

Syntheses of new copper(II) mixed-ligand complexes and their chromotropic properties in solution and in the solid state †

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Reaction of acetylacetonate (Hacac) with aldehyde (RCHO; R = *p*-MeOC₆H₄, *p*-ClC₆H₄ or Ph) in 2:1 mol ratio resulted in the formation of new triketones (HL²), which were previously characterized as bis(β-diketones) of the type [(MeCO)₂CHCHRCH(COMe)₂] (H₂L¹). Mixed-ligand copper(II) complexes with *N,N,N',N'*-tetramethylethane-1,2-diamine (tmen) and the β-diketonate moiety of these triketones, [CuCl(L²)(tmen)], were synthesized and their solvatochromic properties in organic solvents (due to the acceptor properties of the solvent) investigated. The colour of these five-co-ordinated complexes in the solid state gradually changes from green in [CuCl(L²)(tmen)] through bluish green, [CuCl(L²)(tmen)]·CH₂Cl₂, to blue, [CuCl(L²)(tmen)]·MeOH·CH₂Cl₂. Crystallographic studies showed that this phenomenon arises from an intermolecular hydrogen bond between the co-ordinated chloride of one complex and the OH group of a triketonate ligand of an adjacent complex and/or cocrystallized MeOH molecule.

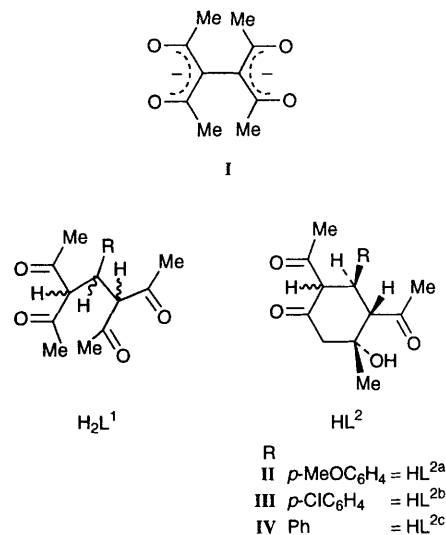
We previously reported the syntheses and characterization of mixed-ligand complexes of the type [M(dik)(diam)]X containing *N*-alkylated diamines (diam) and β-diketonates (dik) [M = Cu or Ni, dik = acetylacetonate (acac), benzoylacetonate (bzac), dibenzoylmethanate (dbm), 1,1,1-trifluoroacetylacetonate (tfac), 1,1,1,5,5,5-hexafluoroacetylacetonate (hfac) or dipivaloylmethanate (dpm); diam = *N,N,N',N'*-tetramethylethane-1,2-diamine (tmen), *N,N'*- or *N,N*-dimethyl (dmen) or diethyl-ethane-1,2-diamine (deen); X = ClO₄⁻, BPh₄⁻ or NO₃⁻].¹⁻⁷ Moreover, binuclear mixed-ligand complexes of the type [M₂(tek)(diam)₂]X₂ were synthesized, where tek is a branched tetraketonate containing two β-diketonates such as tetraacetylthanedide (taed), I, or diacetyldibenzoylthanedide (dabed).⁸⁻¹² These complexes, which are very soluble in organic solvents, show characteristic solvatochromic behaviour in solution.

In continuing these studies we tried to synthesize similar binuclear complexes with a bis(β-diketone) ligand, H₂L¹, containing a spacer between two acetylacetonate moieties. Only a few reports have appeared on metal complexes of these bis(β-diketones).¹³⁻¹⁵ For the synthesis of H₂L¹ we have adopted Shamma's method,¹⁶ which includes condensation of two molecules of acetylacetonate and one of aldehyde (RCHO). However, analysis by ¹H and ¹³C NMR spectroscopy revealed that the correct structure of the product of Shamma's reaction is the triketone HL² rather than the previously evaluated H₂L¹. We report herein the synthesis and characterization of new mononuclear copper(II) mixed-ligand complexes of the type [CuCl(L²)(tmen)]·CH₂Cl₂, utilizing II-IV as ligands.¹⁷

Experimental

Materials

All chemicals were obtained from Wako Pure Chemical Industrial Co. Ltd. Solvents for spectroscopic and conductivity measurements were 'spectro-grade' used as obtained.



Physical measurements

Electronic spectra of solutions were obtained with an UV-3100 PC Shimadzu spectrophotometer using 10 mm quartz cells at room temperature, powder reflectance spectra with the same instrument equipped with an integrating sphere and using BaSO₄ as the reference. Infrared spectra were recorded in KBr pellets with a Shimadzu FT-IR 4000 spectrometer in the range 400–4000 cm⁻¹. Magnetic susceptibility measurements were performed with a Sherwood Scientific Magnetic Susceptibility Balance (M.B.S) at room temperature using [NH₄]₂Fe[SO₄]₂·6H₂O as the standard sample for calibration. Electric conductivity measurements were performed with a Denki Kagaku Keiki AOC-10 instrument at 25 °C. Proton and ¹³C-¹H NMR spectra were obtained with a JEOL JNM-GX 270 Fourier-transform spectrometer, using CDCl₃ as solvent and SiMe₄ as reference (see Fig. 1 for assignment of ¹H NMR signals). Melting-point measurements and TG-DTA were performed with a TG-DTA 2000S Mac Science instrument. The FAB mass spectra were recorded on a Shimadzu concept IS instrument.

† Non-SI unit employed: μ_B ≈ 9.27 × 10⁻²⁴ J T⁻¹.

Syntheses

Compound II. According to Shamma's method,¹⁶ acetylacetone (Hacac) (0.1 mol) and *p*-anisaldehyde (0.05 mol) were mixed in 95% EtOH (30 cm³) and 10 drops of piperidine were added as a base catalyst. The mixture was allowed to stand at room temperature; a few days later white *crystals* of compound **II** appeared, which were recrystallized from benzene–MeOH, washed with 50% EtOH and dried *in vacuo*, m.p. 174.4 °C (Found: C, 67.90; H, 6.55%; *M*⁺, 318. C₁₈H₂₂O₅ requires C, 67.90; H, 7.00%; *M*⁺, 318); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (KBr) 3412m (OH), 1720s, 1693vs (CO), 1612m (CO, C=C). λ_{\max}/nm (2.5 × 10⁻⁴ mol dm⁻³, EtOH) 230 (ϵ 10 420), 276 (1768) and 282 (1540 dm³ mol⁻¹ cm⁻¹). NMR (CDCl₃): ¹H (270.1 MHz), δ 1.3 (3 H, s, CH₃), 1.7 (3 H, s, CH₃), 2.0 (3 H, s, CH₃), 2.5 (1 H, dd, *J* = 14, 2.3, CH₂), 2.6 (1 H, d, *J* = 14, CH₂), 3.2 (1 H, d, *J* = 11, H³), 3.7 (1 H, d, *J* = 12, H¹), 3.77 (3 H, s, aryl OCH₃), 3.92 (1 H, t, *J* = 12, H²), 3.97 (1 H, d, *J* = 2.3, OH⁴), 6.8 (2 H, d, *J* = 8, aromatic CH), and 7.1 (2 H, d, *J* = 9 Hz, aromatic CH); ¹³C (67.94 MHz), δ 28.4, 30.2, 34.4, 44.8, 53.5 (CH₂), 55.2 (OCH₃), 61.7, 68.0, 73.8, 114.6, 128.8, 129.9, 159.0, 203.9, 204.1 and 215.3.

Compound III. Acetylacetone (0.1 mol) and *p*-chlorobenzaldehyde (0.05 mol) were mixed with 10 drops of piperidine in 95% EtOH (30 cm³) to give white *crystals* of compound **III**, m.p. 179 °C (Found: C, 63.25; H, 5.85%; *M*⁺, 322. C₁₇H₁₉ClO₄ requires C, 63.25; H, 5.95%; *M*⁺, 322); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (KBr) 3410s (OH), 1720vs, 1695vs (CO). λ_{\max}/nm (2.5 × 10⁻⁴ mol dm⁻³, EtOH) 223 (ϵ 13 053), 268 (536) and 276 (526 dm³ mol⁻¹ cm⁻¹). NMR (CDCl₃): ¹H (270.1 MHz), δ 1.3 (3 H, s, CH₃), 1.7 (3 H, s, CH₃), 2.0 (3 H, s, CH₃), 2.5 (1 H, dd, *J* = 14, 2.3, CH₂), 2.6 (1 H, d, *J* = 14, CH₂), 3.2 (1 H, d, *J* = 12, H³), 3.7 (1 H, d, *J* = 12, H¹), 3.8 (1 H, d, *J* = 2.3, OH⁴), 3.9 (1 H, t, *J* = 12, H²), 7.1 (2 H, d, *J* = 8.5, aromatic CH) and 7.3 (2 H, d, *J* = 8.5 Hz, aromatic CH); ¹³C (67.94 MHz), δ 28.3, 30.6, 34.4, 44.6, 53.5 (CH₂), 61.4, 67.4, 73.7, 129.0, 129.3, 133.7, 136.8, 203.3, 203.4 and 214.4.

Compound IV. Since the reaction between acetylacetone and benzaldehyde occurs easily, equimolar amounts (0.5 mol) of each were mixed in 70% EtOH (60 cm³) and 20 drops piperidine were added. Compound **IV** was obtained as white *crystals*, m.p. 167.8 °C (Found: C, 71.00; H, 6.95%; *M*⁺, 288. C₁₇H₂₀O₄ requires C, 71.00; H, 7.00%; *M*⁺, 288); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (KBr) 3431s (OH), 1718vs, 1693vs (CO). λ_{\max}/nm (2.5 × 10⁻⁴ mol dm⁻³, EtOH) 260 (ϵ 488), 265 (516) and 284 (568 dm³ mol⁻¹ cm⁻¹). NMR (CDCl₃): ¹H (270.1 MHz), δ 1.3 (3 H, s, CH₃), 1.6 (3 H, s, CH₃), 2.0 (3 H, s, CH₃), 2.5 (1 H, dd, *J* = 14, 2.6, CH₂), 2.6 (1 H, d, *J* = 14, CH₂), 3.2 (1 H, d, *J* = 11.5, H³), 3.8 (1 H, d, *J* = 12.4, H¹), 3.97 (1 H, t, *J* = 12, H²), 3.98 (1 H, d, *J* = 2.6 Hz, OH⁴) and 7.1–7.3 (5 H, m, aromatic ring); ¹³C (67.94 MHz), δ 28.4, 30.4, 34.4, 45.5, 53.5 (CH₂), 61.6, 67.7, 73.9, 127.7, 128.0, 129.3, 138.2, 203.8, 203.9 and 215.1.

Copper(II) complexes. The mixed-ligand copper(II) complexes were synthesized by mixing CuCl₂·2H₂O, tmen, HL² and KOH in the molar ratio 1:1:1:1 in EtOH. After filtration and reduction of the volume of the filtrate under reduced pressure, the *crystals* (with L^{2a}, L^{2b}) or gummy product (with L^{2c}) precipitated, were collected and recrystallized from dichloromethane–diethyl ether. Bluish green *crystals* of [CuCl(L^{2a})(tmen)]·CH₂Cl₂ **1** were obtained (Found: C, 48.85; H, 6.45; N, 4.70%; *M*⁺, 531. C₂₄H₃₉Cl₃CuN₂O₅ requires C, 48.60; H, 6.70; N, 4.70%; *M*⁺, 531). $\mu = 1.89 \mu_{\text{B}}$. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (KBr) 1696s, 1587vs (CO).

With HL^{2b}, depending on ratio of CH₂Cl₂ to ether and temperature, two types of *crystals* were obtained in different yields, which were separated by hand: bluish green **2** and green **3**. The main product was [CuCl(L^{2b})(tmen)]·CH₂Cl₂ **2** (Found: C, 46.35; H, 6.05; N, 4.60%; *M*⁺, 535. C₂₄H₃₆Cl₄CuN₂O₄

requires C, 46.35; H, 5.85; N, 4.50%; *M*⁺, 535). $\mu = 1.90 \mu_{\text{B}}$. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (KBr) 1699vs, 1587vs (CO). Complex [CuCl(L^{2b})(tmen)] **3** (Found: C, 51.20; H, 6.50; N, 5.50. C₂₃H₃₄Cl₂CuN₂O₄ requires C, 51.45; H, 6.40; N, 5.20%). Recrystallization of **2** from a [MeOH (1 drop) + CH₂Cl₂ (0.5 cm³)]–hexane solution resulted in blue *crystals* of [CuCl(L^{2b})(tmen)]·MeOH·CH₂Cl₂ **4** (Found: C, 46.40; H, 5.90; N, 4.25. C₂₅H₄₀Cl₄CuN₂O₅ requires C, 45.90; H, 6.15; N, 4.30%).

With HL^{2c}, bluish green *crystals* of [CuCl(L^{2c})(tmen)]·CH₂Cl₂ **5** were obtained from CH₂Cl₂–hexane solution: (Found: C, 48.70; H, 6.60; N, 4.95%; *M*⁺, 501. C₂₄H₃₇Cl₃CuN₂O₄ requires C, 49.05; H, 6.35; N, 4.80%; *M*⁺, 501). $\mu = 1.94 \mu_{\text{B}}$. $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (KBr) 1696s, 1587vs (CO).

The complex [CuCl(acac)(tmen)]⁶ **6** was obtained by mixing CuCl₂·2H₂O, tmen, Hacac and Na₂CO₃ in a 1:1:1:0.5 molar ratio in EtOH, filtering the mixture and concentrating the filtrate. Recrystallization from CH₂Cl₂–hexane gave an analytically pure sample (Found: C, 42.05; H, 7.65; N, 9.00. Calc. for C₁₁H₂₃ClCuN₂O₂: C, 42.05; H, 7.45; N, 8.90%).

Crystallography

Single *crystals* of complexes **1** and **3** were obtained by slow diffusion of ether into their CH₂Cl₂ solutions. Blue *crystals* of **4** were obtained from its MeOH + CH₂Cl₂ (1 drop:0.5 cm³) solution by slow diffusion of hexane. Blue *crystals* of [CuCl(acac)(tmen)] **6** were obtained by adding hexane to its CH₂Cl₂ solution. Diffraction data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$). Cell constants and the orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 reflections in the ranges 35.48 < 2 θ < 38.64 for **1**, 35.82 < 2 θ < 39.53 for **3**, 36.54 < 2 θ < 39.88 for **4** and 38.93 < 2 θ < 39.84° for **6**. The data were processed using the TEXSAN crystallographic package,¹⁸ and were corrected for Lorentz–polarization effects. Empirical absorption corrections were applied for all *crystals*.

The structures were solved by Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms except for that of OH in **1**, **3** and **4** were placed at calculated positions and included in the final stage of refinements with fixed isotropic parameters. The hydrogen atoms in the OH groups were found in the Fourier-difference maps, and included in refinements with fixed isotropic parameters. Reflection data were collected in the ω –2 θ scan technique up to 2 $\theta = 55^\circ$. Stationary background counts were recorded on each side of the reflection. A total of 3807 reflections for **1**, 6133 for **3**, 7816 for **4** and 3753 for **6** were collected at a rate of 16.0° min⁻¹ (in ω). The final cycle of full-matrix least-squares refinement on *F* was based on 2428, 4015, 3097 and 2536 observed reflections [*I* > 3.00 σ (*I*)], respectively. The maximum and minimum peaks on the final Fourier-difference map of **1** corresponded to 0.41 and –0.28 e \AA^{-3} , respectively, and of **3**, 0.58 and –0.52 e \AA^{-3} . For **4** these values were 0.50 and –0.49 e \AA^{-3} , and of **6**, 0.45 and –0.92 e \AA^{-3} . Final *R* (and *R'*) was 0.043 (0.025) for **1**, 0.046 (0.033) for **3**, 0.059 (0.059) for **4** and 0.050 (0.051) for **6**. For **1**, belonging to monoclinic space group *Cc*, the coordinates of all atoms were inverted and the complete structure was refined again. In this case the final residuals were *R* = 0.049 and *R'* = 0.029, which are higher than those for the first enantiomorph. Crystal data are listed in Table 1.

Atomic scattering factors were taken from ref. 19, and anomalous dispersion effects were included; values for $\Delta f'$ and $\Delta f''$ were taken from ref. 20.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the

CCDC for this material should quote the full literature citation and the reference number 186/89.

Results and Discussion

Nature of proligands

The procedure for the synthesis of the desired bis(β -diketone) pro-ligands was the same as reported by Shamma and co-workers.¹⁶ However, ^1H and ^{13}C NMR chemical shifts for all three showed that the reaction of Hacac and aldehyde (mole ratio 2:1) in the presence of piperidine as base catalyst resulted in the formation of a new type of triketone, HL^2 , via Michael reaction followed by an intramolecular aldol condensation. The compounds H_2L^1 and HL^2 are isomers, which are indistinguishable by elemental analysis and molecular weight determinations. Also their infrared absorption bands are very similar, where that $\approx 3400\text{ cm}^{-1}$ is assigned to the OH group connected to the six-membered ring. This band was previously assigned to the OH vibration of the enolic form.¹⁶

These triketones have four chiral centres but NMR analysis revealed that only one (racemic) stereoisomer was selectively obtained in each case. In the ^1H NMR spectra of **II–IV** the diastereotopic CH_2 protons (H^5 , H^6) give rise to an AB pattern in the range δ 2.5–2.6 (Fig. 1). Moreover, there is weak coupling between the hydroxyl (COH^4) proton and one of the hydrogen atoms in CH_2 , resulting in two doublets ($J \approx 2\text{ Hz}$). The same coupling effect is present in the OH^4 peak which appears as a doublet ($J \approx 2\text{ Hz}$) in the range δ 3.8–3.9. This splitting disappeared on addition of D_2O due to ready exchange of the OH^4 proton with deuterium.

By comparing with acetylacetone, Hacac, which exists as the enol form (80%) in EtOH ,²¹ the β -diketone moiety of these triketones is found to have a low tendency to enolization: the ^1H NMR spectrum of Hacac exhibits signals of both enol and keto forms and the peak at $\delta \approx 13$ is assigned to the OH proton of the enolic form, while in the spectra of **II–IV** the keto form is strongly favoured as is apparent from the absence of corresponding resonances for the enolic form.

Infrared spectra

For all the triketones two sharp bands in the region $1725\text{--}1695\text{ cm}^{-1}$ were observed which are characteristic of the $\nu(\text{C}=\text{O})$ vibration. Also, an intense band appeared at $3450\text{--}3420\text{ cm}^{-1}$ due to the OH stretching vibration. The spectra of the mixed-ligand copper complexes exhibit two bands in the region $1699\text{--}1584\text{ cm}^{-1}$. That at $1699\text{--}1696\text{ cm}^{-1}$ is probably due to unchelated $\nu(\text{C}=\text{O})$ vibrations and that at 1587 cm^{-1} with high intensity is characteristic of the mixed modes of vibration arising due to contributions from $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ of the co-ordinated β -diketonate groups. The shift suggests complex formation through the carbonyl groups at β positions.²²

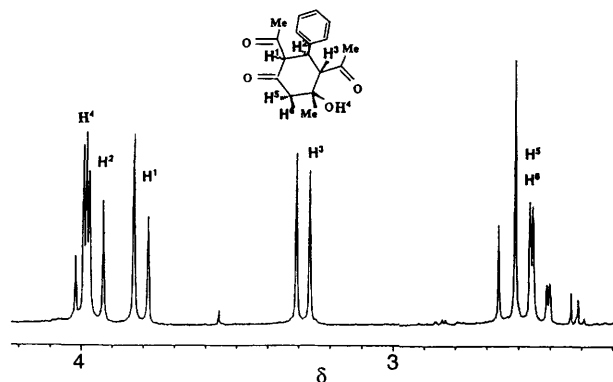


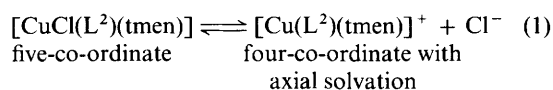
Fig. 1 Proton NMR spectrum of compound **IV** in the range δ 2–4

Solution study

The absorption maxima of the d–d bands of $[\text{CuCl}(\text{L}^2)(\text{tmen})]\cdot\text{CH}_2\text{Cl}_2$ in various organic solvents are given in Table 1. In general, when such a five-co-ordinate copper chelate molecule dissolves in non-polar solvents, e.g. CH_2Cl_2 and $\text{C}_2\text{H}_4\text{Cl}_2$, the structure remains square pyramidal. However, in polar solvents such as water or alcohols the co-ordinated Cl^- will be surrounded by solvent molecules which pull it out of the co-ordination sphere. At the same time other solvent molecules will try to attack the copper(II) ion directly to form a solvated chelate cation. This phenomenon, in which a structural change from a square pyramid to an elongated octahedral occurs, results in a change in electronic configuration and d-orbital splitting of Cu^{2+} , leading to a colour change: as a five-co-ordinate species in non-polar solvents such as dichloroethane the colour is green, and as a solvated square-planar molecule in polar solvents such as MeOH the colour is blue.

When the anion is $\text{X} = \text{ClO}_4^-$ or BPh_4^- in $[\text{Cu}(\text{dik})(\text{tmen})]\text{X}$ the axial sites of the chelate cation are open to direct attack by polar solvent molecules. In the case of anions with co-ordination ability, such as chloride in the present case, the situation is different and the solvent molecules must first drive out the firmly bound Cl^- anion from the co-ordination sphere. The Cu–Cl bond is weakened by this interaction, and the chloride anion finally dissociates. Subsequently the chelate cation will be readily solvated. Thus, the most important characteristic of the solvent for a colour change must be its power to solvate the anion, i.e. its acceptor ability which is expressed in terms of the acceptor number A_N .²⁴ Fig. 2 shows the observed absorption maxima for complexes **1**, **2** and **5** in organic solvents versus the solvents A_N . A linear relation with good reliability factor ($R > 0.97$) was found for all three complexes; regression versus donor number, D_N ,²⁵ reveals no relation and also a multiple regression of A_N and D_N results in no improvement. In the case of $[\text{CuCl}(\text{acac})(\text{tmen})]$, not only A_N , but an appropriate combination of A_N and D_N , seems to be important.^{7,26}

The equilibrium (1) involving dissociation and formation of



the five-co-ordinate complex is shifted to the right with increasing solvent acceptor properties. The conductivity of complexes **1**, **2** and **5** was measured in different organic solvents and the data are presented in Table 1. Compared with the reported conductivity data for 1:1 species,²³ in high acceptor solvents such as MeOH, EtOH and Me_2SO the extent of ionization is high and the blue, four-co-ordinated species with axial solvation is predominant. However, in solvents with low

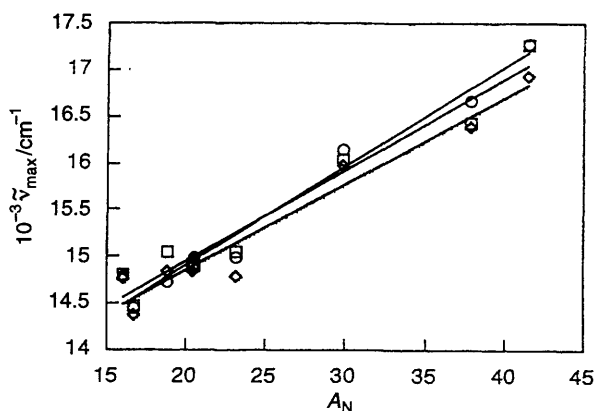
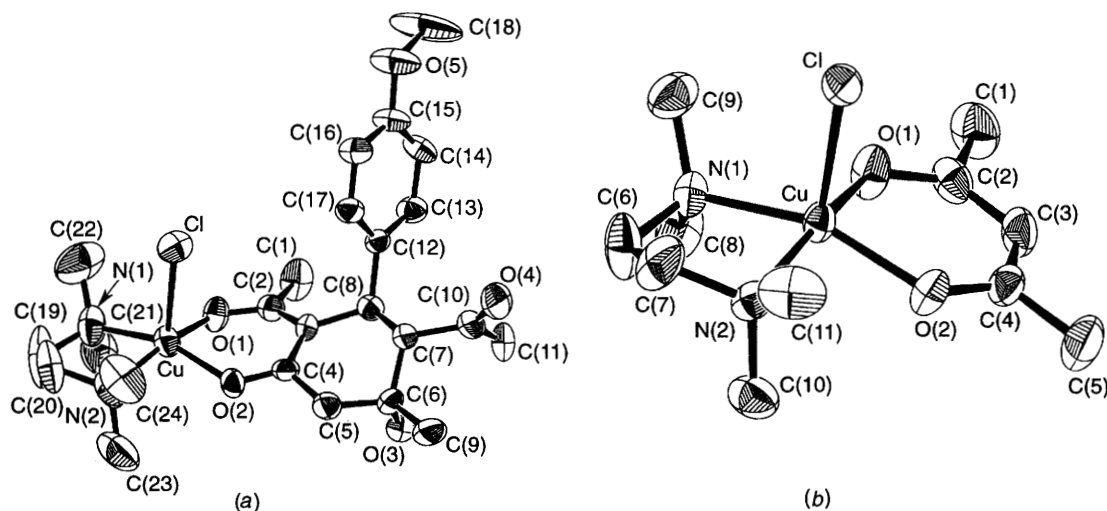


Fig. 2 Variation of absorption maxima ($\bar{\nu}_{\text{max}}$) with acceptor number (A_N) of the solvent for complexes **1** (\circ), **2** (\square) and **5** (\diamond)

Table 1 Values of $\tilde{\nu}_{\max}$, ϵ_{\max} ^a and conductivity (Λ_M)^b of [CuCl(L²)(tmen)]·CH₂Cl₂ in solid state^c and various solvents at room temperature

| | 1 | | | 2 | | | 5 | | | Colour | Conductivity of 1:1 electrolytes, ^d Λ | |
|---|-------|----------------------|-------------------|-------------|----------------------|-------------------|-------------|----------------------|-------------------|--------|--|-------------|
| | A_N | $\tilde{\nu}_{\max}$ | ϵ_{\max} | Λ_M | $\tilde{\nu}_{\max}$ | ϵ_{\max} | Λ_M | $\tilde{\nu}_{\max}$ | ϵ_{\max} | | | Λ_M |
| Solid | — | 15.81 | — | — | 15.33 | — | — | 14.87 | — | — | Bluish green | |
| MeOH | 41.5 | 17.27 | 137.2 | 79.2 | 17.26 | 135.4 | 79.8 | 16.92 | 137.6 | 81.6 | Blue | 80–115 |
| EtOH | 37.9 | 16.67 | 146.4 | 30.4 | 16.43 | 151.3 | 28.5 | 16.39 | 156.7 | 30.1 | Blue | 35–45 |
| Me ₂ SO | 29.8 | 16.14 | 137.6 | 41.1 | 16.03 | 139.7 | 28.6 | 15.97 | 158.2 | 30.6 | Blue | 50–70 |
| HCONMe ₂ | 16.0 | 14.79 | 137.1 | 19.1 | 14.80 | 125.9 | 24.4 | 14.77 | 137.0 | 23.0 | Green | 65–90 |
| MeCN | 18.9 | 14.72 | 149.3 | 21.4 | 15.05 | 140.6 | 23.3 | 14.84 | 149.2 | 25.4 | Green | 120–160 |
| MeNO ₂ | 20.5 | 14.98 | 148.8 | 27.6 | 14.90 | 147.8 | 34.1 | 14.96 | 157.2 | 35.6 | Green | 75–95 |
| CH ₂ Cl ₂ | 20.4 | 14.88 | 173.2 | 1.4 | 14.91 | 171.5 | 3.8 | 14.84 | 173.7 | 4.0 | Green | |
| 1,2-C ₂ H ₄ Cl ₂ | 16.7 | 14.45 | 170.0 | 4.3 | 14.47 | 170.8 | 4.47 | 14.37 | 175.9 | 6.26 | Green | 10–20 |

^a 0.01 mol dm⁻³ solutions; $\tilde{\nu}_{\max}$ in 10³ cm⁻¹, ϵ_{\max} in dm³ mol⁻¹ cm⁻¹. ^b Conductivities (Ω^{-1} cm² mol⁻¹) of 1.0 × 10⁻³ solutions were measured at 25 °C. ^c Solid reflectance spectra show broad peaks. ^d Ref. 23.

**Fig. 3** The ORTEP diagrams for compounds **1** (a) and **6** (b) with the labelling scheme

A_N such as CH₂Cl₂ and 1,2-C₂H₄Cl₂ the ionization is low and green, five-co-ordinated species are favoured.

The ligand-field strengths of L^{2a}, L^{2b} and L^{2c} were estimated, by comparing $\tilde{\nu}_{\max}$ of their mixed-ligand copper(II) complexes (**1**, **2**, **5**) in the non-polar solvent dichloroethane. By comparison to [CuCl(acac)(tmen)] ($\tilde{\nu}_{\max}$ 14.03 × 10³ cm⁻¹), the following order was obtained: L^{2a} ≈ L^{2b} > L^{2c} > acac.

Solid-state study

The solid reflectance spectra of all the mixed-ligand copper complexes **1–6** were measured. In the case of the acac complex **6** the $\tilde{\nu}_{\max}$ (14.21 × 10³ cm⁻¹) is very similar to that of in 1,2-dichloroethane (14.03 × 10³ cm⁻¹), which means that the complex has same structure in both states: five-co-ordinate, square pyramidal (green). However, for [CuCl(L²)(tmen)]·CH₂Cl₂ complexes (bluish green), the $\tilde{\nu}_{\max}$ in solid state (15.81 × 10³, 15.33 × 10³, 14.87 × 10³ cm⁻¹ for **1**, **2** and **5**, respectively) are considerably higher than in 1,2-C₂H₄Cl₂ (see Table 2). Moreover, for green [CuCl(L^{2b})(tmen)] **3**, without cocrystallized solvent molecules, the $\tilde{\nu}_{\max}$ values in the solid state (14.21 × 10³ cm⁻¹) and in 1,2-C₂H₄Cl₂ (14.47 × 10³ cm⁻¹) are similar, as for **6**. On the other hand, when this species is recrystallized from 1,2-C₂H₄Cl₂–MeOH, blue crystals of [CuCl(L^{2b})(tmen)]·MeOH·CH₂Cl₂ **4** ($\tilde{\nu}_{\max}$ = 15.60 × 10³ cm⁻¹) were obtained.

In order to explain these differences the crystal structures of complexes **1**, **3**, **4** and **6** were determined by X-ray diffraction analysis. Selected bond distances and angles are given in Table 3. The ORTEP²⁷ diagrams showing the molecular structures of **1** (which confirms the stereochemistry of L²) and **6** are given in

Fig. 3. The Cu atom has a square-pyramidal co-ordination, where the two N atoms of tmen and the two O atoms of the β -diketonate moiety (L² or acac) form the basal plane and the Cl atom occupies the apical site. The displacement of Cu atom from the average basal plane is 0.309 Å in **1**, 0.329 Å in **3**, 0.268 Å in **4** and 0.322 Å in the acac complex **6**.

In the green crystal of complex **6** the Cu–Cl bond length is 2.500(2) Å and the metal–donor distances in the basal plane are Cu–O(1) 1.956(4), Cu–O(2) 1.969(4), Cu–N(1) 2.085(4) and Cu–N(2) 2.049(4) Å; there is no intermolecular interactions between individual molecules [Fig. 4(a)].

In the green crystal of complex **3** there is weak hydrogen bonding C–O(4)···H–O(3) (1.97 Å) between two adjacent molecules as evidenced by the O(3)···O(4) distance of 2.918(4) Å; but the Cl atom has no participation in weak intermolecular interactions [Fig. 4(b)]. In this case the Cu–Cl bond length is 2.486(1) Å and in the basal plane the distances are Cu–O(1) 1.939(2), Cu–O(2) 1.943(3), Cu–N(1) 2.082(3) and Cu–N(2) 2.060(3) Å. Since both **3** and **6** exist as individual molecules (without any interaction *via* the chloride anions) in the solid state they present similar electronic spectral behaviour in the solid-state and in 1,2-C₂H₄Cl₂ solution.

In bluish green crystals of complex **1**, the orientation of the molecules in the unit cell involves weak intermolecular hydrogen-bond interactions Cu–Cl···H–O(3) (2.26 Å) as evidenced by Cl···O(3) 3.199(4) Å [Fig. 4(c)]. This interaction results in elongation of the Cu–Cl bond length to 2.527(2) Å, followed by compression of the copper–donor atom distances in the basal plane: Cu–O(1) 1.925(4), Cu–O(2) 1.926(4), Cu–N(1) 2.055(6) and Cu–N(2) 2.072(5) Å. Here, the copper atom is closer to the basal plane (0.309 Å compared with 0.329 Å

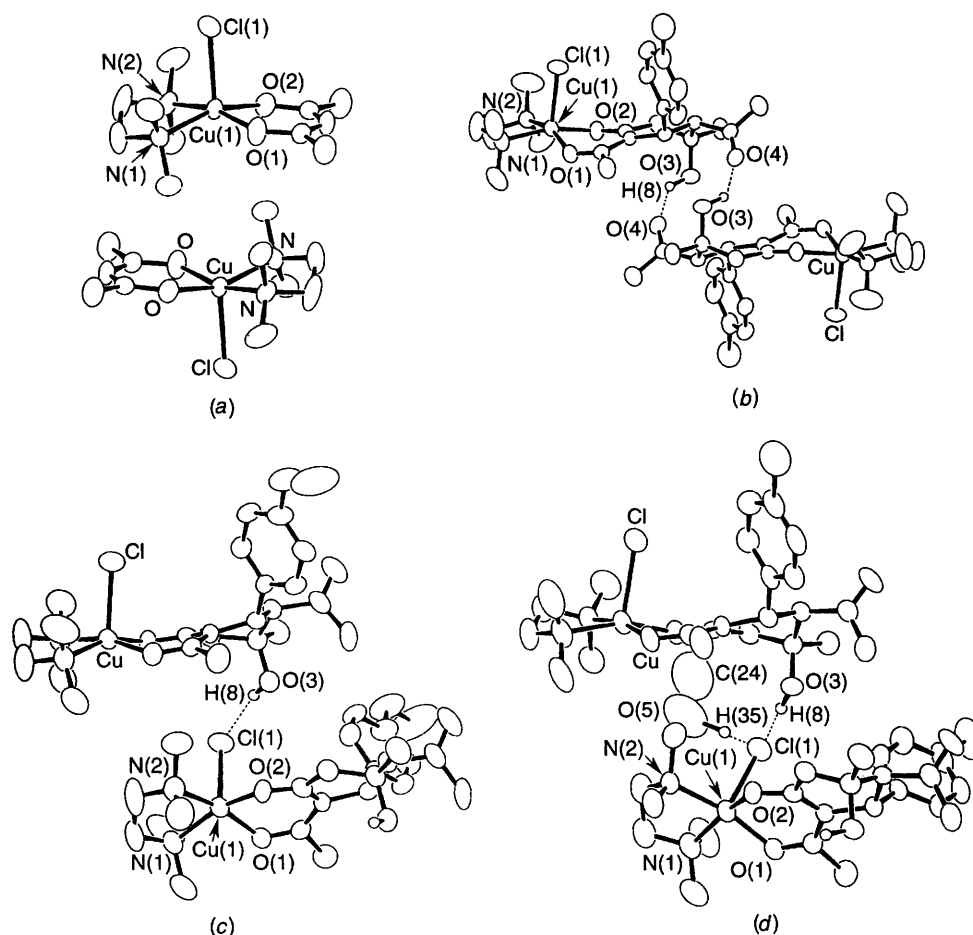


Fig. 4 Orientation of molecules in the unit cell for compounds **6** (a), **3** (b), **1** (c) and **4** (d). The intermolecular hydrogen bonds are shown by dashed lines

Table 2 Crystal data for compounds **1**, **3**, **4** and **6**

| | 1 [CuCl(L ^{2a})(tmen)]·CH ₂ Cl ₂ | 3 [CuCl(L ^{2b})(tmen)] | 4 [CuCl(L ^{2b})(tmen)]·MeOH·CH ₂ Cl ₂ | 6 [CuCl(acac)(tmen)] |
|---|---|---|---|---|
| Formula | C ₂₅ H ₃₉ Cl ₃ CuN ₂ O ₅ | C ₂₃ H ₃₄ Cl ₂ CuN ₂ O ₄ | C ₂₅ H ₄₀ Cl ₄ CuN ₂ O ₅ | C ₁₁ H ₂₃ ClCuN ₂ O ₂ |
| <i>M</i> | 617.50 | 536.98 | 653.96 | 314.31 |
| Colour | Bluish green | Green | Blue | Green |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Monoclinic |
| Crystal size/mm | 0.20 × 0.50 × 0.60 | 0.20 × 0.25 × 0.25 | 0.40 × 0.40 × 0.60 | 0.30 × 0.35 × 0.45 |
| Space group | <i>Cc</i> (no. 9) | <i>P</i> $\bar{1}$ (no. 2) | <i>P</i> ₂ ₁ / <i>c</i> (no. 14) | <i>P</i> ₂ ₁ / <i>n</i> (no. 14) |
| <i>a</i> /Å | 11.678(1) | 12.048(2) | 11.966(3) | 9.6428(8) |
| <i>b</i> /Å | 22.284(1) | 12.318(2) | 23.480(6) | 12.2285(8) |
| <i>c</i> /Å | 11.816(1) | 10.618(2) | 11.249(4) | 13.1211(7) |
| α /° | — | 95.40(1) | — | — |
| β /° | 91.000(7) | 114.02(1) | 91.66(2) | 107.360(5) |
| γ /° | — | 63.311(10) | — | — |
| <i>U</i> /Å ³ | 3074.2(4) | 1278.3(4) | 3159(1) | 1476.7(2) |
| <i>Z</i> | 4 | 2 | 4 | 4 |
| <i>D</i> _c /g cm ⁻³ | 1.334 | 1.395 | 1.375 | 1.414 |
| μ /cm ⁻¹ | 10.05 | 10.93 | 10.64 | 16.53 |
| <i>F</i> (000) | 1292.00 | 562.00 | 1364.00 | 660.00 |
| <i>R</i> ^a | 0.043 | 0.046 | 0.059 | 0.050 |
| <i>R</i> ^b | 0.025 | 0.033 | 0.059 | 0.051 |
| Goodness of fit indicator | 2.51 | 2.46 | 2.44 | 5.28 |

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R' = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, $w = 1/\sigma^2(F_o)$.

in **3**). As a result of this structural distortion, the interaction of the d orbitals of the copper with the molecular orbitals of the ligands in the basal plane is increased, which affects the degeneracy of the d orbitals, electronic absorption and colour of complex (from green to bluish green). Since the ligand-field strengths of compounds **II** and **III** are almost the same, the same structure would be expected for **1** and **2**.

In blue crystals of complex **4**, again weak hydrogen-bond interaction occurs Cu—Cl···H—O(3) (2.14 Å), Cl···O(3)

3.237(5) Å. Moreover, cocrystallization of MeOH molecules with the complex causes an additional hydrogen bond between the OH of MeOH and the chloride anion, O(5)—H···Cl—Cu (1.98 Å), Cl···O(5) 3.11(1) Å [Fig. 4(d)]. Owing to these two hydrogen-bonding interactions, the Cu—Cl distance is increased to 2.607(2) Å. This elongation results in shortening of the copper—donor atom distances in the basal plane: Cu—O(1) 1.921(4), Cu—O(2) 1.908(4), Cu—N(1) 2.034(5) and Cu—N(2) 2.062(6) Å. Again this brings more distortion from a square-

Table 3 Selected bond lengths (Å) and angles (°)

| | 1 | 3 | 4 | 6 |
|--------------|----------|-----------|----------|----------|
| Cu–N(1) | 2.055(6) | 2.082(3) | 2.034(5) | 2.085(4) |
| Cu–N(2) | 2.072(5) | 2.060(3) | 2.062(6) | 2.049(4) |
| Cu–Cl | 2.527(2) | 2.486(1) | 2.607(2) | 2.500(2) |
| Cu–O(1) | 1.925(4) | 1.939(2) | 1.921(4) | 1.956(4) |
| Cu–O(2) | 1.926(4) | 1.943(3) | 1.908(4) | 1.969(4) |
| O(1)–C(2) | 1.273(6) | 1.264(4) | 1.279(7) | 1.268(6) |
| O(2)–C(4) | 1.270(7) | 1.278(4) | 1.275(7) | 1.286(6) |
| C(2)–C(3) | 1.396(7) | 1.415(5) | 1.409(8) | 1.388(8) |
| C(3)–C(4) | 1.423(8) | 1.386(4) | 1.386(8) | 1.379(8) |
| C(1)–C(2) | 1.515(8) | 1.510(5) | 1.511(9) | 1.490(7) |
| C(4)–C(5) | 1.495(7) | 1.514(5) | 1.511(8) | 1.490(8) |
| <hr/> | | | | |
| N(1)–Cu–N(2) | 84.9(3) | 85.2(1) | 85.1(2) | 85.2(2) |
| N(1)–Cu–O(1) | 90.1(2) | 88.5(1) | 89.9(2) | 88.3(2) |
| N(1)–Cu–O(2) | 159.2(2) | 163.0(1) | 161.1(2) | 158.4(2) |
| N(2)–Cu–O(1) | 89.9(2) | 91.4(1) | 91.1(2) | 88.7(2) |
| N(2)–Cu–O(2) | 165.0(2) | 159.2(1) | 166.8(2) | 164.4(2) |
| O(1)–Cu–O(2) | 89.8(2) | 88.9(1) | 89.6(2) | 92.1(2) |
| Cl–Cu–N(1) | 101.4(2) | 100.7(1) | 103.1(2) | 100.2(1) |
| Cl–Cu–N(2) | 100.4(2) | 102.14(9) | 100.0(2) | 96.6(1) |
| Cl–Cu–O(1) | 94.4(1) | 98.49(8) | 93.0(1) | 98.5(1) |
| Cl–Cu–O(2) | 99.4(1) | 96.26(8) | 95.8(1) | 101.1(1) |

pyramidal structure (of the type **3** or **6**) which results in the blue colour.

It can be concluded that due to intermolecular hydrogen-bonding interactions in the solid state in complexes **1**, **2**, **4** and **5**, their colours are more bluish, along with electronic absorption at higher wavenumbers (in spite of their green solution in non-polar solvents such as 1,2-C₂H₄Cl₂, in which all molecules are separate, without any intermolecular interaction, similar to solid **3**).

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