 8 | III–V | 12 |
| I–IV | 9 | II–VII | 9 |
| I–V | 9 | IV–V | 18 |
| II–III | 1 | IV–VI | 8 |
| II–VI | 6 | V–VII | 16 |

$^a$Atoms with asterisks were not used in the plane calculation.

TABLE VI. Shortest Contact Distances (A).

| *Intramolecular contacts* | | | |
|---|---|---|---|
| O(1)···O(2) | 2.75(1) | O(1)···O(5) | 3.23(2) |
| O(3)···O(4) | 2.76(1) | O(4)···O(5) | 3.16(1) |
| O(1)···O(4) | 2.81(1) | O(2)···O(5) | 3.08(2) |
| O(2)···O(3) | 2.46(1) | O(3)···O(5) | 2.98(1) |
| O(1)···O(3) | 3.79(1) | Cu···Ni | 2.931(2) |
| O(2)···O(4) | 3.82(1) | N(1)···N(2) | 2.56(1) |
| O(2)···N(2) | 2.74(1) | N(1)···O(2) | 3.73(1) |
| O(3)···N(1) | 2.74(1) | N(2)···O(3) | 3.70(1) |
| *Intermolecular bonding* (i) 1 − x, ½ + y, ½ − z | | | |
| O(1)···O(5$^i$) | 2.79(2) | O(4)···O(5$^i$) | 2.72(1) |

are projected onto the *ac* plane of the cell. The nickel atom is four coordinated and square planar being retained in the inner $N_2O_2$ chamber, whilst the copper atom, which is incorporated in the outer $O_2$-$O_2$ chamber, is five coordinate and square pyramidal being also bonded to a water molecule. This copper atom is displaced 0.20 Å from the plane of the four equatorial oxygen atoms toward the axial water. The metal–oxygen distances to the bridging oxygens (mean 1.93 Å) are chemically equivalent and, because of the additional bond, significantly longer than the corresponding distances with the terminal O(1) and O(2) oxygens (1.88 Å). The long axial Cu–O distance (2.26 Å) agrees well with the axial Cu–N (pyridine) distances (2.27 Å) in bispyridinedicopper(II) [1] in which the metal atoms are five-coordinate square pyramidal.

Although the X-ray results do not allow one to distinguish between Ni and Cu atoms, structural comparisons between NiCu(aapen)$H_2O$ and related compounds leave no doubt as to the positions of these atoms. It is a matter of experience that Ni–O and Ni–N distances in chelates with the same skeleton are quite typical for square-planar Ni(II). As shown in Fig. 3, comparison of these distances in NiZn(py)$(BAA)_2$en and NiVO$(BAA)_2$en [4], containing the Schiff base ligand derived from ethylenediamine and 1-phenyl-1,3,5-hexanetrione $H_4(BAA)_2$en, clearly shows that they agree well with those found in NiCu(aapen)$H_2O$ and differ significantly from the corresponding Cu–O and Cu–N distances in $Cu_2$-

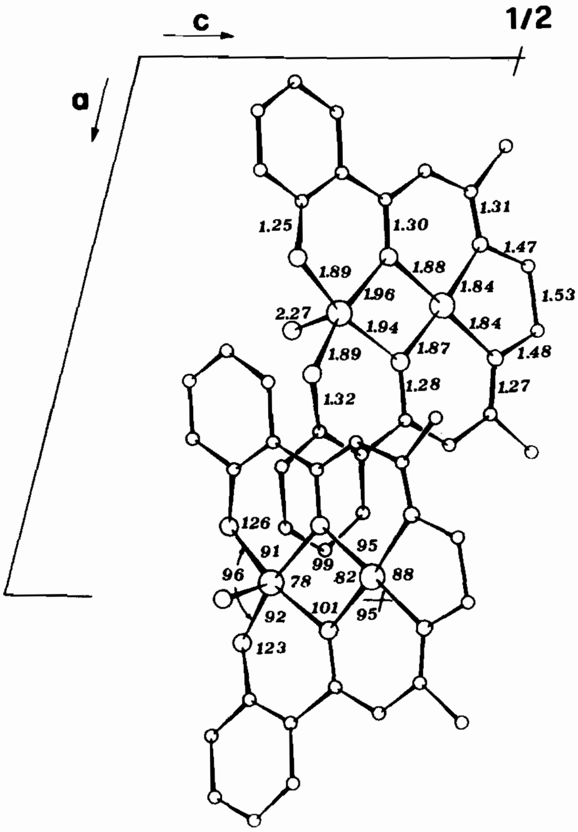


Fig. 2. Projection of the structure down the *b* axis.

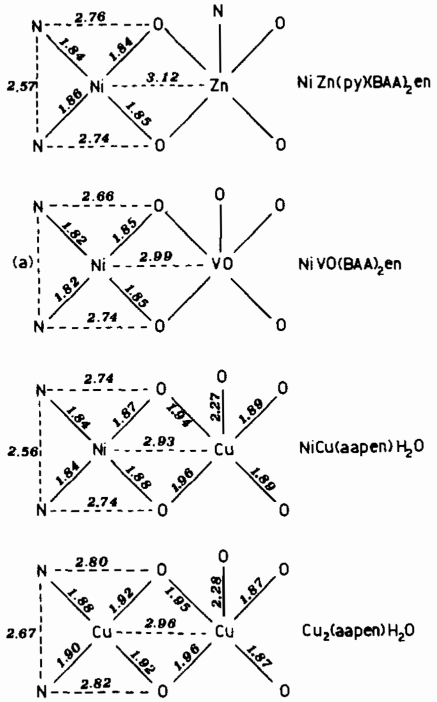


Fig. 3. Comparison of corresponding distances in NiZn(py)-(BAA)en, NiVO(BAA)$_2$en, NiCu(aapen)$H_2O$ and Cu$_2$-(aapen)$H_2O$. Only the skeletons of the molecules are reported. Distances have been approximated to the second decimal digit. Standard deviations are ±0.001 Å. [a]Distance not reported.

(aapen)$H_2O$. On the contrary, distances involving the Cu(II) ion are fully comparable in the isomorphous pair. N···O and N···N contact distances around nickel ion are also very similar in the complexes and shorter than around the copper ion.

The electronic d.r.s. spectrum of NiCu(aapen)$H_2O$ shows a broad ligand field band centered at 15,500 cm$^{-1}$; this was interpreted assuming that the 'inside' Ni(II) tetracoordinate is square planar and diamagnetic retaining its $N_2O_2$ occupancy and copper(II) being pentacoordinate in the $O_2O_2$ site. The magnetic moments in the 80–300 K temperature range (2.00 B.M. (81.7°), 2.10 B.M. (159.3°), 2.16 B.M. (217.9°) 2.27 B.M. (295.9°)) vary very little; indicating that there is no spin-coupling in the complex.

No unusually short intermolecular contacts are present except two O···O distances (2.79 and 2.72 Å, see Table VI) which are within the range of commonly accepted hydrogen-bonded O···O separations. As indicated in Fig. 4, molecules related by the screw axes are bridged by hydrogen bonding from the water molecule of one unit to the terminal oxygen atoms of the successive unit.

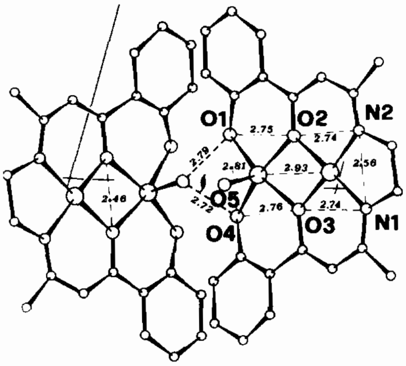


Fig. 4. Hydrogen bonding and contact distances (Å).

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## References

1 R. Graziani, M. Vidali, U. Casellato and P. A. Vigato, *Transition Met. Chem.*, *3*, 138 (1978).
2 R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, D. P. Gavel and J. M. Kuszaj, *Inorg. Chem.*, *15*, 1633 (1976).

3 R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic and D. P. Gavel, *Inorg. Chem.*, *15*, 1646 (1976).

4 M. D. Glick, R. L. Lintvedt, D. P. Gavel and B. K. Tomlonovic, *Inorg. Chem.*, *15*, 1654 (1976).

5 R. Graziani, M. Vidali, U. Casellato and P. A. Vigato, *Acta Cryst.*, *B32*, 1681 (1976).

6 R. Graziani, M. Vidali, U. Casellato and P. A. Vigato, *Transition Met. Chem.*, *3*, 99 (1978).

7 R. Graziani, M. Vidali, U. Casellato and P. A. Vigato, *Transition Met. Chem.*, *3*, 239 (1978).

8 G. Wittig, *Ann. Chem.*, *446*, 173 (1920).

9 D. T. Cromer and J. T. Waber, *Acta Cryst.*, *18*, 104 (1965).