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# X-ray structures and properties of five-coordinate copper(II) complexes with a quadridentate $N_4$ ligand and with a quinquedentate $N_5$ ligand

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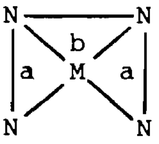
## Abstract

Complexes Cu(biquinen)($H_2O$)($BF_4$)$_2$ (**1**), Cu(biquinen)($H_2O$)($ClO_4$)$_2$ (**2**) and Cu(biquidien)($ClO_4$)$_2$ (**3**) with the $N_4$ Schiff base biquinen (1,2-bis(8-quinolylmethyleneimino)ethane) and with the $N_5$ Schiff base biquidien (1,5-bis(8-quinolylmethyleneimino)-3-aza-pentane) were prepared. **1** crystallizes in the trigonal space group $P3_2$ with $a=1018.0(3)$, $c=2032.2(7)$ pm *and* $Z=3$; **2** in the monoclinic space group *Cc* with $a=1865.7(9)$, $b=995.1(5)$, $c=1715.7(8)$ pm, $\beta=128.59(2)°$ and $Z=4$; **3** in the triclinic space group $P\bar{1}$ with $a=1419.6(8)$, $b=1095.8(6)$, $c=917.7(6)$ pm, $\alpha=74.16(2)$, $\beta=75.55(2)$, $\gamma=88.95(2)°$ and $Z=2$. In all three complexes the copper is five-coordinate with a $N_4O$ set of donor atoms in **1** and **2** and a $N_5$ set of donor atoms in **3**. The coordination geometry of the chromophors Cu(biquinen)($H_2O$)$^{2+}$ in **1** and **2** and Cu(biquidien)$^{2+}$ in **3** is distorted trigonal bipyramidal, with the water in **1** and **2** being coordinated in an equatorial position. In aqueous solution **1** and **2** give the same Vis absorption spectrum with a broad band at 609 nm, whereas for **3** this weak d–d band is shifted to 578 nm. In water/dioxane (3:1) the imine nitrogens of the Schiff base biquinen have p$K_a$ values of 9.25 and 6.63, respectively ($I=0.5$ M $NaClO_4$; $T=25$ °C).

## Introduction

When open-chain quadridentate $N_4$ ligands are bound to metals M the thermodynamic stability and also the geometry of coordination of complexes **I** thus formed is clearly affected by the size of the chelate rings a and b and by the nature of the terminal nitrogen atoms. The combination 6–5–6 (i.e., a = 6-membered ring, b = 5-membered ring) affords more stable complexes than the combination 5–5–5, which is, for example, demonstrated by the copper(II) complexes obtained with $H_2N–(CH_2)_3–NH–(CH_2)_2–NH–(CH_2)_3–NH_2$ (log $K=21.7$) and $H_2N–(CH_2)_2–NH–(CH_2)_2–NH–(CH_2)_2–NH_2$ (log $K=20.1$), respectively [1]. Extending this concept to metal complexes formed with open-chain Schiff base ligands such as **II** and **III** one would expect, therefore, that **III** (6–5–6 type) forms more stable complexes than **II** (5–5–5 type). As discussed in detail by Goodwin and co-workers [2, 3], however, the environmental requirements of the terminal N atoms in **II** and **III** must be considered. Molecular models show that ligand **II** can easily function as a planar quadridentate whereas in the case of **III** crowding of the H atoms in the 2-position of the quinoline rings (*) is produced when the molecule functions as a planar quadridentate group. It was suggested, therefore, that in the light-blue species [Cu(biquinen)]$^{2+}$ (obtained from copper(II) perchlorate and **III**) the ligand is coordinated in a distorted fashion, which avoids clashing of the H atoms [2], and that the coordination geometry of the species [Cu(biquinen)X]$^{+}$ (X = Cl, I) is trigonal bipyramidal [3]. X-ray structure de-



I

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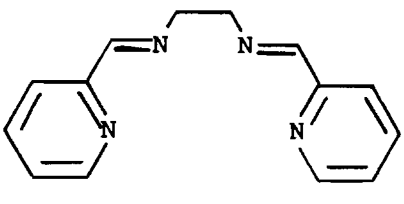
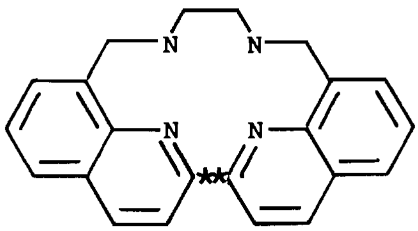
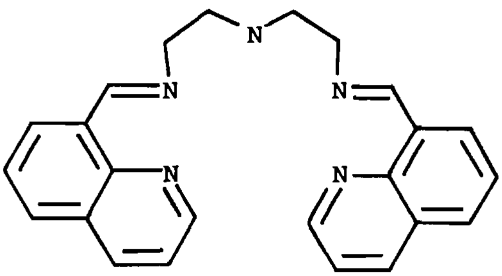


II



III = biquinen



IV = biquidien

terminations of such biquinen complexes are still missing, however.

In the course of our work on the kinetic behavior of four-coordinate planar and distorted copper(II) complexes [4] we decided to include the biquinen complexes of copper(II) in these studies and to carry out first a structural and spectroscopic analysis of Cu(biquinen)$(BF_4)_2 \cdot H_2O$ (**1**), Cu(biquinen)$(ClO_4)_2 \cdot H_2O$ (**2**) and also Cu(biquidien)$(ClO_4)_2$ (**3**) with the quinquedentate ligand biquidien (IV).

## Experimental

### *Ligands and complexes*

The synthesis of the solid compound biquinen (1,2-bis(8-quinolylmethyleneimino)ethane (III)) followed the sequence 2-methylaniline → 8-methylquinoline [5] → 8-(dibromomethyl)quinoline [6] → quinoline-8-aldehyde [6] → biquinen [2] and was carried out according to published methods. The Schiff base biquidien (1,5-bis(8-quinolylmethyleneimino)-3-aza-pentane (IV)) was prepared from stoichiometric amounts of quinoline-8-aldehyde [6] and diethylenetriamine in EtOH. After evaporation of the solvent and of the water formed the residual yellow oil was used for complex formation without further purification. Complexes **1** and **2** were obtained from III and $CuCl_2 \cdot 2H_2O$ in warm EtOH according to Goodwin and Lions [2] by addition of an excess of $NaClO_4$ and $[(n\text{-}Bu)_4N]BF_4$, respectively. Complex **3** formed upon addition of an ethanolic solution of $Cu(ClO_4)_2 \cdot 6H_2O$ to the warm solution of IV in EtOH. The blue–black crystals of **1–3** were recrystallized from water (m.p. > 250 °C, dec.). *Anal.* Found for **1**: C, 44.43; H, 3.49; N, 9.38. Calc. for $C_{22}H_{20}B_2CuF_8N_4O$: C, 44.52; H, 3.40; N, 9.44%. Found for **2**: C, 42.96; H, 3.05; N, 9.04. Calc. for $C_{22}H_{20}Cl_2CuN_4O_9$: C, 42.70; H, 3.26; N, 9.05%. Found for **3**: C, 43.74; H, 3.46; N, 10.68. Calc. for $C_{24}H_{23}Cl_2CuN_5O_8$: C, 44.77; H, 3.60; N, 10.88%.

**Caution**: Although the preparations described have been carried out several times without any problems, it should be remembered that perchlorate salts have been known to detonate violently and great care should be taken when they are handled.

### *UV–Vis spectra*

The absorption spectra were taken on a Varian spectrophotometer (model DMS 300).

### *Potentiometric titrations*

The $pK_a$ values of III were derived from titration curves obtained potentiometrically in the pH range 2–12 with an automatic Metrohm titration apparatus (model E 536). The solution of the ligand, acidified with $HClO_4$, was titrated with 0.1 M NaOH. Since the solubility of III in water is limited, the solvent was water/1,4-dioxane (3:1). The ionic strength was adjusted to 0.5 M ($NaClO_4$). The system was calibrated with a selection of standard buffers covering the pH range studied. The $pK_a$ values were determined on the basis of hydrogen ion activities as following from the pH data obtained at $I = 0.5$ M.

### *X-ray structure determination*

The crystals selected for the structural analysis were a three-sided prism of **1** (0.125 mm side length × 1.13 mm length), a prism of **2** (dimensions 0.15 × 0.2 × 0.6 mm) and a prism of **3** (dimensions 0.06 × 0.2 × 0.8 mm). Intensities were measured with a four-circle diffractometer (Siemens-Stoe) using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 71.069$ pm). Cell constants were determined by least-squares methods from the $2\theta$ angles of about 40 reflections ($T = 25$ °C), measured on the same instrument.

The measured intensities were corrected for background and Lp effects; a numerical absorption correction was applied.

The structures were solved by direct methods and atomic positions and anisotropic temperature factors refined by least-squares methods to the $R$ values given in Table 1. Final parameter shifts were less than 0.1 standard deviations. Hydrogen atoms were positioned geometrically (C–H distance 108 pm) and not refined. The crystallographic calculations were performed with the programs SHELX-76 and SHELXS-86 on an IBM 200 D computer at Technische Hochschule Darmstadt, using scattering factors for C, H, N and O as stored in SHELX-76 [7]. Table 1 summarizes relevant crystallographic data and information on data processing. The final positional parameters are given in Table 2; the bond distances and bond angles in Table 3.

## Results and discussion

### *Properties of the ligands and complexes*

The ligand biquinen (**III**) was prepared according to published procedures, whereas the new ligand biquidien (**IV**) was obtained from quinoline-8-aldehyde and diethylenetriamine. To characterize the base properties of **III**, its acidified solution in water/dioxane was titrated with NaOH. The p$K_a$ values obtained are compiled in Table 4. Only three of the four p$K_a$ values expected can be derived from the titration curve, but interestingly enough the first point of inflection is observed after addition of 2(!) equivalents of NaOH. This points strongly to hydrolysis of **III** in acid medium, which leads to ethylenediamine and 2(!) equivalents of quinoline-8-aldehyde. The lowest p$K_a$ value obtained, p$K_a(3) = 3.79$, is thus to be assigned to the free aldehyde. An independent titration of quinoline-8-aldehyde in water/dioxane leads to p$K_a = 3.90$ (see Table 4), which confirms this assignment. At higher pH reconstitution of the Schiff base **III** obviously takes place, since both p$K_a(2) = 6.63$ and p$K_a(1) = 9.25$ are clearly smaller than the independently determined p$K_a$ values of ethylenediamine (see Table 4). The data obtained for p$K_a(1)$ and p$K_a(2)$ have thus to be assigned to the two imine nitrogen atoms in **III**. The overall result is, therefore, that the $N_4$ ligand **III** carries two rather strongly basic imine nitrogens and two much less basic quinoline nitrogens.

The blue–black complexes **1**–**3** were recrystallized from water and characterized by elemental analysis (the somewhat low value obtained for the carbon content of **3** might be due to incomplete combustion of the perchlorate salt). All three complexes behave as $AB_2$ electrolytes in water. Their paramagnetism corresponds to what one expects for non-coupled $3d^9$ metal centers ($\mu_{eff} = 1.9$ $\mu_B$ for **3** at 24 °C [2]).

### *Spectroscopic results*

It is found that the UV–Vis absorption spectra of complexes **1** and **2** are identical, which confirms

TABLE 1. Summary of crystal data for complexes **1**–**3**

| | Cu(biquinen)$(BF_4)_2 \cdot H_2O$ (**1**) | Cu(biquinen)$(ClO_4)_2 \cdot H_2O$ (**2**) | Cu(biquidien)$(ClO_4)_2$ (**3**) |
|---|---|---|---|
| Formula | $C_{22}H_{20}B_2CuF_8N_4O$ | $C_{22}H_{20}Cl_2CuN_4O_9$ | $C_{24}H_{23}Cl_2CuN_5O_8$ |
| Molecular weight | 593.57 | 618.87 | 643.92 |
| Space group | trigonal, $P3_2$ | monoclinic, $Cc$ | triclinic, $P\bar{1}$ |
| $a$ (pm) | 1018.0(3) | 1865.7(9) | 1419.6(8) |
| $b$ (pm) | | 995.1(5) | 1095.8(6) |
| $c$ (pm) | 2032.2(7) | 1715.7(8) | 917.7(6) |
| Angles (°) | | 128.59(2)[a] | 74.16(2)[b]; 75.55(2)[a]; 88.95(2)[c] |
| $Z$ | 3 | 4 | 2 |
| $D_{calc}$ (g cm$^{-3}$) | 1.57 | 1.65 | 1.61 |
| Reflections collected (2$\theta$ range up to 50) | 3623 | 1895 | 4362 |
| Symmetry-independent reflections | 2263 | 1895 | 2480 |
| Reflections with $F > 2\sigma(F)$ | 2234 | 1857 | 2201 |
| $R_1 = \Sigma\lvert F_o - F_c\rvert / \Sigma F_o$ | 0.0638 | 0.0387 | 0.0873 |
| $R_2 = \Sigma w^{1/2}\lvert F_o - F_c\rvert / \Sigma w^{1/2}\lvert F_o\rvert$ | 0.0610 | 0.0363 | 0.0760 |
| Absorption coefficient (cm$^{-1}$) | 9.7 | 11.5 | 10.4 |

[a]Angle $\beta$. [b]Angle $\alpha$. [c]Angle $\gamma$.

TABLE 2. Final positional parameters ($\times 10^4$) (excluding hydrogens) for the cations in complexes **1**–**3**

| Atom | **1** | | | **2** | | | **3** | | |
|---|---|---|---|---|---|---|---|---|---|
| | *x/a* | *y/b* | *z/c* | *x/a* | *y/b* | *z/c* | *x/a* | *y/b* | *z/c* |
| Cu1 | 10027(01) | 4351(01) | 6981 | 5000 | 8677(01) | 5000 | 7423(01) | 2489(01) | 1908(02) |
| N1 | 8964(12) | 5208(12) | 6477(05) | 5428(04) | 6961(06) | 5786(05) | 6413(06) | 2774(10) | 3918(11) |
| C1 | 7557(18) | 4310(16) | 6262(06) | 4904(06) | 6378(08) | 5968(06) | 6014(09) | 1744(13) | 5060(17) |
| C2 | 6562(18) | 4692(22) | 6007(07) | 5014(08) | 5013(10) | 6275(08) | 5587(09) | 1768(15) | 6596(17) |
| C3 | 7087(24) | 6236(27) | 5975(07) | 5672(08) | 4304(10) | 6427(08) | 5574(09) | 2906(18) | 6952(16) |
| C4 | 8615(22) | 7318(21) | 6136(07) | 6204(06) | 6268(08) | 6049(06) | 5959(08) | 3985(15) | 5806(16) |
| C5 | 9186(27) | 8937(25) | 6062(08) | 6324(06) | 4877(08) | 6362(06) | 5936(10) | 5206(18) | 6131(17) |
| C6 | 10673(33) | 9893(25) | 6168(09) | 7135(08) | 4208(10) | 6615(07) | 6286(11) | 6252(16) | 4994(22) |
| C7 | 11595(20) | 9320(17) | 6374(07) | 7764(07) | 4839(11) | 6593(08) | 6661(08) | 6179(12) | 3463(17) |
| C8 | 11090(15) | 7827(14) | 6461(06) | 7640(07) | 6159(09) | 6348(08) | 6729(08) | 5069(12) | 3058(14) |
| C9 | 9501(17) | 6736(17) | 6360(05) | 6882(05) | 6897(09) | 6063(06) | 6382(07) | 3898(12) | 4263(14) |
| C10 | 12233(18) | 7452(19) | 6607(07) | 6874(06) | 8310(10) | 5873(07) | 7112(08) | 5163(12) | 1417(15) |
| N2 | 11952(12) | 6023(12) | 6731(05) | 6263(05) | 9139(07) | 5577(06) | 7412(07) | 4271(09) | 829(11) |
| C11 | 13242(14) | 5792(15) | 6829(08) | 6406(06) | 10575(10) | 5531(07) | 7733(11) | 4510(14) | −876(14) |
| C12 | 12910(14) | 4778(16) | 7355(08) | 5506(06) | 11179(08) | 4650(07) | 7505(11) | 3363(17) | −1254(16) |
| N3 | 11298(12) | 3566(14) | 7359(05) | 4783(05) | 10566(06) | 4595(05) | 7093(17) | 2422(23) | −99(27) |
| N3′ | | | | | | | 7828(14) | 2213(19) | −230(23) |
| C13 | 10832(15) | 2211(16) | 7519(06) | 4132(06) | 11265(09) | 4434(07) | 7361(13) | 1069(18) | −218(20) |
| C14 | 9288(16) | 1114(15) | 7636(06) | 3070(06) | 9365(11) | 4122(06) | 7017(14) | 202(15) | 1285(22) |
| C15 | 9000(17) | −346(15) | 7740(06) | 3328(06) | 10760(10) | 4283(07) | 7769(09) | −93(12) | 3335(18) |
| C16 | 7594(21) | −1484(17) | 7900(08) | 2742(07) | 11701(13) | 4201(07) | 8226(09) | 220(12) | 4448(15) |
| C17 | 6424(21) | −1271(17) | 7986(06) | 1913(09) | 11354(15) | 3997(10) | 8328(09) | −767(14) | 5688(18) |
| C18 | 6597(17) | 220(16) | 7876(06) | 1655(08) | 10054(16) | 3831(09) | 8813(10) | −640(15) | 6780(17) |
| C19 | 8044(13) | 1395(13) | 7648(06) | 2203(06) | 9014(13) | 3838(07) | 9215(09) | 500(17) | 6650(15) |
| C20 | 5498(19) | 601(20) | 7990(07) | 1903(07) | 7678(13) | 3547(08) | 9161(09) | 1590(14) | 5390(15) |
| C21 | 5730(17) | 1968(22) | 7902(06) | 2432(06) | 6763(12) | 3524(08) | 8626(08) | 1417(13) | 4311(14) |
| C22 | 7163(13) | 3069(14) | 7676(06) | 3310(06) | 7164(11) | 3876(07) | 9615(09) | 2788(15) | 5114(16) |
| N4 | 8203(11) | 2778(12) | 7519(04) | 3625(05) | 8419(07) | 4204(05) | 7382(08) | 666(10) | 2382(14) |
| O1 | 9620(09) | 2724(09) | 6072(04) | 4936(04) | 7628(06) | 3701(04) | | | |
| C23 | | | | | | | 9547(09) | 3751(14) | 3875(17) |
| C24 | | | | | | | 9002(08) | 3532(12) | 2897(14) |
| N5 | | | | | | | 8547(06) | 2454(09) | 3088(10) |

that in aqueous solution there is complete dissociation of the tetrafluoroborate and perchlorate salt of the chromophor Cu(biquinen)$(H_2O)^{2+}$. For both cations Cu(biquinen)$(H_2O)^{2+}$ and Cu(biquidien)$^{2+}$ the same UV absorption pattern is observed, i.e. a very strong band at approx. 220 nm, a weak shoulder at approx. 260 nm and a strong absorption at approx. 310 nm (see Table 5). The fact that the free ligand biquinen (**III**) produces the same type of UV spectrum (see Table 5) proves that these bands are characteristics of the aromatic system in ligands **III** and **IV**.

The low intensities of the very broad absorptions* at 609 nm (Cu(biquinen)$(H_2O)^{2+}$) and 578 nm (Cu(biquidien)$^{2+}$) are typical for d–d transitions. For a qualitative comparison Table 5 presents also the absorption data for some four-coordinate copper(II) complexes. One clearly sees that the d–d absorption of the species Cu(biquinen)$(H_2O)^{2+}$ is considerably red-shifted as compared to the planar $CuN_4$ chromophors $Cu(en)_2{}^{2+}$ and Cu(3-2-3-$N_4$)$^{2+}$, which confirms that there are steric problems arising for the ligand biquinen in a planar $N_4$ arrangement. In addition, one has to consider, of course, that the ligand field strength produced by the $N_4$ ligand biquinen is probably rather different from that produced by en (= ethylenediamine) and 3-2-3-$N_4$ (= $H_2N$–$(CH_2)_3$–NH–$(CH_2)_2$–NH–$(CH_2)_3$–$NH_2$).

For the solid state (Nujol spectra) it is again found that complexes **1** and **2** produce the same spectrum with a broad absorption peaking at 580 nm and a shoulder at approx. 400 nm. As found for the solution, the maximum absorption of the biquidien complex **3** is slightly blue-shifted (570 instead of 580 nm).

### *X-ray structures*

As summarized in Table 1 the crystals formed by complexes **1**–**3** belong to different crystal systems

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*Since the shape of these broad bands was not further analysed it might well be that they represent the sum of several overlapping absorptions.

TABLE 3. Interatomic distances (pm) and bond angles (°) for the coordination core of complexes **1**–**3**[a]

| **1** | | **2** | | **3**[c] | |
|---|---|---|---|---|---|
| Distances[b] | | | | | |
| Cu–O(1) | 237.5 | Cu–O(1) | 239.4 | Cu–N(1) | 213.0 |
| Cu–N(1) | 198.3 | Cu–N(1) | 200.7 | Cu–N(2) | 193.5 |
| Cu–N(2) | 191.3 | Cu–N(2) | 195.9 | Cu–N(3′) | 200.7 |
| Cu–N(3) | 198.4 | Cu–N(3) | 195.7 | Cu–N(4) | 192.4 |
| Cu–N(4) | 205.8 | Cu–N(4) | 203.5 | Cu–N(5) | 213.4 |
| Cu–F[d] | 302 | Cu–O[e] | 284 | Cu–O[e] | 322 |
| Angles[f] | | | | | |
| N(1)–Cu–N(2) | 90.7 | N(1)–Cu–N(1) | 90.7 | N(1)–Cu–N(2) | 90.0 |
| N(1)–Cu–N(3) | 170.8 | N(1)–Cu–N(3) | 164.4 | N(1)–Cu–N(3′) | 155.2 |
| N(2)–Cu–N(3) | 82.9 | N(2)–Cu–N(3) | 82.6 | N(2)–Cu–N(3′) | 86.1 |
| N(1)–Cu–N(4) | 97.9 | N(1)–Cu–N(4) | 98.6 | N(1)–Cu–N(4) | 101.8 |
| N(2)–Cu–N(4) | 163.3 | N(2)–Cu–N(4) | 169.9 | N(2)–Cu–N(4) | 162.3 |
| N(3)–Cu–N(4) | 89.9 | N(3)–Cu–N(4) | 89.3 | N(3′)–Cu–N(4) | 77.7 |
| O(1)–Cu–N(1) | 87.8 | O(1)–Cu–N(1) | 91.3 | N(1)–Cu–N(5) | 88.4 |
| O(1)–Cu–N(2) | 99.1 | O(1)–Cu–N(2) | 85.3 | N(2)–Cu–N(5) | 103.0 |
| O(1)–Cu–N(3) | 86.7 | O(1)–Cu–N(3) | 102.1 | N(3′)–Cu–N(5) | 116.3 |
| O(1)–Cu–N(4) | 95.5 | O(1)–Cu–N(4) | 90.6 | N(4)–Cu–N(5) | 90.6 |

[a] The numbering of the atoms follows that shown in Figs. 1–3 (complexes **1** and **2**) and Fig. 4 (complex **3**), respectively. The symbol Cu is equivalent to Cu1 in Figs. 1–4. [b] Error limits: ±1 pm (complexes **1** and **3**) and ±0.7 pm (complex **2**). [c] The middle (third) nitrogen atom of the ligand biquidien (**IV**) in complex **3** is disordered, leading to nitrogens N(3) and N(3′). Since Fig. 4 is based on N(3′) instead of N(3), the distances and angles including atom N(3) have been omitted in Table 3. The data compiled in Table 2 lead to a distance Cu–N(3) of 203.1 pm and to an angle N(3)–Cu–N(3′) of 30.1°. [d] Shortest Cu–F (tetrafluoroborate) distance observed. [e] Shortest Cu–O (perchlorate) distance observed. [f] Error limits: ±0.5° (complex **1**), ±0.3° (complex **2**) and ±0.7° (complex **3**).

TABLE 4. $pK_a$ values

| | $pK_a(1)$ | $pK_a(2)$ | $pK_a(3)$ |
|---|---|---|---|
| biquinen (III)[a] | 9.25±0.02 | 6.63±0.03 | 3.79±0.01[b] |
| en[a] | 9.92±0.01<br>(10.04±0.05)[c] | 6.99±0.01<br>(7.31±0.02)[c] | |
| Quinoline-8-aldehyde[a] | 3.90±0.01<br>(4.97)[d] | | |

[a] From titration carried out in water/dioxane (3:1) at $I=0.5$ M ($NaClO_4$) and $T=25$ °C. [b] Determined from the first point of inflection of the titration curve observed after addition of 2(!) equivalents of NaOH. [c] Solvent water, $I=0.5$ M, $T=25$ °C [1]. [d] $pK_a$ value for quinoline in water, $I=0.1$ M, $T=25$ °C [1].

and different space groups. The structures of **1** and **2** could be refined to $R_2=0.061$ and $R_2=0.0363$, respectively, whereas for complex **3** refinement was not better than $R_2=0.0760$, due to the fact that the central N atom of the $N_5$ ligand **IV** (biquidien) in complex **3** is disordered.

Figures 1 and 2 give views of complex **1** which suggest an interpretation of the coordination geometry to be such that the copper is located in the center of a somewhat distorted $N_4$ plane with the water oxygen occupying an axial position on top of the copper. In particular Fig. 2 shows very clearly the internal distortion by which the ligand biquinen avoids clashing of the H atoms attached to carbon atoms C1 and C22 that would occur upon planar $N_4$ coordination. In contrast to the interpretation based on a quadratic pyramid, Fig. 3 gives a view of the coordination geometry in **1** which apparently brings it closer to a distorted trigonal bipyramid with the water oxygen occupying an equatorial position.

A decision on the more likely type of coordination geometry in **1** can be made only by considering the bond angles and distances (see Table 3) in detail. For an ideal quadratic pyramid one would expect a $CuN_4$ base plane in which all four Cu–N distances are equal. It is found, however, that there are two equal distances (Cu–N(1) and Cu–N(3)) and one longer one (Cu–N(4)) and one shorter one (Cu–N(2)). The fact of finding 198 pm for both the distances Cu–N(1) and Cu–N(3) is more in line with the

TABLE 5. UV–Vis absorption data for complexes 1–3 in aqueous solution at 25 °C

| Complex | $\lambda_{max}$ (nm) | ($\epsilon_{max}$ ($M^{-1}$ $cm^{-1}$)) | Reference |
|---|---|---|---|
| $Cu(biquinen)(BF_4)_2 \cdot H_2O$ (1) and | 609 | (124) | this work |
| $Cu(biquinen)(ClO_4)_2 \cdot H_2O$ (2) | 318 | ($35.5 \times 10^3$) | |
| | 260 | (sh) | |
| | 223 | ($100 \times 10^3$) | |
| | 580[a] | | |
| | 400[a] | (sh) | |
| $Cu(biquidien)(ClO_4)_2$ (3) | 578 | (128) | this work |
| | 310 | ($23.4 \times 10^3$) | |
| | 250 | (sh) | |
| | 222 | ($76 \times 10^3$) | |
| | 570[a] | | |
| | 400[a] | (sh) | |
| biquinen[b] | 300[c] | | this work |
| | 250 | (sh) | |
| | 217[c] | | |
| $Cu(en)_2(BF_4)_2$ | 556 | | 8 |
| | 526 | | |
| $Cu(3\text{-}2\text{-}3\text{-}N_4)^{2+}$[d] | 531 | (151) | 8 |

[a]Solid state absorption spectrum of finely ground complex (Nujol). [b]Saturated aqueous solution ($< 2.5 \times 10^{-5}$ M). [c]Ratio of absorptivities: $\epsilon(217)/\epsilon(300) \approx 4/1$. [d]$3\text{-}2\text{-}3\text{-}N_4 = H_2N\text{-}(CH_2)_3\text{-}NH\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_3\text{-}NH_2$.

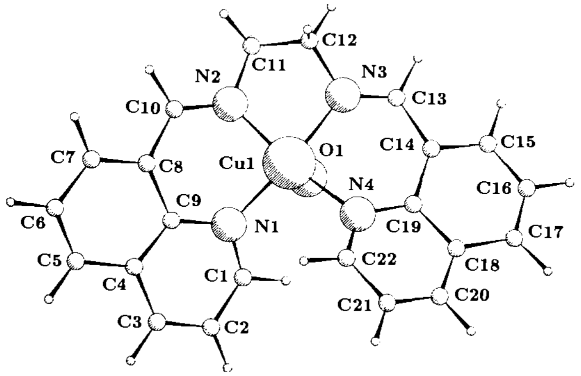

Fig. 1. View of the coordination geometry of $Cu(biquinen)(H_2O)(BF_4)_2$ (1) as projected on to the plane N1, N2, N4.

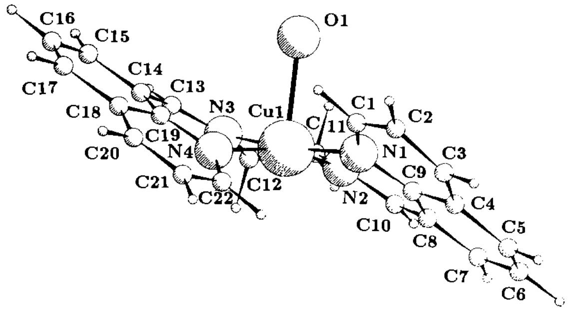

Fig. 2. Coordination geometry of complex 1 as viewed into the angle N1–Cu1–N4.

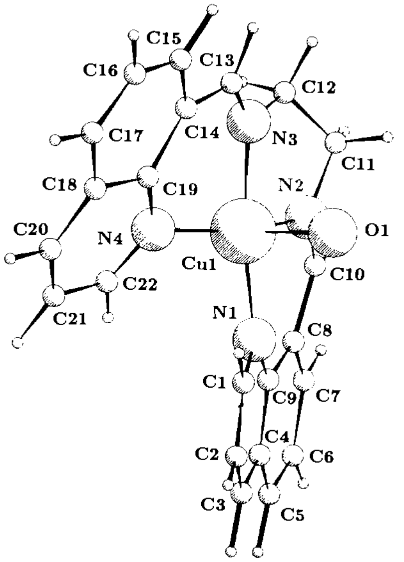

Fig. 3. Coordination geometry of complex 1 as viewed into the angle N4–Cu1–O1.

distorted trigonal bipyramid shown in Fig. 3, where nitrogens N(1) and N(3) occupy the axial positions. The angles N(3)–Cu–N(4) and N(1)–Cu–N(2) are 89.9 and 90.7°, respectively, whereas the angle N(1)–Cu–N(3) is 170.8° instead of 180°.

Without going into further details one can summarize the discussion on complex 1 by saying that the $N_4O$ penta-coordination in this complex appears to be closer to a distorted trigonal bipyramid (with the water in an equatorial position) than to a distorted quadratic pyramid. The Cu–F distance of $\geqslant 302$ pm indicates that the tetrafluoroborate anions are not coordinated.

Complex **2** is the perchlorate salt of the cation $Cu(biquinen)(H_2O)^{2+}$ instead of the tetrafluoroborate salt in complex **1**. Comparing **1** and **2** means to look for anion effects on the coordination sphere of the copper. It follows from Table 3 that the corresponding distances and angles of **2** are indeed very close to those of **1**. The distances Cu–N(1) and Cu–N(3) (200.7 and 195.7 pm, respectively) do not agree as well as in the case of **1** and the angle N(1)–Cu–N(3) = 164.4° deviates slightly more from the expected value of 180°, but, in general, the arrangement of the $N_4O$ set of donor atoms around the copper again appears to be closer to a distorted trigonal bipyramid than to a distorted quadratic pyramid. The perchlorate anions are obviously not coordinated (Cu–O(perchlorate) $\geqslant 284$ pm).

The introduction of the quinquedentate ligand biquidien (IV) in complex **3** leads to a $N_5$ set of donor atoms instead of the $N_4O$ set in **1** and **2**. To our knowledge complex **3** represents the first example of a five-coordinate copper(II) complex of the $CuN_5$ type in which all five nitrogen atoms are part of just one chelate ligand.

As shown in Fig. 4 and Table 3 the most adequate description of the coordination geometry in complex **3** is that of a distorted trigonal bipyramid. Both the distances found for the Cu–N bonds and the angles formed by the nitrogen atoms surrounding the copper are in favor of this interpretation, with both quinoline nitrogens acting as equatorial donor atoms. It has to be pointed out that the central aliphatic nitrogen atom of the ligand biquidien, which occupies the third equatorial position, is disordered in **3**, leading to nitrogens N(3) and N(3′), respectively. This disordering does not effect, however, the interpretation of the coordination geometry to be distorted trigonal bipyramidal. In view of the structure of the $CuN_5$ chromophor in **3** it is not surprising to see that the perchlorate anions are not coordinated (Cu–O(perchlorate) $\geqslant 322$ pm).

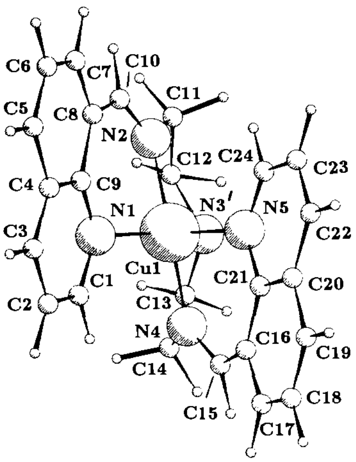

Fig. 4. Coordination geometry of complex $Cu(biquidien)(ClO_4)_2$ (**3**) as viewed into the angle N1–Cu1–N5.

The stereochemistry of five-coordinate copper(II) complexes was recently reviewed and discussed in great detail by B. J. Hathaway [8]. As a matter of fact, the regular square-based pyramidal geometry as well as the regular trigonal bipyramidal geometry is only of rare occurrence. These regular geometries are limited to complexes with ligand systems that favor the regularity. As an example one could mention the square pyramidal copper complexes of the general type $Cu(N_4\text{-macrocycle})X$ [9] and the trigonal bipyramidal complexes $[Co(NH_3)_6][CuCl_5]$ [10] or $[Cu(tren)(NH_3)](ClO_4)_2$ [11]. Considering the fact that in the ligands biquinen and biquidien the nitrogen atoms are chemically not equivalent and, in addition, part of just one chelate ligand with limited steric flexibility, one is not surprised to find strongly distorted coordination geometries in complexes **1–3**.

Comparing the five-coordinate complexes **1–3** from a preparative point of view one would classify **3** as being coordinatively "saturated", whereas in **1** and **2** the water can be easily replaced by anions $X^-$ to form the cation $Cu(biquinen)X^+$, which has been shown for X = Cl, I already [3]. From the point of kinetics the species $Cu(biquinen)X^+$ might be an interesting one to study the kinetics of ligand substitution in five-coordinate copper(II) complexes according to reaction (1).

$$Cu(biquinen)X^+ + Y^- \rightleftharpoons Cu(biquinen)Y^+ + X^- \quad (1)$$

## Supplementary material

Further information concerning details of the structure analysis is available from the authors on request.

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