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# Spectroscopic Studies on Mixed Ligand Copper(II) Complexes

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**Summary.** Mixed copper(II) complexes, Cu(*bzyoxb*)(*diam*)*X* (where *bzyoxb* = benzyl-(2-oxobutanoat) *diam* = N,N,N′,N′-tetramethylethylenediamine (*tmen*) and *N*-methyl-1,4-diazacycloheptane (*medach*), and $X = ClO_4^-$, $Cl^-$ and $CH_3CO_2^-$ ($OAc^-$)), have been prepared. Their structures and properties were characterized by elemental analysis, UV-Vis, IR and Far IR spectroscopy and magnetic measurements. The square planar complexes were only obtained in presence of perchlorate anion, whereas the five coordinated complexes were obtained for both $Cl^-$ and $OAc^-$ counter-anions. The d–d absorption bands of perchlorate complexes were found to be linearly correlated with the donor number of solvents or coordinating anions. The results are discussed in terms of the extended donor–acceptor concept.

**Keywords.** Copper(II) complexes; Donor numbers; Solvatochromism; Five- and four-coordination.

**Spektroskopische Untersuchungen an solvatochromen Kupfer(II)-Komplexen mit gemischten Liganden**

**Zusammenfassung.** Gemischte Kupfer(II)-Komplexe Cu(*bzyoxb*)(*diam*)*X* (*bzyoxb* = benzyl-(2-oxobutanoat), *diam* = N,N,N′,N′-tetramethylethylendiamin (*tmen*) und N-methyl-1,4-diazacycloheptan (*medach*), $X = ClO_4^-$, $Cl^-$ und $CH_3CO_2^-$ ($OAc^-$)) wurden hergestellt und mittels Elementar-analyse, UV-Vis-, IR- und ferner IR-Spektroskopie und magnetischen Methoden untersucht. Die quadratisch-planaren Komplexe mit *tmen* und *medach* konnten nur als Perchlorate isoliert werden. Das Zentralatom im Chlorid- und im Acetat-Komplex ist fünffach koordiniert. Die d-d-Absorptionsbande der Perchloratkomplexe korreliert linear mit der Donorzahl von Lösungmitteln und Anionen. Die Ergebnisse werden auf der Basis des erweiterten Donor-Acceptor–Konzeptes diskutiert.

## Introduction

In preceding communications [1,2], thermodynamic and quantum mechanical studies of solvatochromic copper(II)-complexes and the donor numbers of anions in various solvents ($DN_{X,Solv}$) have been reported. A large number of studies on the solvatochromic phenomena of Cu(*β-dik*)(*diam*)*X* have been carried out by *Sone*, *Fukuda* and *Linert* [3–5]. This type of complexes can be used as color indicators for the solvent's donor strength [6–9]. From this point of view some mixed complexes of the composition (Cu(*bzyoxb*)(*diam*)*X* (*bzyoxb* = benzyl-(2-oxobutanoat), *diam* = N,N,N′,N′-tetramethylethylenediamine (*tmen*) and N-methyl-1,4-diazacycloheptane (*medach*) and $X^- = ClO_4^-$, $Cl^-$ and $OAc^-$) were recently prepared to investigate the effect of coordination of both amines and anions on the structures of these complexes and their solvatochromic properties in solutions.

## Experimental

Chemicals were obtained from Merck and Rathburn Chemicals. Solvents were purified using standard methods [10, 11]. The water content of the solvents was found by means of *Karl–Fischer* titration to be below 30 mg/l. The respective tetrabutylammonium salts were prepared according to [12]. For the anions $OAc^-$ and $CO_3^{2-}$, the ammonium salts were used.

*Synthesis of [Cu(bzyoxb)(diam)]X*: 10 mmol of $CuX_2 \cdot xH_2O$ were dissolved in 30 ml of ethanol (EtOH) and 10 mmol of benzyl-(2-oxobutanoat) (*bzyoxb*) in 30 ml $CHCl_3$ and 10 mmol of anhydrous $Na_2CO_3$ (solid) were added under vigorous stirring. Then a solution of diamine ligand (10 mmol) in 10 ml $CHCl_3$ was added under stirring, the resultant solution was filtered off and let stand overnight. The crude crystals obtained were recrystallized from nitromethane. The obtained complexes appear as fine crystals or crystalline powders; their colors, analytical data, magnetic moments and melting points are given in Table 1.

**Table 1.** Colors, analytical data[a] and magnetic moments of Cu(*bzyoxb*)(*diam*)*X* complexes (calculated values in parentheses)

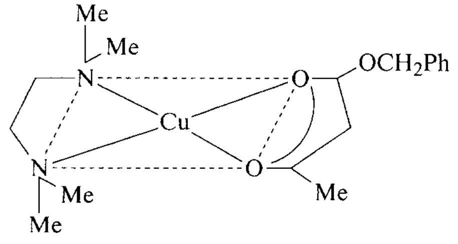
| No. | Chelate | Color | C% | H% | N% | $\mu_{eff}$(BM) | m.p. (°C) |
|---|---|---|---|---|---|---|---|
| 1 | [Cu(*bzyoxb*)(*tmen*)]$ClO_4$ | violet | 42.69 (43.41) | 5.60 (5.79) | 5.74 (5.96) | 1.72 | 154–160 |
| 2 | [Cu(*bzyoxb*)(*medach*)]$ClO_4$ | violet | 42.75 (43.59) | 4.97 (5.38) | 5.52 (5.98) | 1.68 | 195–200 |
| 3 | [Cu(*bzyoxb*)(*tmen*)Cl] | green | 48.88 (50.24) | 6.39 (6.70) | 6.77 (6.89) | 1.85 | 110–115 |
| 4 | [Cu(*bzyoxb*)(*tmen*)OAc] | green | 54.24 (53.07) | 6.75 (7.03) | 5.97 (6.51) | 1.66 | 133–138 |

[a] Calculated values are in parentheses

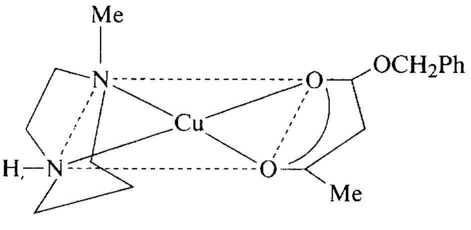
Electronic spectra of complexes in organic solvents and with different anions in nitromethane (*NM*) solution were obtained with a Hitachi U-2000 Spectrophotometer using 10 mm quartz cells thermostated at 25 °C. The following solvents have been used: 1,2-dichloroethane (*DCE*), nitromethane (*NM*), acetonitrile (*AN*), acetone (*AC*), methanol (*MeOH*), formamide (*FA*), dimethylformamide (*DMF*), dimethylsulfoxide (*DMSO*), diethylformamide (*DEF*) and hexamethylphosphoric triamide (*HMPA*). Magnetic measurements of solid complexes were performed by a magnetic suspectibility balance from Johnson Matthey Alfa products (Model MK). The IR-spektra between 600 and 4000 $cm^{-1}$ were recorded with a Perkin Elmer spectrophotometer. FT Far-IR spectra have been recorded with a NICOLET 20F Far-IR Vacuum Spectrometer (FTIR) with a TGS (room temperature) detector using polyethylene wafers. The data were treated with the *Happ–Genzel* apodization function.

## Results and Discussion

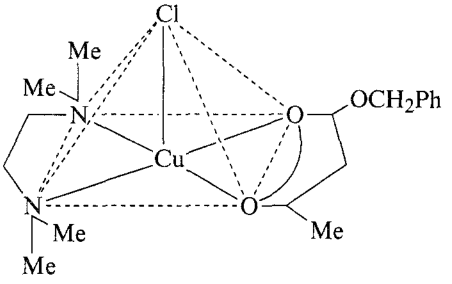
The molecular structures of the complexes under investigation are given in formulae **1–4**



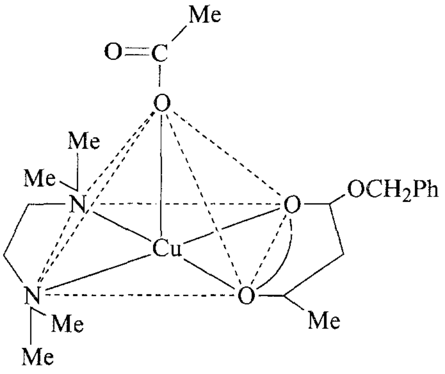
**1**) [Cu(*bzyoxb*)(*tmen*)]$ClO_4$



**2**) [Cu(*bzyoxb*)(*medach*)]$ClO_4$



3) [Cu(*bzyoxb*)(*tmen*)Cl]



4) [Cu(*bzyoxb*)(*tmen*)OAc]

The characteristic IR vibrational frequencies of the complexes are given in Table 2. The observed bands are assigned according to normal coordinate analysis of similar complexes, namely of [Cu(*acac*)$_2$] [13] and [Cu(*acac*)(*tmen*)]$^+$ [14]. The anion vibrational modes are deduced from the IR data of these complexes. The perchlorate anion does not coordinate to the copper(II), the very broad and strong band at 1100 cm$^{-1}$ and the sharp and strong band at 630 cm$^{-1}$ indicates the ionic character of ClO$_4^-$ [13]. On the other hand, the acetate and chloride anions are coordinated. The acetate complex **4** shows two bands at 1656 and 1380 cm$^{-1}$ which may be assigned as antisymmetric and symmetric vibrations for the carboxylate anion ($\Delta\nu = 276$ cm$^{-1}$). This confirms that this anion coordinates as a monodentate ligand [15]. The chloride complex **3** shows a strong band at 261 cm$^{-1}$ which is assigned to Cu–Cl stretching vibration [16]. The coordination of Cl$^-$ ion can be also supported by a negative silver nitrate test performed in aqueous solution. The magnetic data of the complexes are found in the range of $\mu_{\text{eff}} = 1.66$–$1.85$ BM as shown in Table 1, and agree with those of other four- and five-coordinated Cu(II)-complexes [3, 14].

Table 3 collects the d–d transition absorption frequencies of the copper(II)-complexes under investigation in different solvents. The d–d bands of the square planar species **1** and **2** exhibit a red-shift with increasing solvent donor numbers (DN) [17] as shown in Fig. 1. Complex **1**, [Cu(*bzyoxb*)(*tmen*)]$^+$, exhibits a stronger red-shift than complex **2** [Cu(*bzyoxb*)(*medach*)]$^+$, in all coordinating solvents. This indicates that the coordination of donor solvents to the central metal ion is more pronounced for the former than for the latter. This may be due to the rigidity of the *medach* ligand [4]. Stability constants for the coordination of donor solvents with [Ni(*acac*)(*medach*)]$^+$ and [Ni(*acac*)(*tmen*)]$^+$ support this interpretation [18]. Exceptions are found for *DMF* and *FA* solutions. These amide solvents might coordinate *via* their nitrogen site to the Cu(II) center of the complex **2** [19], whereas the bulky substituents of *DEF* make this impossible and *DEF* therefore coordinates *via* its carbonyl oxygen. A linear regression of $\nu_{\max}/kK$ *vs.* DN (Fig. 2) yields: $\nu_{\max}/kK = 17.82$–$0.075$ DN, $r = 0.97$ and $\nu_{\max}/kK = 17.51 - 0.057$ DN, $r = 0.81$ for complexes **1** and **2**, respectively. The solvatochromicity of the former complex is thus pronounced than that of the latter one and the steric hindrance of the rigid and bulky *medach* ligand corroborates the linear correlation between $\nu_{\max}$ and DN. The

**Table 2.** IR absorption frequencies of Cu(*bzyoxb*)(*diam*)*X* complexes (the same numbers as in Table 1) and their assignments

| **1** | **2** | **3** | **4** | Assignment |
|---|---|---|---|---|
| *IR-absorption maxima* | | | | |
| 1569 | 1573 | 1565 | 1573 | C=O |
| 1527 | 1527 | 1522 | 1523 | C=C |
| 1477 | 1477 | 1477 | 1477 | C=C |
| *Far-IR absorption maxima* | | | | |
| 623 s | 623 vs | 629 s | 627 s | diketonate ring |
| 605 vw | | 616 w | 603 w | Ring deformation, Cu–O$^{a}$ |
| | 591 m | 590 w | | |
| 571 vw | 577 m | 570 w | 571 vw | Ring deformation, CuO$^{a}$ |
| 553 s | 557 s | | 551 m | |
| | 543 s | | | |
| 510 s | – | | 510 w | |
| 505 m | 505 m | 504 s | 504 m | Cu–O |
| – | 498 m | 493 s | 498 s | Cu–O$^{a}$ |
| 487 vs | 487 w | | 486 w | |
| | 477 m | 480 m | | Cu–O |
| 475 vs | | 474 m | 474 s | |
| | 466 w | | 467 | |
| | 453 m | 447 m | | |
| 400 s | | | | |
| 388 w | – | | 386 s | Cu–O$^{a}$ |
| 283 s | 284 w | | 283 m | Cu–O$^{a}$ |
| – | – | 261 vs | – | Cu–Cl |
| | 256 s | | | |
| 250 w | 250 w | 250 w | 250 s | Cu–N |
| – | – | 196 w | 196 w | |
| 182 w | 185 s | 174 w | 179 m | Cu–N |
| 158 s | 161 m | 161 vw | 163 w | Cu–N |
| 153 vs | 150 s | 151vs | 151 vs | Cu–N |
| 129 w | 129 m | | | |
| 122 vs | 123 m | 124 s | | |
| 103 s | 106 m | 104 s | 104 s | |
| 97 vs | 100 m | 97 m | 96 m | |
| 88 s | 81 s | | 80 s | |

*vs* very strong, *s* strong, *m* medium, *w* weak and *vw* very weak

[a] Stretching vibration

d–d transition bands of chloride and acetate complexes **3** and **4** in various solvents show more complicated behaviour with solvent parameters than those of perchlorate complexes. For the fivefold coordinated complexes the shift of d–d bands linearly correlates with the appropriate combination of AN and DN of the solvent (AD) as shown in Fig. 3, *i.e.*, AD = 0.063 DN + 0.091 AN [2].

**Table 3.** Absorption maxima $\nu_{max}/10^3\,cm^{-1}$ (extinction coefficients are in the range 100–110 $dm^3\,mol^{-1}\,cm^{-1}$) for the Cu(*bzyoxb*)(*diam*)*X* complexes in various organic solutions at 25 °C

| Complex[a] | *HMPA* | *DMSO* | *DEF* | *DMF* | *FA* | MeOH | *AC* | *AN* | *NM* | *DCE* |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 14.95 | 15.48 | 15.74 | 15.42 | 16.0 | 16.41 | 16.86 | 16.57 | 17.62 | 17.26 |
| **2** | 15.28 | 16.06 | 16.27 | 15.08 | 15.37 | 16.72 | 17.12 | 16.92 | 17.56 | 17.11 |
| **3** | 14.53 | 14.87 | 14.23 | 14.64 | 15.95 | 16.10 | 13.82 | 14.13 | 13.93 | 13.62 |
| **4** | 14.45 | 14.79 | 14.66 | 15.35 | 16.08 | 15.56 | 14.39 | 14.55 | 14.47 | 13.91 |

[a] The same numbers as in Table 1

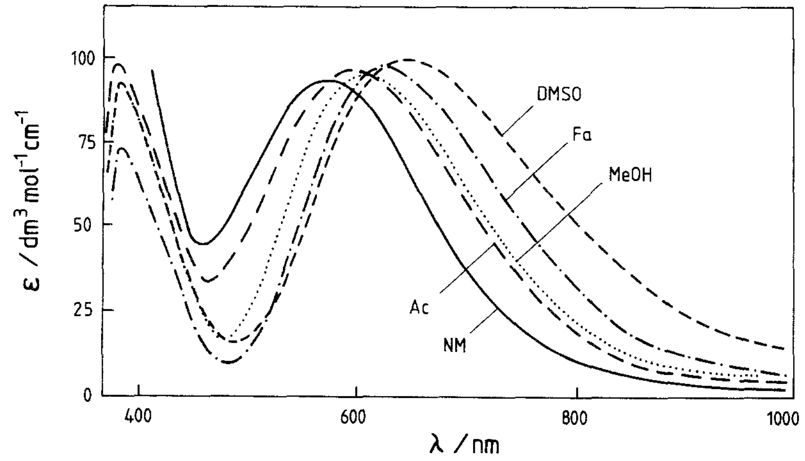


**Fig. 1.** Absorption spectra of [Cu(*bzyoxb*)(*tmen*)]$ClO_4$ in *NM*, *AC*, MeOH, *FA*, and *DMSO* solutions at 25 °C

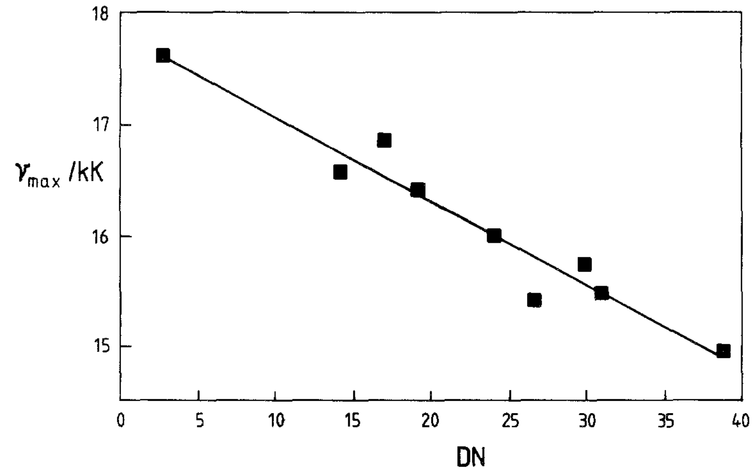


**Fig. 2.** Relation of $\nu_{max}/10^3\,cm^{-1}$ of [Cu(*bzyoxb*)(*tmen*)]$ClO_4$ with *Gutmann*'s DN of solvents

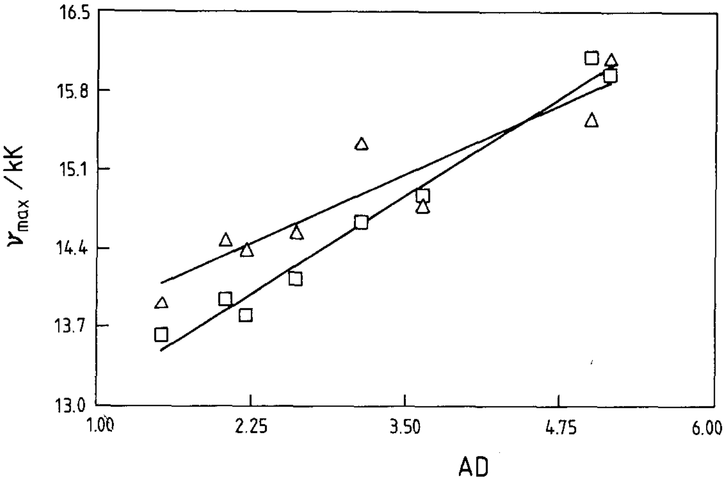


**Fig. 3.** Relation of $\nu_{max}/10^3\,cm^{-1}$ of [Cu(*bzyoxb*)(*tmen*)Cl] (□) and [Cu(*bzyoxb*)(*tmen*)OAc] (△) complexes with AD (where AD = 0.063 DN + 0.091 AN) for different solvents

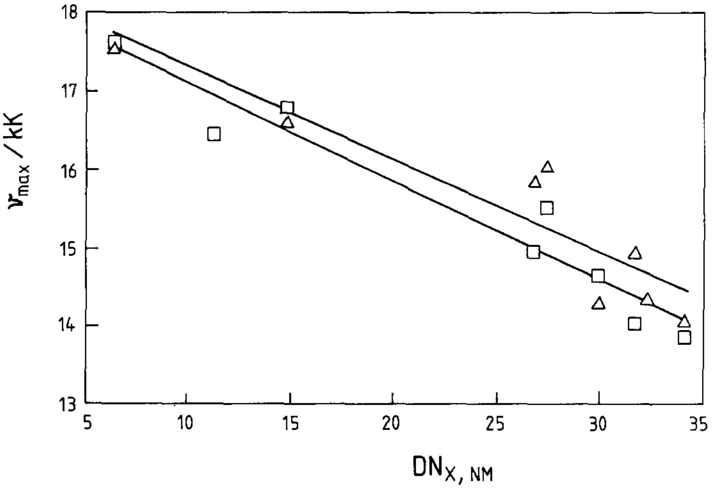


**Fig. 4.** Relation of $\nu_{max}/10^3\,cm^{-1}$ of [Cu(*bzyoxb*)(*tmen*)]$ClO_4$(□) and [Cu(*bzyoxb*)(*medach*)]$ClCO_4$ (△) complexes with $DN_{X,MN}$ of anions in *NM* solution

**Table 4.** Absorption maxima $\upsilon_{max}/10^3\,cm^{-1}$ (extinction coefficients are in the range 110–130 $dm^3\,mol^{-1}\,cm^{-1}$) of [Cu(*bzyoxb*)(*diam*)]$ClO_4$ complexes with various anions in *NM* solution at 25 °C

| Complex[a] | $ClO_4^-$ | $CF_3SO_3^-$ | $OAc^-$ | $CO_3^{2-}$ | $I^-$ | $Br^-$ | $SCN^-$ | $N_3^-$ | $Cl^-$ |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 17.62 | 16.81 | 15.52 | 16.45 | 14.95 | 14.04 | 14.65 | - | 13.87 |
| **2** | 17.56 | 16.65 | 16.06 | 16.21 | 15.86 | 14.96 | 14.32 | 14.37 | 14.08 |

[a] The same numbers as in Table 1

In all investigated solvents the perchlorate complexes exhibit higher $\nu_{max}$ values than the corresponding chloride and acetate complexes. This indicates that the perchlorate complexes in non- or very weak coordinating solvents (*DCE* or *NM*) remain square planar species since the ability of perchlorate anions to coordinate to the central metal ion is very weak. This can be expected from the donor number of the $ClO_4^-$ anions in *NM* (6.36) [2] and is supported by IR spectroscopy as discussed above. In contrary the coordination of $Cl^-$ and $OAc^-$ to the central metal ion ($Cu^{2+}$) leading to the formation of five-coordinated species [4, 5] shifts d–d bands strongly to lower frequencies at about 14 *kK* in non-coordinating solvents. This can be assigned to a distorted square-pyramidal geometry [20]. In general the chloride-complex exhibits a stronger red shift than acetate-complex. This reflects a stronger coordination ability of the former than of the latter in agreement with their donor numbers [2].

Table 4 shows a strong effect of anions on the d–d bands of perchlorate complexes **1** and **2** dissolved in *NM*. The shift to lower frequencies yield a linear correlation of $\nu_{max}$ values *vs.* the donor number of anions in *NM* [2] (see Fig. 4): $\nu_{max}/kK = 18.35 - 0.126\ DN_{x,NM}$, $r = 0.97$ and $\nu_{max}/kK = 18.49 - 0.118\ DN_{x,NM}$, $r = 0.92$ for **1** and **2** respectively.

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