Syntheses and Crystal Structures of Copper and Silver Complexes with New Imine Ligands − Air-Stable, Photoluminescent Cu^IN_4 Chromophores

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Keywords: N ligands / Copper / Silver / Luminescence / Electrochemistry

A series of new imine ligands [**1** ($C_{12}H_{12}N_2S_2$), **2** ($C_{12}H_{12}N_2S_2$), **3** ($C_{24}H_{18}N_4S_2$), and **5** ($C_{30}H_{27}N_7$)] have been synthesized (**1** and **2** are structural isomers). Cu^I and Ag^I complexes of the nonconjugated dithiophene-diimine ligands **1**, **2** and the tripodal imine-amine ligand **5** have also been prepared and thoroughly characterized by spectroscopic techniques as well as by X-ray diffraction. In cyclic voltammetry at a glassy carbon milli electrode in anhydrous dichloromethane under dry N_2, the corresponding Cu^I complexes [**6** ($2C_{12}H_{12}N_2S_2{\cdot}CuClO_4$), **7** ($2C_{12}H_{12}N_2S_2{\cdot}CuClO_4$), and **12** ($C_{30}H_{27}N_7{\cdot}CuClO_4$)] show quasi-reversible $Cu^{II/I}$ couples with high redox potentials (1.001 V for **6**, 0.958 V for **7**, and 0.692 V for **12**, vs. Ag/AgCl). This indicates that the π-acid ligands **1**, **2**, and **5** preferentially stabilize copper(I) over copper(II). The Cu^IN_4 chromophores in the complexes **6**, **7**, and **12** display photoluminescence in dichloromethane at room temperature. The related silver complexes of the same three ligands **10** ($2C_{12}H_{12}N_2S_2{\cdot}AgClO_4$), **11** ($2C_{12}H_{12}N_2S_2{\cdot}AgClO_4$), and **13** [$C_{30}H_{27}N_7{\cdot}Ag(CH_3CN)ClO_4$] reveal similar structural features but lack specific photophysical properties.

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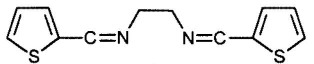
Introduction

Metal complexes of N-donor ligands are of considerable current interest because they catalyze many organic transformations,[1] including the cyclization of 1,2-allene derivatives,[2] the asymmetric cyclization reaction of isocyanoacetic acid or isocyanomethyl toluenesulfonate with aldehydes,[3] asymmetric intramolecular carbene C−H insertion reactions[4] and the enantioselective addition of allyltin reagents to aldehydes.[5,6] Further interest is in photoluminescent complexes of copper(I). The photophysics of compounds derived from 1,10-phenanthroline species, which contain the Cu^IN_4 chromophore, is well established.[7−9] However, materials based on other ligands with N-donor atoms are less abundant in the literature.[10−12] In this context we have synthesized a series of new nonconjugated diimine and imine-amine nitrogen donor ligands (**1**−**5**) and attempted the formulation and thorough spectral and structural characterization of their complexes with Cu^I, as well as with the related Ag^I ion. The linear ligands **1**−**4** also contain peripheral thiophene substituents, which may have some unique effect on the photophysical properties of the anticipated Cu^IN_4 chromophores, depending on the proximity of the sulfur atoms (although they are considered to be weak nucleophiles) to the complexation site. Another variant of this study involves transition metal complexes with tetradentate tripodal Schiff-base ligands, due to their diverse structural and physical properties, as well as their possible application as magnetic imaging agents and models of metalloenzymes such as superoxide dismutases.[13,14] Correspondingly, Cu^I and Ag^I complexes with the tripodal ligand **5** were prepared and characterized. The Cu^I complex of **5** is also photoluminescent.



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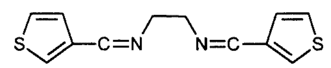

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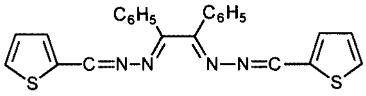

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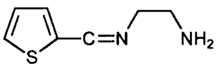

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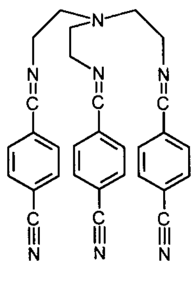

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Herein we report the detailed structures and preliminary photophysical properties of three new Cu^IN_4 chromophores derived from ligands **1**, **2**, and **5**; chemical spectral and structural data are provided for the Ag^I complexes of these ligands as well. The bulky ligand **3** does not form stable complexes with these metal ions, while the asymmetric ligand **4** yields a stable structure only with divalent copper ions.

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Results and Discussion

Synthesis and Structure

Compounds **1** and **2** were synthesized by condensing ethylenediamine with 2-thiophenecarboxaldehyde or 3-thiophenecarboxaldehyde, respectively. These compounds are flexible about the central C−C bond. A 1:2 condensation reaction of benzil dihydrazone with 2-thiophenecarboxaldehyde yields a bulkier ligand **3**, which is considerably more rigid. The molecular structures of **2** and **3** are shown in Figure 1. Ligand **2** is located in the crystal on an axis of twofold rotational symmetry, the torsion angle about the central C−C bond that connects the two equivalent parts of the molecule being 70.6(3)°. The inner nitrogen atoms are exposed to the surrounding species, and provide excellent sites for metal ion binding. The N−C−C−N torsion angle about the central bond in **3** is 49.6(2)°. The nitrogen atoms are involved in partly delocalized π-electron systems (one part of the molecule is nearly planar; Figure 1), and therefore are less-effective donor sites for complex formation.

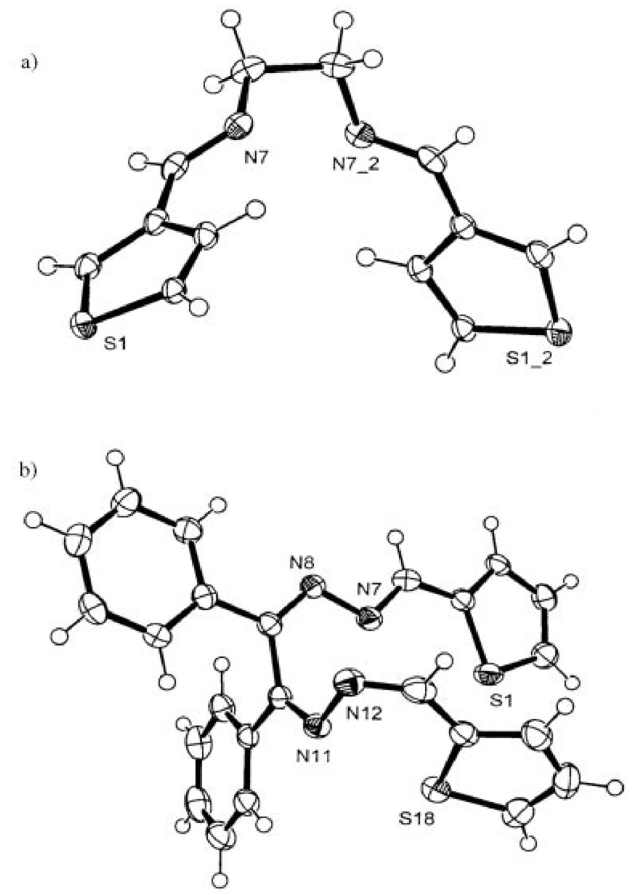

Figure 1. Molecular structures of (a) ligand **2** (located on a twofold symmetry axis), and (b) ligand **3**; the heteroatoms are indicated by darkened circles and are labeled; 50% probability thermal ellipsoids at 110 K are shown

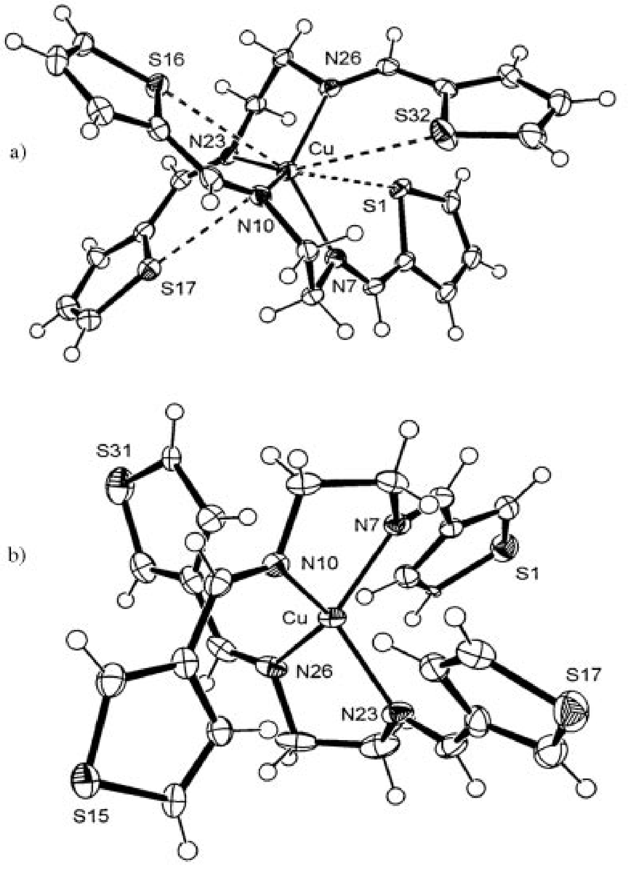

Figure 2. Complexes of Cu^I with (a) ligand **1**, and (b) ligand **2**; note in (a) the additional attractive interactions of the metal ion with the inward turning sulfur sites (dotted lines); in this and the following structural illustration the counterions and solvent moieties are omitted for clarity

In this work we have been able to synthesize and crystallize stable Cu^I and Ag^I complexes of **1** and **2**, but no metal ion complexes of **3** could be obtained. The copper(I) derivatives were prepared by treating ligands **1** and **2** with $[Cu(CH_3CN)_4]ClO_4$ in anhydrous methanol under argon in a 1:2 metal/ligand ratio. The resulting bright orange-yellow solids $[Cu(\mathbf{1})_2](ClO_4)$ (**6**) and $[Cu(\mathbf{2})_2](ClO_4)$ (**7**) are extremely stable in air both in the solid state and in solution (CH_3OH and CH_2Cl_2). The observed structures of the cationic species in **6** and **7** are illustrated in Figure 2. The high propensity of the copper ion to form tetrahedrally structured complexes determines the 1:2 stoichiometry of the metal/ligand reaction. In **6** and **7** the Cu−N bond lengths within the Cu^IN_4 chromophore are in the range 2.004−2.111(2) and 2.039−2.071(3) Å, respectively. However, in **6** all the S-atom sites of the 2-thiophene substituents are oriented towards, and weakly interact with, the central metal ion; the corresponding Cu···S distances range from 3.24 to 3.60 Å (Figure 2, a). Such interactions are not possible in the 3-thiophene derivative **7**. As a result the thiophene rings in this structure (as well as in the related complexes described below) tend to exhibit twofold orientational disorder about the C−C bond through which they are connected to the central part of the ligand. The Cu^IN_4 moieties are distorted tetrahedra with two N−Cu−N angles near 85° (which involve nitrogen atoms from the same ligand) and four N−Cu−N angles greater than 115° (for N atoms of the two different ligands).

The corresponding [Cu(**1**)$_2$](ClO$_4$)$_2$ complex with divalent copper, of a deep-green color, is stable in CH$_3$OH or CH$_3$CN only for a few minutes, and could not be characterized. An alternative reaction of **1** with Cu(CF$_3$SO$_3$)$_2$ yielded a somewhat more stable product, [Cu(**1**)$_2$](CF$_3$SO$_3$)$_2$ (**8**), which is stable in air, and in solution in CH$_3$OH or CH$_3$CN, for about 2−3 h. However, upon slow recrystallization from the solution mixture the ligand framework in **8** is partially hydrolyzed, transforming after about 8 h to a different species of composition [Cu(**4**)$_2$](CF$_3$SO$_3$)$_2$ (**9**) characterized by a light pink color.[15] In situ partial hydrolysis of a diimine ligand within the coordination sphere of copper is rare. No stable complexes of ligand **2** with Cu^{II} ions could be obtained under similar experimental conditions. The structure of the [Cu(**4**)$_2$]$^{2+}$ cation in **9** is depicted in Figure 3. It shows a nearly square-planar complex with the metal ion located on a center of inversion, with Cu−N distances of 1.997(2) and 2.038(2) Å and N−Cu−N bond angles between the *cis*-related nitrogen sites of 83.40(6)° within the ligand and 96.60(6)° between the two ligands.

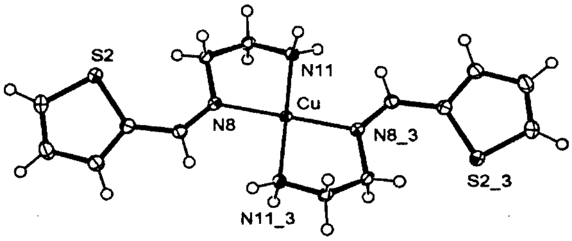

Figure 3. Molecular structure of the square-planar complex **9** of Cu^{II}, the metal ion being located in the crystal on a crystallographic center of inversion

The structures of the respective Ag^{I} complexes of **1** and **2** {[Ag(**1**)$_2$](ClO$_4$) (**10**) and [Ag(**2**)$_2$](ClO$_4$) (**11**)} are shown in Figure 4. They were prepared readily by treating the ligands with Ag(ClO$_4$) at room temperature. These two 1:2 metal/ligand complexes are stable in the solid state for about two weeks, and in solution (MeOH or MeCN) for at least 12 h. Their structures have a distorted tetrahedral geometry similar to that observed for the corresponding copper(I) derivatives.

The coordination parameters are: (a) in **10**, Ag−N bond lengths of 2.293−2.298(3) Å, N−Ag−N bond angles within the same ligand of nearly 76°, and involving two different ligands greater than 120°; (b) in **11**, the corresponding values are 2.273−2.353(3) Å, 76−77° and greater than 118°, respectively. In **10**, the silver ions are also approached, in a convergent manner, by the four thiophene S-sites at an Ag···S distance range of 3.22−3.37 Å. The latter may represent additional weakly attractive interactions between the metal ion and the ligand species.

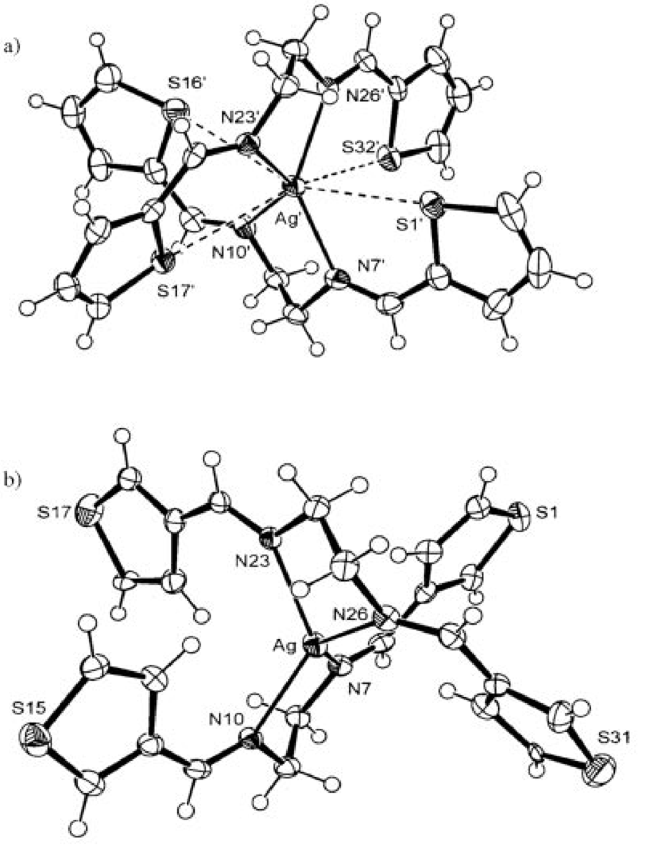

Figure 4. Structures of complexes of Ag^{I} with (a) ligand **1**, and (b) ligand **2**; note in (a) the additional attractive interactions of the metal ion with the inward turning sulfur sites (dotted lines), as in the corresponding Cu^{I} complex shown in Figure 2a

Ligand **5** is a 1:3 condensate of tris(2-aminoethyl)amine (tren) and 4-cyanobenzaldehyde. It contains an amino nitrogen atom, as well as three imino N-donors, and may act as a tetradentate ligand of adjustable conformation. Correspondingly, in complexation reactions with Cu^{I} and Ag^{I} one molecule of **5** should function as two molecules of **1** or **2**. The yellow-reddish Cu^{I} complex [Cu(**5**)](ClO$_4$) (**12**) was obtained by treating **5** with [Cu(CH$_3$CN)$_4$]ClO$_4$ in equimolar proportions in methanol under argon. Complex **12** is also fairly stable in air, both in the solid state and in solution. A similar reaction of **5** with Ag(ClO$_4$) in acetonitrile at room temperature yielded [Ag(**5**)(CH$_3$CN)](ClO$_4$) (**13**). The molecular structures of the two complexes are illustrated in Figure 5.

Indeed, complex **12** has a tripodal structure with the Cu^{I} cation trapped inside the ligand by internal coordination to the four N-donor sites. The Cu−N(imino) distances are within the range 2.000−2.008(2) Å, while the Cu−N(amino) bond length is 2.206(2) Å. The geometry of the Cu^{I}N$_4$ moiety in this structure resembles a trigonal pyramid with the amino nitrogen atom at its apex. The Cu^{I}N$_4$ chromophore with a trigonal-pyramidal geometry around the metal ion is not common.[16] The N(imino)−Cu−N(amino) bond angles are constrained by the proximity of the two nitrogen sites to low values within the range 84.6−85.3(1)°, while the geometrically less constrained N(imino)−Cu−N(imino) bond angles in the base of the pyramid are characterized by larger values of be-

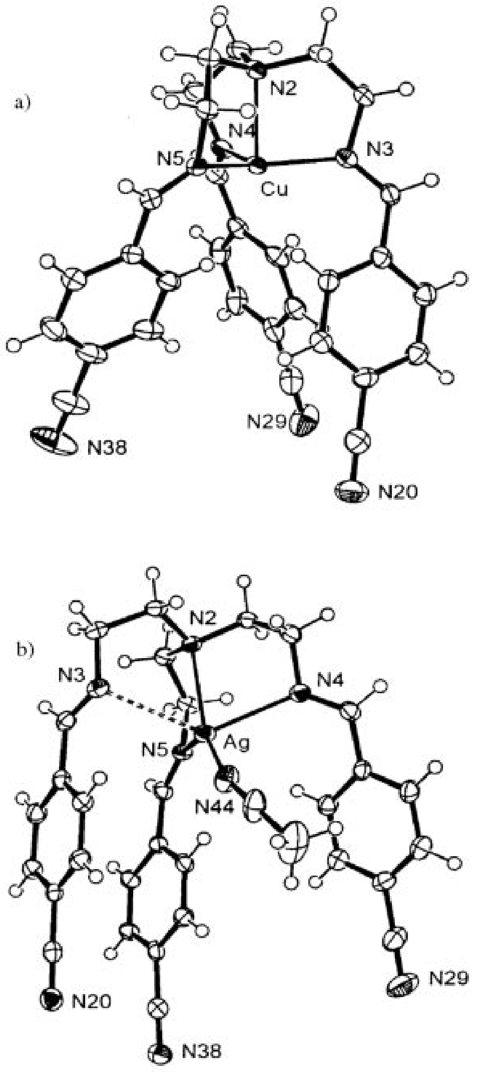

Figure 5. Structures of the tripodal complexes of ligand **5** with (a) Cu^I and (b) Ag^I; the Cu^IN_4 moiety in (a) is characterized by a trigonal-pyramidal geometry; the coordination geometry around the silver ion in (b) is affected by the additional coordinated acetonitrile ligand

tween 116.6 and 121.4(1)°. The geometry of the corresponding silver complex **13** is disrupted by coordination of one acetonitrile ligand which coordinates to the metal ion with an Ag−N distance of 2.211(3) Å. The latter also coordinates strongly to three N-atom donor sites of the ligand at 2.315−2.461(2) Å, and more weakly to the fourth (imino) nitrogen at 2.763(2) Å.

IR and NMR Characterization

Ligands **1** and **2** exhibit strong IR absorption bands at 1635 and 1641 cm^{-1}, respectively, for the $\nu(C{=}N)$ stretching vibration. On coordination with Cu^I this band shifts to much lower energies (1611 and 1614 cm^{-1} for **6** and **7**, respectively). In case of the Ag^I complexes **10** and **11**, however, this band appears at 1631 and 1640 cm^{-1}, respectively. For the ligand **5** and its Cu^I and Ag^I complexes, **12** and **13**, this $\nu(C{=}N)$ stretching vibration appears at 1642, 1635, and 1633 cm^{-1}, respectively, and the $\nu(C{\equiv}N)$ stretching vibrations appear at 2221, 2228, and 2226 cm^{-1}, respectively. Complexes **6**, **7**, **10**, **11**, **12**, and **13** give characteristic well-resolved bands around 1088, 1080, 1085, 1081, 1090, and 1091 cm^{-1}, respectively, for the noncoordinated $\nu(ClO_4^-)$ vibrations.[17]

The ^1H and ^{13}C NMR spectra of the ligands **1**, **2**, and **5** in $CDCl_3$ consist of sharp and well-resolved signals for each of the organic groupings present. The Cu^I and Ag^I complexes **6**, **7** and **10**, **11** show almost the same pattern as the ligand in their ^1H NMR spectra in $(CD_3)_2SO$. While the ^1H NMR spectrum of **13** shows the same pattern as that of the ligand, the ^1H NMR spectrum of **12** shows different chemical shifts. In case of the ligand **5** and its Ag^I complex **13** all the phenylic protons appear at the same position (δ = 7.67 ppm for ligand **5** and δ = 7.93 ppm for the Ag^I complex **13**) but for the Cu^I complex **12** they appear at two different positions (δ = 8.07 and 7.46 ppm). In the EI mass spectra ligands **1** and **2** show exactly the same type of fragmentation pattern.

Electrochemistry

The redox behavior of the Cu^I complexes **6**, **7**, and **12** has been examined by cyclic voltammetry in dichloromethane at a glassy carbon working electrode under dry N_2 (Figure 6). Quasi-reversible oxidative voltammograms attributed to the $Cu^{II/I}$ couple were observed with half-wave potential ($E_{1/2}$) values of 1.001, 0.958 and 0.692 V vs. Ag/AgCl, 1 M KCl for **6**, **7**, and **12**, respectively. The couple is more reversible in the case of **6** and **7** than for **12**. The peak-to-peak (ΔE_p) separation values for this couple are 190, 205, and 310 mV for **6**, **7**, and **12**, respectively, at a scan rate of 50 $mV{\cdot}s^{-1}$ and these values increase when the scan rate is increased. The higher potential of this couple in **6** and **7** than in **12** indicates that the Cu^I complexes **6** and **7** are more stable than **12**; this has been observed experimentally: a dichloromethane solution of **6** or **7** is stable in air

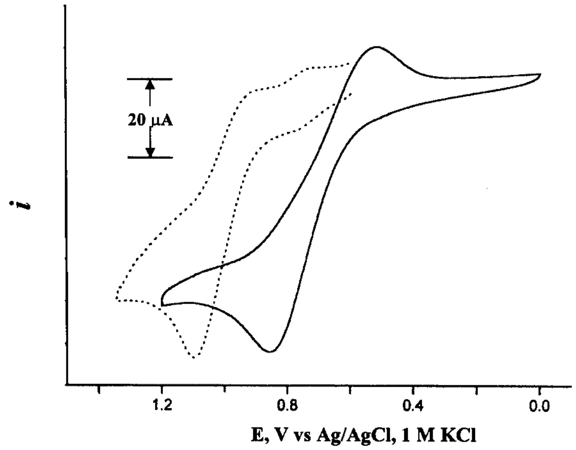

Figure 6. Cyclic voltammograms of **6** (broken line) and **12** (full line) [approximately 10^{-3} M in dichloromethane, 0.2 M Bu_4NClO_4] at a glassy carbon electrode, scan rate 50 $mV{\cdot}s^{-1}$

for at least 10 d, whereas a solution of **12** is stable only for about 3−4 d. The $Cu^{II/I}$ potential in the $Cu^{I}N_4$ chromophore increases with the π-acidity of the ligand and the extent of tetrahedral distortion in the corresponding copper(II) species.[18] The π-acidity of ligands **1** and **2** is larger than that of **5**. In this context, it should be mentioned that, to the best of our knowledge, the highest potential for the $Cu^{II/I}$ couple so far reported in a $Cu^{I}N_4$ chromophore is 1.55 V vs. SCE.[8]

UV/Vis and Photophysical Data

There is a difference in the absorption spectra of the ligands **1** and **2** in dichloromethane. While ligand **1** shows two charge-transfer bands at 284 and 261 nm with intensities (ε) of 24975 and 28160 $M^{-1}cm^{-1}$, respectively, ligand **2** shows only one charge-transfer band at 250 nm (ε = 31 945). These intra-ligand charge-transfer bands appear at 282 and 266 nm for the Cu^{I} complex **6** and at 254 nm for **7**. In addition to these bands, **6** shows two metal-to-ligand charge-transfer (MLCT) bands at 415 (ε = 2480) and 345 nm (ε = 8785). These two MLCT bands appear at 410 (ε = 2405) and 347 nm (ε = 7250) for complex **7**. The deep green color of copper(II) complexes of the ligand **1** and pale pink color of the copper(II) complex of ligand **4** are due to the d-d transition band at 613 nm (ε = 215) and 587 nm (ε = 150), respectively. Ligand **5** shows an intra-ligand charge-transfer band at 255 nm (ε = 38 120) in dichloromethane. This band appears at 251 nm (ε = 30 730) for its copper(I) complex **12** and at 248 nm (ε = 26 500, in CH_3CN) for its silver(I) complex **13**. The copper(I) complex shows an MLCT band at 379 nm (ε = 2526).

Ligands **1**, **2**, and **5** are not photoluminescent in dichloromethane. Upon excitation at 350 nm (MLCT envelope) in dichloromethane at room temperature both complexes **6** and **7** yield a single, structureless, broad emission band with maxima at 445 and 456 nm, respectively, with quantum yields (φ) of $2.9 \cdot 10^{-4}$ and $7.2 \cdot 10^{-5}$ (against quinine sulfate[19] in 0.1 N H_2SO_4; Figure 7), respectively. In complex **6** all the four S-atoms are directed towards the metal ion, so the metal coordination sphere is sterically more hindered. This may be the reason for the larger quantum yield (φ) of **6** than **7**. The chemical nature, the size and the position of the substituents in the ligand can affect the geometry of the excited state, which influences the emission properties.[9] It has been found for 2,9-disubstituted phenanthroline derivatives that the Cu^{I} geometry is stabilized by enforcing a tetrahedral geometry that inhibits the flattened square-planar coordination geometry in the Cu^{II} state formed upon excitation.[20]

On excitation at 380 nm (MLCT band), complex **12** exhibits a single structureless broad emission band with a maximum at 505 nm and a quantum yield (φ) of $5.8 \cdot 10^{-5}$ (against quinine sulfate[19] in 0.1 N H_2SO_4; Figure 7). The photophysical properties of the $Cu^{I}N_4$ chromophore have been analysed mainly for complexes of Cu^{I} with derivatives of 1,10-phenanthroline.[9] These complexes are of the bis-type in which all the nitrogen donor atoms are essentially of the same type. Complex **12** is only the second known example of a photoluminescent $Cu^{I}N_4$ chromophore where the nitrogen donor atoms are of the imino as well as the amino type, and come from the same ligand. The only photoluminescent $Cu^{I}N_4$ chromophore of this type known so far has been reported recently.[12]

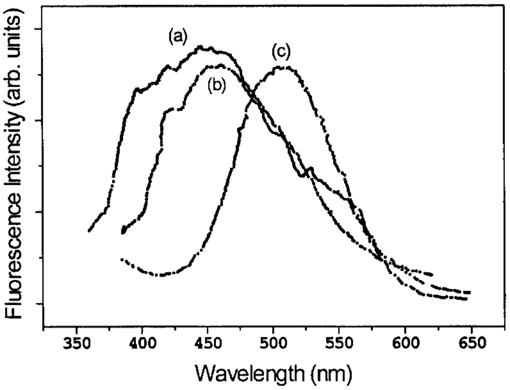

Figure 7. Emission spectra of (a) **6**, (b) **7**, and (c) **12** at room temperature in dichloromethane; excitation wavelength is 350 nm for **6** and **7**, 380 nm for **12**; absorbances for **6**, **7**, and **12** are 0.68, 0.73, and 0.80, respectively

Conclusions

In a search for new metal ion complexes with interesting features, we have synthesized a series of copper(I) and silver(I) compounds with targeted diimine and tripodal ligands, and examined their structural, photophysical, and electrochemical properties. The copper(I) complexes are of particular interest here, as they reveal a more unique photophysical behavior. The emission quantum yield (φ) of complex **6** at room temperature in dichloromethane was found to be four to five times larger than that of complexes **7** and **12**. The $Cu^{II/I}$ redox potential values of all three compounds are rather high, indicating that the copper(I) state is much more stable than the corresponding copper(II) state.

Experimental Section

General Procedures: The complex $[Cu(CH_3CN)_4]ClO_4$ was synthesized by a reported procedure.[21] All other reagents were procured commercially. Copper was estimated gravimetrically as CuSCN. Microanalyses were performed with Perkin−Elmer 2400II elemental analyzer and CE instruments. Melting points were determined by an electrothermal IA9000 series digital melting point apparatus and are uncorrected. IR spectra (KBr disc) were recorded with a Nicolet Magna-IR spectrophotometer (Series II), UV/Vis spectra with a Shimadzu UV-160A spectrophotometer, ^{1}H and ^{13}C NMR spectra with a Bruker DPX200 spectrometer and EI (electron impact) mass spectra with a VG Autospec M-250 instrument. Cyclic voltammetry was performed at room temperature at a planar glassy carbon milli electrode using μ-Autolab II with GPES software, version 4.8.5 (EcoChemie, The Netherlands) in purified and anhydrous dichloromethane under dry nitrogen with a conventional three-electrode configuration. Under the experimental conditions employed here, the ferrocene/ferrocenium couple appears at 0.42 V vs. Ag/AgCl in 1 M KCl with a ΔE_p of 110 mV at a scan rate of 50 $\mathrm{mV \cdot s^{-1}}$ (Figure 6). The photophysical studies were performed in air with a Shimadzu RF-540 spectrofluorophotometer.

Ligand 1: Distilled ethylenediamine (1 mL, 15 mmol) and freshly distilled 2-thiophenecarboxaldehyde (2.80 mL, 30 mmol) were refluxed in 60 mL of anhydrous methanol for 6 h. On evaporating the solvent a light yellow solid was obtained, which on recrystallization from *n*-hexane gave colorless needles suitable for X-ray analysis. Yield: 2.98 g (80%); m.p. 91−93 °C. $C_{12}H_{12}N_2S_2$ (248.36): calcd. C 58.01, H 4.87, N 11.28, S 25.83; found C 58.05, H 4.83, N 11.32, S 25.87. EI-MS: *m*/*z* (%) = 248.1 (20) $[M^+]$, 124 (55) $[M^+/2]$. FTIR (KBr): $\tilde{\nu}$ = 507 (m), 577 (m), 648 (w), 715 (vs), 792 (vs), 841 (s), 860 (s), 955 (s), 1051 (s, split), 1192 (m), 1235 (vs), 1284 (s), 1326 (m), 1430 (s), 1635(vs), 2848 (wb), 2908 (wb), 3099 (s) $\mathrm{cm^{-1}}$. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 8.35 (s, 2 H), 7.35 (d, J = 4 Hz, 2 H), 7.27 (d, J = 4 Hz, 2 H), 7.04 (dd, J = 2 and 4 Hz, 2 H), 3.91 (s, methylene, 4 H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ = 155.96, 142.27 (quaternary), 130.46, 128.70, 127.27, 60.92 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 284 (24975), 261 nm (28160 $\mathrm{M^{-1} \cdot cm^{-1}}$).

Ligand 2: This compound was prepared by following a similar procedure starting with distilled ethylenediamine (1 mL, 15 mmol) and freshly distilled 3-thiophenecarboxaldehyde (2.63 mL 30 mmol) to obtain shiny white crystals, suitable for X-ray analysis. Yield: 2.66 g (71%); m.p. 97 °C. $C_{12}H_{12}N_2S_2$ (248.36): calcd. C 58.01, H 4.87, N 11.28, S 25.83; found C 58.08, H 4.91, N 11.27, S 25.90. EI-MS: *m*/*z* (%) = 248.1 $[M^+]$ (20), 124 $[M^+/2]$ (55). FTIR (KBr): $\tilde{\nu}$ = 575 (m), 625 (s), 717 (m), 789 (vs), 828 (s), 878 (m), 902 (m), 1021 (vs), 1070 (m), 1160 (s, split), 1240 (vs), 1291 (s), 1346 (w), 1354 (m), 1426 (m), 1458 (s), 1641 (vs), 2844 (wb), 3049 (m, split), 3091 (s) $\mathrm{cm^{-1}}$. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 8.28 (s, 2 H), 7.57 (d, J = 4 Hz, 2 H), 7.51 (d, J = 4 Hz, 2 H), 7.30 (dd, J = 2 and 4 Hz, 2 H), 3.90 (s, methylene, 4 H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ = 156.98, 140.32 (quaternary), 128.44, 126.30, 125.66, 61.57 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 250 nm (31945 $\mathrm{M^{-1} \cdot cm^{-1}}$).

Ligand 3: Benzil dihydrazone (1.87 g, 7.85 mmol), synthesized by a reported procedure,[22] was dissolved in 50 mL of anhydrous methanol. To this solution, freshly distilled 2-thiophenecarboxaldehyde (1.47 mL, 15.70 mmol) was added. The resulting yellowish mixture was refluxed for 6 h, maintaining dry conditions. Then it was slowly cooled to room temperature to yield a yellowish crystalline solid, which was filtered off and dried in air. Crystals suitable for X-ray analysis were obtained by slow concentration of an acetonitrile solution. Yield 2.15 g (64%); m.p. 159−160 °C. $C_{24}H_{18}N_4S_2$ (426.54): calcd. C 67.56, H 4.26, N 13.14, S 15.05; found C 67.58, H 4.29, N 13.19, S 14.99. FTIR (KBr): $\tilde{\nu}$ = 525(m), 596 (m), 610 (m), 685 (vs), 712 (vs), 764 (vs, split), 835 (w), 919 (m), 1050 (s), 1074 (m), 1175 (m), 1212 (s), 1237 (m, split), 1299 (w), 1326 (m), 1424 (vs), 1445 (s), 1490 (s), 1605 (vs), 2840 (wb), 2917 (w), 3105(s) $\mathrm{cm^{-1}}$. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ = 8.65 (s, 2 H), 8.05−7.99 (m, 6 H), 7.97−7.90 (m, 6 H), 7.30 (d, 2 H), 7.10 (d, 2 H), 6.96 (dd, 2 H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ = 164.86 (quaternary), 162.40 (quaternary), 155.65, 148.31, 139.22 (quaternary), 134.19, 133.50, 131.75, 128.80, 127.22 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 328 (35 600), 276 (28 690), 257 nm (26845 $\mathrm{M^{-1} \cdot cm^{-1}}$). EI-MS: *m*/*z* (%) = 426.1 $[M^+]$ (15).

$[Cu(1)_2]ClO_4$ (6): Solid $[Cu(CH_3CN)_4]ClO_4$ (0.165 g, 0.5 mmol) was added to 30 mL of an anhydrous, degassed methanol solution of **1** (0.25 g, 1 mmol) under argon, and stirred for 1 h maintaining dry conditions. An orange-yellow compound precipitated. This was filtered off, washed with 2 mL of methanol and dried in vacuo over fused $CaCl_2$. Yield: 0.18 g (55%). Single crystals were grown by diffusion of *n*-hexane into a concentrated dichloromethane solution of the complex. $C_{24}H_{24}ClCuN_4O_4S_4$ (659.70): calcd. C 43.67, H 3.67, Cu 9.63, N 8.49, S 19.45; found C 43.62, H 3.73, Cu 9.69, N 8.46, S 19.49. FTIR (KBr): $\tilde{\nu}$ = 625 (m), 641 (w), 722 (m, split), 853 (w), 1088 (vs), 1108 (vs), 1187 (m), 1234 (s), 1288 (s), 1321 (m), 1435 (s), 1611 (vs), 2850 (wb), 2910 (m), 3099 (s) $\mathrm{cm^{-1}}$. ^1H NMR [200 MHz, $(CD_3)_2SO$, TMS]: δ = 8.68 (s, 4 H), 7.52 (d, J = 4 Hz, 4 H), 7.27 (d, J = 4 Hz, 4 H), 7.05 (dd, J = 2 and 4 Hz, 4 H), 4.17 (s, methylene, 8 H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 415 sh (2480), 345 sh (8785), 282 (22080), 266 nm (31250 $\mathrm{M^{-1} \cdot cm^{-1}}$).

$[Cu(2)_2]ClO_4$ (7): This complex was prepared similarly by treating $[Cu(CH_3CN)_4]ClO_4$ (0.165 g, 0.5 mmol) with **2** (0.25 g, 1 mmol) in 50 mL of anhydrous methanol under argon. Yield: 0.16 g (48%). Single crystals were grown by direct diffusion of *n*-hexane into a dichloromethane solution of the complex. $C_{24}H_{24}ClCuN_4O_4S_4$ (659.70): calcd. C 43.67, H 3.67, Cu 9.63, N 8.49, S 19.45; found C 43.69, H 3.74, Cu 9.74, N 8.44, S 19.47. FTIR (KBr): $\tilde{\nu}$ = 628 (m), 722 (m, split), 787 (m), 832 (s), 910 (w), 1080 (vs), 1105 (vs), 1161 (m), 1236 (m), 1326 (w), 1371 (w), 1462 (s), 1614 (vs), 3096 (s) $\mathrm{cm^{-1}}$. ^1H NMR [200 MHz, $(CD_3)_2SO$, TMS]: δ = 8.42 (s, 4 H), 7.76 (br., 4 H), 7.55 (br., 4 H), 7.05 (br. 4 H), 4.08 (s, methylene, 8 H) ppm. UV/Vis (CH_3OH): λ_{max} (ε) = 410 sh (2405), 347 sh (7250), 254 nm (34320 $\mathrm{M^{-1} \cdot cm^{-1}}$).

$[Cu(1)_2](CF_3SO_3)_2$ (8): Ligand **1** (0.25 g, 1 mmol) was dissolved in 20 mL of acetonitrile. To this colorless solution 5 mL of an acetonitrile solution of $Cu(CF_3SO_3)_2$ (0.18 g, 0.5 mmol) was added dropwise with constant stirring. The solution turned bottle green. Diethyl ether was then added dropwise to this solution until precipitation occurred. The reaction mixture was kept in a refrigerator for 10 min. The green precipitate was then filtered off, washed with diethyl ether, and dried in air. Yield: 0.44 g (51%). $C_{26}H_{24}CuF_6N_4O_6S_6$ (858.12): calcd. C 36.36, H 2.82, Cu 7.40, N 6.53, S 22.42; found C 36.41, H 2.85, Cu 7.47, N 6.49, S 22.48. FTIR (KBr): $\tilde{\nu}$ = 528 (w), 535 (m), 641 (s), 736 (s), 867 (m), 1118 (m), 1211 (m), 1268 (vs, split), 1338 (m), 1418 (s), 1621 (vs), 2912 (wb), 3095 (m) $\mathrm{cm^{-1}}$. UV/Vis (CH_3CN): λ_{max} (ε) = 613 (215), 287 (34225), 264 nm (35075 $\mathrm{M^{-1} \cdot cm^{-1}}$).

$[Cu(4)_2](CF_3SO_3)_2$ (9): Complex **8** (0.43 g, 0.5 mmol) was dissolved in 15 mL of acetonitrile. To this solution 10 mL of diethyl ether was added. This green solution was kept in the refrigerator for 8 h. Light pink colored crystals, suitable for X-ray analysis were deposited. These were filtered and dried in vacuo over fused $CaCl_2$. Yield: 0.095 g (28%). $C_{16}H_{20}CuF_6N_4O_6S_4$ (670.14): calcd. C 28.66, H 3.01, Cu 9.48, N 8.36, S 19.14; found C 28.72, H 2.95, Cu 9.43, N 8.42, S 19.18. FTIR (KBr): $\tilde{\nu}$ = 515 (m), 576 (m), 635 (s), 755 (m), 1042 (vs, split), 1112 (m), 1170 (vs), 1265 (vs, split), 1486 (m), 1625 (vs), 2895 (w), 3305 (vb) $\mathrm{cm^{-1}}$. UV/Vis (CH_3CN): λ_{max} (ε) = 587 (150), 281 (28470), 269 nm (28750 $\mathrm{M^{-1} \cdot cm^{-1}}$).

$[Ag(1)_2](ClO_4)$ (10): Ligand **1** (0.25 g, 1 mmol) was dissolved in 15 mL of methanol. To this solution 5 mL of a methanol solution of $AgClO_4$ (0.105 g, 0.5 mmol) was added dropwise with constant stirring, causing an off-white solid to precipitate. It was kept in air for 1 h, then filtered off, washed with 2 mL of methanol and dried in vacuo over fused $CaCl_2$. Yield: 0.19 g (54%). Single crystals suitable for X-ray analysis were grown by slow concentration of an acetonitrile solution. The compound crystallizes with half a molecule of the acetonitrile solvent. $C_{24}H_{24}AgClN_4O_4S_4$ (704.03): calcd. C 40.92, H 3.44, N 7.96, S 18.22; found C 40.95, H 3.39, N 10.89, S 18.26. FTIR (KBr): ṽ = 505 (m), 581 (w), 623 (s), 715 (vs), 842 (s), 951 (m), 1085 (vs, split), 1217 (m), 1285 (m), 1326 (w), 1430 (s), 1459 (m), 1631 (vs), 2861 (wb), 3100 (m) $\mathrm{cm^{-1}}$. ^{1}H NMR [200 MHz, $(CD_3)_2SO$, TMS]: δ = 8.83 (s, 4 H), 7.74 (d, *J* = 4 Hz, 4 H), 7.61 (d, *J* = 4 Hz, 4 H), 7.14 (dd, *J* = 2 and 4 Hz, 4 H), 4.06 (s, methylene, 8 H) ppm. UV/Vis (CH_3CN): λ_{max} (ε) = 281 (28385), 260 nm (32155 $\mathrm{M^{-1}\cdot cm^{-1}}$).

$[Ag(2)_2](ClO_4)$ (11): Silver perchlorate (0.105 g, 0.5 mmol) was added to a solution of **2** (0.25 g, 1 mmol) in 20 mL of methanol. The reaction mixture was stirred at room temperature for 1 h. A light yellow compound precipitated. This was filtered off, washed with a few drops of methanol and dried in vacuo over fused $CaCl_2$. Yield: 0.16 g (46%). Single crystals suitable for X-ray analysis were grown by slow evaporation of the methanol solution of the complex. $C_{24}H_{24}AgClN_4O_4S_4$ (704.03): calcd. C 40.92, H 3.44, N 7.96, S 18.22; found C 40.97, H 3.48, N 7.91, S 18.28. FTIR (KBr): ṽ = 579 (w), 625 (vs), 715 (w), 790 (vs), 867 (m, split), 951 (m), 1081 (vs, split), 1237 (m), 1291 (s), 1346 (m), 1407 (m), 1457 (s), 1522 (m), 1640 (vs), 2843 (wb), 2904 (w), 3098 (m) $\mathrm{cm^{-1}}$. ^{1}H NMR [200 MHz, $(CD_3)_2SO$, TMS]: δ = 8.68 (s, 4 H), 8.15 (d, *J* = 4 Hz, 4 H), 7.73 (d, *J* = 4 Hz, 4 H), 7.63 (dd, *J* = 2 and 4 Hz, 4 H), 3.94 (s, methylene, 8 H) ppm. UV/Vis (CH_3CN): λ_{max} (ε) = 248 nm (37535 $\mathrm{M^{-1}\cdot cm^{-1}}$).

Ligand 5: 4-Cyanobenzaldehyde (3.93 g, 30 mmol) was dissolved in 150 mL of anhydrous methanol. To this solution distilled tris(2-aminoethyl)amine (1.5 mL, 10 mmol) was added dropwise. The re-

Table 1. Crystal and experimental data related to the structural analyses

Compound	**2**[a]	**3**	**6**[b]	**7**[b]	**9**[c]
Empirical formula	$C_{12}H_{12}N_2S_2$	$C_{24}H_{18}N_4S_2$	$2C_{12}H_{12}N_2S_2\cdot CuClO_4$	$2C_{12}H_{12}N_2S_2\cdot CuClO_4$	$2C_7H_{10}N_2S\cdot Cu(CF_3SO_3)_2$
Formula mass	248.36	426.54	659.70	659.70	670.14
Crystallization solvent	–	–	–	–	–
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a [Å]	22.0020(9)	11.2690(3)	23.3760(2)	17.7670(2)	13.0240(2)
b [Å]	5.4920(3)	7.5640(2)	14.1940(2)	17.3330(1)	10.2440(2)
c [Å]	10.3350(4)	24.4540(8)	17.7390(4)	17.8660(2)	10.1090(4)
α [°]	90	90	90	90	90
β [°]	100.836(3)	91.429(1)	111.005(5)	91.412(4)	111.150(1)
γ [°]	90	90	90	90	90
V [Å^3]	1226.6(1)	2083.7(1)	5494.7(2)	5500.3(1)	1257.9(1)
Z	4	4	8	8	2
μ(Mo-K_α) [$\mathrm{mm^{-1}}$]	0.41	0.27	1.23	1.23	1.29
T [K]	110	110	110	110	110
D_c [$\mathrm{g\cdot cm^{-3}}$]	1.345	1.360	1.595	1.593	1.769
$2\theta_{max}$ [°]	56.5	55.0	55.8	55.8	56.4
No. unique reflections	1457	4703	12630	12868	2985
No. reflections ($I > 2\sigma$)	1192	2733	8664	9930	2524
No. refined parameters	73	271	685	918	169
$R1$ ($I > 2\sigma$)	0.037	0.053	0.042	0.049	0.030
$R1$ (all data)	0.049	0.116	0.082	0.070	0.040
$wR2$ (all data)	0.101	0.142	0.103	0.145	0.079
$\lvert\Delta\rho\rvert_{max}$ [e·Å^{-3}]	0.36	0.39	0.57	1.08	0.41

Compound	**10**[b]	**11**[b]	**12**	**13**
Empirical formula	$2C_{12}H_{12}N_2S_2\cdot AgClO_4$	$2C_{12}H_{12}N_2S_2\cdot AgClO_4$	$C_{30}H_{27}N_7\cdot CuClO_4$	$C_{30}H_{27}N_7\cdot Ag(C_2H_3N)ClO_4$
Formula mass	724.56	704.03	726.69	754.49
Crystallization solvent	$1/2C_2H_3N$		$C_2H_3N+1/2C_4H_{10}O$	$1/2C_2H_3N$
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1$	$P2_1/c$	$P\bar{1}$	$C2/c$
a [Å]	12.9450(1)	23.0490(2)	12.1820(2)	15.3070(2)
b [Å]	14.5890(2)	14.3170(2)	12.4590(2)	20.0510(3)
c [Å]	16.9380(2)	18.2170(2)	12.6410(4)	22.6490(5)
α [°]	90	90	84.618(1)	90
β [°]	110.281(1)	107.011(1)	78.889(1)	104.893(1)
γ [°]	90	90	65.524(1)	90
V [Å^3]	3000.5(1)	5748.5(1)	1713.2(1)	6717.9(2)
Z	4	8	2	8
μ(Mo-K_α) [$\mathrm{mm^{-1}}$]	1.08	1.12	0.77	0.73
T [K]	110	110	110	110
D_c [$\mathrm{g\cdot cm^{-3}}$]	1.60	1.627	1.409	1.492
$2\theta_{max}$ [°]	55.9	55.8	55.0	56.5
No. unique reflections	7283	13665	7581	8032
No. reflections ($I > 2\sigma$)	6780	9261	5405	5668
No. refined parameters	721	685	443	439
$R1$ ($I > 2\sigma$)	0.031	0.051	0.051	0.041
$R1$ (all data)	0.036	0.097	0.084	0.075
$wR2$ (all data)	0.072	0.114	0.137	0.107
$\lvert\Delta\rho\rvert_{max}$ [e·Å^{-3}]	0.77	0.86	0.71	0.76

[a] Molecules are located on symmetry axes of twofold rotation. [b] The crystallographic asymmetric unit contains two independent moieties of the complex. [c] The metal complex is located on centers of inversion.

action mixture was refluxed for 8 h maintaining dry conditions. Then, it was transferred into a beaker and left in the air overnight. A yellowish solid precipitated. This was filtered off, washed with 5 mL of methanol, dried in the air, and then recrystallized from acetonitrile. Yield: 3.2 g (66%); m.p. 135−137 °C. $C_{30}H_{27}N_7$ (485.27): calcd. C 74.19, H 5.61, N 20.20; found C 74.26, H 5.66, N 20.14. EI-MS: *m/z* (%) = 486.2 [MH^+] (30). FTIR (KBr): $\tilde{\nu}$ = 553 (s), 646 (m), 834 (vs), 927 (m), 1023 (m), 1067 (vs), 1158 (w), 1221 (w), 1287 (m), 1375 (s), 1440 (m), 1503 (m), 1642 (vs), 2221 (vs), 2841 (wb), 3428 (vb) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ = 8.19 (s, 3 H), 7.67 (m, 12 H), 3.74 (t, methylene, 6 H), 2.97 (t, methylene, 6 H) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ = 159.73, 139.86 (quaternary), 132.31, 128.26, 118.30 (quaternary), 113.79 (quaternary), 60.08, 55.20 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 255 nm (38120 $\text{M}^{-1}\cdot\text{cm}^{-1}$).

[Cu(5)]ClO$_4$ (12): Complex **5** (0.243 g, 0.5 mmol) was dissolved in 35 mL of anhydrous methanol by warming. Argon was purged through the solution and it was then cooled to room temperature. After 15 min, solid [$Cu(CH_3CN)_4$]ClO_4 (0.165 g, 0.50 mmol) was added to the degassed methanol solution. The reaction mixture was stirred at room temperature under argon for 1 h, maintaining dry conditions. A reddish yellow compound precipitated. This was filtered off, washed with 2 mL of methanol, and dried in vacuo over fused $CaCl_2$. Yield: 0.148 g (46%). Single crystals were grown by direct diffusion of diethyl ether into a concentrated acetonitrile solution of the complex. The compound crystallizes with one molecule of acetonitrile and half a molecule of diethyl ether. $C_{30}H_{27}ClCuN_7O_4$ (648.58): calcd. C 55.53, H 4.20, Cu 9.80, N 15.11; found C 55.61, H 4.25, Cu 9.91, N 15.08. FTIR (KBr): $\tilde{\nu}$ = 556 (s), 624 (s), 829 (s), 890 (m), 1090 (vs, split), 1286 (m), 1390 (w), 1460 (m), 1635 (vs), 2228 (vs), 2858 (wb), 3449 (vb) cm^{-1}. ^{1}H NMR [200 MHz, $(CD_3)_2SO$, TMS]: δ = 8.75 (s, 3 H), 8.07 (d, 6 H), 7.46 (d, 6 H), 3.88 (s, methylene, 6 H), 3.12 (s, methylene, 6 H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 379 (2526), 251 nm (30730 $\text{M}^{-1}\cdot\text{cm}^{-1}$).

[Ag(5)(CH$_3$CN)]ClO$_4$ (13): Silver perchlorate (0.105 g, 0.5 mmol) was added to a solution of **5** (0.243 g, 0.5 mmol) in 25 mL of acetonitrile. The reaction mixture was stirred at room temperature for 1 h and was then kept in a refrigerator for 24 h. Large colorless blocks, which were suitable for X-ray analysis, separated. They were filtered off, washed with a few drops of methanol, and dried in vacuo over fused $CaCl_2$. Yield 0.155 g (42%). One molecule of the acetonitrile solvent was found coordinated to the silver ion (another noncoordinated acetonitrile was found included in the lattice with partial occupancy). $C_{32}H_{30}AgClN_8O_4$ (733.79): calcd. C 52.34 H 4.12, N 15.27; found C 52.60, H 4.10, N 15.32. FTIR (KBr): $\tilde{\nu}$ = 552 (s), 623 (s), 833 (s), 927 (m), 972 (w), 1091 (vs, split), 1220 (w), 1288 (m), 1374 (m), 1505 (m), 1563 (w), 1633 (vs), 2226 (vs), 2842 (wb), 3442 (vb) cm^{-1}. ^{1}H NMR [200 MHz, $(CD_3)_2SO$, TMS]: δ = 8.61 (s, 3 H), 7.93 (m, 12 H), 3.81 (br., methylene, 6 H), 2.98 (br., methylene, 6 H), 2.07 (s, 3 H) ppm. UV/Vis (CH_3CN): λ_{max} (ε) = 248 nm (26500 $\text{M}^{-1}\cdot\text{cm}^{-1}$). ***Caution:*** Perchlorates are potentially explosive and should not be prepared and stored in large amounts.

Crystallography: The diffraction measurements were carried out with a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). Crystalline samples of the analyzed compounds were covered with a thin layer of light oil and freeze-cooled to 110 K in order to minimize solvent escape (if present), structural disorder (particularly of the anions) and thermal motion effects, and to increase the precision of the results. The crystal and experimental data for all the compounds are summarized in Table 1. The structures were solved by direct (SHELXS-86, SIR-92, SIR-97)[23,24] and Patterson methods (DIRDIF-96),[25] and refined by full-matrix least squares on F^2 (SHELXL-97).[26] Intensity data of the silver-containing structures were corrected for absorption effects. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in idealized positions, and were refined using a riding model with fixed thermal parameters [$U_{ij} = 1.2 \cdot U_{ij}$(eq.) of the atom to which they are bonded]. CCDC-188495 to -188503 for compounds **2**, **3**, **6**, **7**, **9**, **10**, **11**, **12**, and **13**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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