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New copper(II) complexes incorporating unsymmetrical tetradentate ligands with *cis*-N_2O_2 chromophores: synthesis, molecular structure, substituent effect and thermal stability

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Abstract—Five new tetradentate unsymmetrical ligands, ethylene-*N*-(acetylacetoneimine)-*N′*-(*ortho*-hydroxyl arylaldimine) (aryl = 3,5-dibromophenyl, 3-methylphenyl, 3,6-dimethylphenyl, 3,5-dichlorophenyl, 3,5-dibromoacetophenone), have been prepared and characterized for studies of the general structure of their copper(II) complexes and assessment of the substituent effects on central metal ions. Upon reaction with copper(II) ions, the ligands derived from aryls, where aryls are 3,5-dibromophenyl, 3-methylphenyl, 3,6-dimethylphenyl and 3,5-dibromoacetophenone, give the corresponding copper(II) complexes while the ligand derived from 3,5-dichlorophenyl undergoes partial hydrolysis leading to the cleavage of an acetylacetone moiety. The general coordination configuration has been revealed by an X-ray crystallographic study of one of the complexes, ethylene-*N*-(acetylacetoneiminato)-*N′*-(*o*-hydroxy-3,5-dibromoacetophenoneiminato)copper(II), which exhibits an approximately square-planar geometry with a slight tetrahedron distortion. An ESR study of the copper(II) complexes in solution indicates electronic effects from substituents influence the reactivity of central metal ions. In addition, a key step in preparation of the unsymmetrical ligands has been dramatically improved to ensure synthetic reproducibility and eliminate the decomposition of an intermediate, 7-amino-4-methyl-5-azo-3-heptene-2-one, AMAHO. Thermal stability of the complexes has been also evaluated to assess the compatibility of the two donating moieties. © 1997 Elsevier Science Ltd

Keywords: unsymmetrical Schiff bases; copper(II) complexes; salicylaldehydes; ethylenedamines; acetylacetones; substituent effects.

Recent interest in the design, synthesis and characterization of unsymmetrical Schiff base ligands derived from ethylenediamine for transition metal ion complexes has come from the realization that coordinated ligands around central metal ions in natural systems are unsymmetrical [1]. Symmetrical Schiff base ligands derived from ethylenediamine have been widely used in model complexes [1–6], mostly due to facile and inexpensive preparation of ligands, excellent chelating properties for easy incorporation of metal ions and easy formation of different geometries for modeling studies. For instance, simple and often one pot condensation of two components, ethylenediamine either with salicylaldehydes or with acetylacetones, can easily lead to the formation of tetradentate Schiff base ligands, which can incorporate a variety of metal ions for different purposes. Although unsymmetrical ligands can clearly offer many advantages over their symmetrical counterparts in the elucidation of the composition and geometry of metal ion binding sites in metalloproteins, and in the development leading to the duplication of enzymatic efficiency and selectivity of natural systems with synthetic materials, the difficulty of preparation of such

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ligands has hampered progress because simple condensation methodology with three components is no longer applied.

Several approaches have been developed in the preparation of unsymmetrical Schiff base ligands derived from ethylenediamine, salicylaldehyde and acetylacetone [7–9] to explore the properties of their metal complexes. One important feature of the complexes formed from such unsymmetrical ligands is expected to be unique structural properties, which may sterically and electronically differ from those of conventional (symmetrical) ligands due to a unique combination of aromatic donors (salicylaldehyde portion) and nonaromatic doors (acetylacetone portion) bridged by ethylenediamine units. The acetylacetoneiminato side has been found to be a very reactive nucleophilic center which can lead to the formation of binuclear metal complexes containing two metal centers in close proximity [10]. Few investigations have focused on the other important part of ligands, i.e. the salicylaldiminato side. Substituents in the aromatic ring are expected to play a key role in determining the general properties of the metal complexes because they can influence the reactivity of the central metal ions and stability of the complexes. Fine-tuning of the electronic properties of the complexes simply by changing substituents on the aromatic rings should be possible since the acetylacetone side is relatively fixed, and the contribution from this side is constant (Fig. 1); therefore, intrinsic electronic effects from substituents can be clearly manifested. In this paper we report five new tetradentate ligands, H_2L, ethylene-*N*-(acetylacetoneimine)-*N′*-(*ortho*-hydroxyl arylaldimine) (aryl = 3,5-dibromophenyl, 3-methylphenyl, 3,6-dimethylphenyl, 3,5-dichlorophenyl and 3,5-dibromoacetophenone), where several substituents have been used in the aromatic rings. Ligands H_2L are prepared by an improved procedure which significantly simplifies tedious purification and enhances reproducibility of an active intermediate, AMAHO. The substituents in these ligands have been found to dramatically affect stability of the complexes. Upon reaction with copper(II) ions, the ligands H_2L derived from aryls, where aryls are 3,5-dibromophenyl, 3-methylphenyl, 3,6-dimethylphenyl and 3,5-dibromoacetophenone, give the corresponding copper(II) complexes while the ligand derived from 3,5-dichlorophenyl undergoes partial hydrolysis leading to the cleavage of the acetylacetone moiety. The general coordination configuration has been revealed by an X-ray crystallographic study of one of the complexes, ethylene-*N*-(acetylacetoneiminato)-*N′*-(*ortho*-hydroxy-3,5-dibromoacetophenoneiminato)copper(II), which exhibits an approximately square-planar geometry with a slight tetrahedron distortion. The substituent effects studied by ESR indicate that electronic factors have a profound effect on the central metal ions. Thermal analysis study indicates that both salicylaldiminato and acetylacetoneiminato donating moieties are thermally compatible.

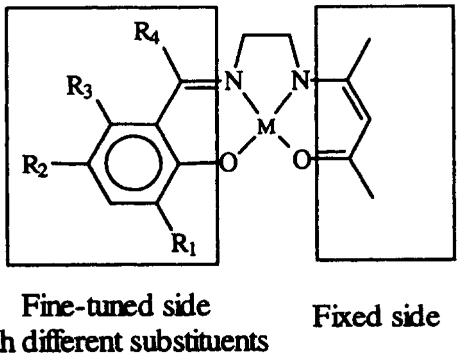


Fig. 1. Schematic representation of unsymmetrical ligands with one donating side fixed and the other fine-tuned.

EXPERIMENTAL

3-Methyl, and 3,6-dimethyl-salicylaldehydes were synthesized according to a literature procedure [11]. 3,5-dibromo-2-hydroxyacetophenone was obtained by bromination of 2-hydroxyacetophenone [12]. Chemical-grade metal chloride or acetate was used for the preparation of the complexes. IR spectra were obtained as KBr pellets on a Schimadzu IR-408 spectrophotometer, calibrated against polystyrene. UV–vis spectra were measured using a Schimadzu UV-240 spectrophotometer with analytical grade solvents. ^1H NMR spectra were recorded on a Varian 200 spectrometer with the use of TMS as reference for ^1H shifts. All the chemical shifts are reported in ppm and coupling constants in Hz. Microanalysis data (C, H and N analysis) were obtained using a Perkin–Elmer 240 C elemental analyzer. ESR spectra were recorded on a JOEL-F1XG spectrometer using MnO or DPPH as references. Thermogravimetric analysis was carried out on Seiko 320 TG/DTA instrument.

Synthesis

7-Amino-4-methyl-5-azo-3-heptene-2-one(AMAHO). The procedure for preparation of this intermediate was a modification of a reported method [7]. Acetylacetone (8.5 cm^3, 0.083 mol) in 50 cm^3 of chloroform was added dropwise to a solution of chloroform (150 cm^3) containing ethylenediamine (7.68 g, 0.128 mol), which was kept at 0–5°C with vigorous stirring during the reaction. After complete addition which took approximately 5 h, the mixture was stirred for another 15 min at room temperature. A clear solution of the mixture without any precipitate was rapidly evaporated *in vacuo* on an oil-bath, 60°C, to remove any free diamines and solvents, and yield a pale-yellow viscous liquid. Yield: 85–90%. The ^{1}H-

NMR data were consistent with that reported in the literature [8].

1-(2′-Hydroxyphenyl)-2,5-diaza-6-methylnona-1,6-diene-8-one (**1**). 7-Amino-4-methyl-5-aza-3-heptene-2-one (4.26 g, 0.03 mmol) dissolved in 30 cm^3 of chloroform was added dropwise to a stirred solution of chloroform (50 cm^3) containing 3-methylsalicylaldehyde (4.08 g, 0.03 mmol) at room temperature over a period of 15 min. The mixture was refluxed for 10 min and evaporated on a rotary evaporator to remove the solvent. The residue was cooled to give a solid which was collected by suction, washed with *n*-hexane and recrystallized from chloroform/petroleum ether (1 : 1 v/v) to yield analytically pure yellow needles of **1**, yield: 83%, m.pt 74–76°C. Found: C, 62.0; H, 6.5; N, 9.9. Calc. for $C_{15}H_{20}N_2O_2$: C, 61.6; H, 6.4; N, 9.6%. ν_{max}/cm^{-1} (KBr): 3400 (br, OH), 1628 (s, C=N), 1600 (s, C=O), 1558, 1516, 1494, 1452 (m, C=C and Ar). δ_H ($CDCl_3$/TMS): 1.92 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 3.71 (m, 4H, CH_2CH_2), 4.96 (s, 1H, C=CH), 7.08 (m, 3H, Ar-H), 8.32 (s, 1H, ArCH=N), 10.82 (s, 1H, NH) ppm.

Ligands **2**, **3**, **4** and **5** were prepared in a manner similar to compound **1**.

Ligand **2**: yield: 84% after recrystallization from chloroform and petroleum ether, m.pt 76–78°C. Found: C, 70.1; H, 8.1; N, 10.2. Calc. for $C_{16}H_{22}N_2O_2$: C, 70.1; H, 8.0; N, 10.2%. ν_{max}/cm^{-1} (KBr): 3300 (br, OH), 1604 (s, C=N and C=O), 1560, 1505, 1460, 1440 (m, C=C and Ar). δ_H ($CDCl_3$/TMS): 1.90 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 3.90 (m, 4H, CH_2CH_2), 5.13 (s, 1H, C=CH), 7.40–7.75 (m, 2H, Ar—H), 8.81 (s, 1H, ArCH=N), 11.00 (br, 1H, NH) ppm.

Ligand **3**: yield: 80% after recrystallization from acetone and petroleum ether, m.pt 84–86°C. Found: C, 41.6; H, 3.6; N, 6.9. Calc. for $C_{14}H_{16}N_2O_2Br_2$: C, 41.6; H, 4.0; N, 6.9%. ν_{max}/cm^{-1} (KBr): 3350 (br, OH), 1642 (s, C=N), 1604 (s, C=O), 1550, 1560, 1433 (m, C=C and Ar). δ_H ($CDCl_3$/TMS): 1.92 (s, 3H, CH_3), 2.0 (s, 3H, CH_3), 3.67 (m, 4H, CH_2CH_2), 4.99 (s, 1H, C=CH), 7.30–7.74 (m, 2H, Ar—H), 8.28 (s, 1H, ArCH=N), 10.91 (s, 1H, NH) ppm.

Ligand **4**: yield: 80% after recrystallization from chloroform and petroleum ether, m.pt 146–148°C. Found: C, 43.3; H, 4.0; N, 6.7. Calc. for $C_{15}H_{18}N_2O_2Br_2$: C, 43.1; H, 4.3; N, 6.7%. ν_{max}/cm^{-1} (KBr): 3400 (br, OH), 1600 (s, C=N), 1575 (s, C=O), 1540, 1512, 1490, 1443 (m, C=C and Ar). δ_H ($CDCl_3$/TMS): 1.80 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.73 (m, 4H, CH_2CH_2), 4.99 (s, 1H, C=CH), 7.57–7.70 (m, 2H, Ar—H), 10.80 (s, 1H, NH), 16.80 (br, 1H, OH) ppm.

Ligand **5**: yield: 82% after recrystallization from acetone, m.pt 86–88°C. Found: C: 53.1; H: 4.8; N: 8.8. Calc. for $C_{14}H_{16}N_2O_2Cl_2$: C, 53.3; H, 5.1; N, 8.9%. ν_{max}/cm^{-1} (KBr): 3350 (br, OH), 1640 (s, C=N), 1610 (s, C=O), 1572, 1518, 1500, 1440 (m, C=C and Ar). δ_H ($CDCl_3$/TMS): 1.88 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 3.80 (m, 4H, CH_2CH_2), 5.03 (s, 1H, C=CH), 7.57–7.70 (m, 2H, Ar—H), 10.80 (s, 1H, NH), 16.80 (br, 1H, OH) ppm.

*Ethylene-*N*-(acetylacetoneiminato)-*N′*-(3-methylsalicylaldiminato)copper*(II) (**6**). Copper(II) acetate (0.91 g, 5 mmol) was dissolved in 50 cm^3 of methanol with the help of a minimum of water. To this solution was added a chloroform solution (50 cm^3) containing compound **1** (1.3 g, 5 mmol). The mixture was stirred for 15 min at room temperature and refluxed for another 15 min. Removal of the solvent gave a solid upon cooling. Crystallization of the solid from chloroform/acetone (1 : 2 v/v) produced analytically pure sample **6**, yield: 81%, m.pt > 250°C. Found: C: 55.8; H: 5.4; N: 8.8. Calc. for $C_{15}H_{18}CuN_2O_2$: C, 55.9; H, 5.6; N, 8.7%; ν_{max}/cm^{-1} (KBr): 1632 (s, C=N), 1590 (s, C=O), 1530, 1508, 1470, 1435 (m, C=C and Ar).

Complexes **7** and **8** were prepared in the same way as complex **6**. Complex **9** was also prepared in a similar way as described above except that 50 mmol of copper(II) chloride instead of copper(II) acetate was used for the reaction. The reaction mixture was stirred for 30 min at room temperature, then refluxed for 15 min, followed by a similar work-up.

Complex **7**: yield: 87% after recrystallization from chloroform and methanol, m.pt > 250°C. Found: C: 57.0; H: 5.8; N: 8.3. Calc. for $C_{16}H_{20}CuN_2O_2$: C, 57.1; H, 5.9; N, 8.3%. ν_{max}/cm^{-1} (KBr): 1630 (s, C=N), 1595 (s, C=O), 1560, 1520, 1440 (m, C=C and Ar).

Complex **8**: yield: 83% after recrystallization from chloroform and methanol, m.pt > 250°C. Found: C: 35.7; H: 3.3; N: 5.7. Calc. for $C_{14}H_{14}Br_2CuN_2O_2$: C, 36.1; H, 3.0; N, 6.0%). ν_{max}/cm^{-1} (KBr): 1635 (s, C=N), 1580 (s, C=O), 1510, 1440, 1400 (m, C=C and Ar).

Complex **9**: yield: 85% after recrystallization from chloroform, m.pt > 250°. Found: C, 37.5; H, 3.1; N, 5.7. Calc. for $C_{15}H_{16}Br_2CuN_2O_2$: C, 37.3; H: 3.3; N: 5.8%. ν_{max}/cm^{-1} (KBr): 159 (br, C=N and C=O), 1512, 1442, 1410 (m, C=C and Ar).

Complex **10**: 0.05 mmol of copper(II) chloride dissolved in ethanol (15 cm^3) with the help of a minimum of water was added to a stirred solution of chloroform (30 cm^3) containing compound **5** (1.57 g, 0.005 mmol). The mixture changed color from pink, to colorless, to green during the first 30 min at room temperature. The mixture was then heated to 50°C for 15 min and cooled to give a gray solid, which was purified by recrystallization twice from THF, yield, 70%, m.pt > 250°C. Found: C, 38.7; H, 4.1; N, 10.0. Calc. for $C_9H_9N_2OCl_3 \cdot H_2O$: C, 37.9; H, 3.9; N, 9.8%. ν_{max}/cm^{-1} (KBr): 3300, 3250 (sh, NH_2), 1642 (s, C=N), 1578, 1520, 1485, 1445 (m, Ar).

Crystal and data collection and structure determination of complex 9 · 1/2CHCl$_3$

Crystal data and data collection parameters: $C_{15.5}H_{14.5}N_2O_2Br_2Cl_{1.5}Cu$, $M = 539.47$, monoclinic, space group $C2/c$, $a = 15.7655(21)$, $b = 17.6793(3)$, $c = 13.843(3)$ Å, $\beta = 101.352(14)°$, $U = 3782.8(11)$ Å^3, cell dimensions are obtained from 25 reflections with 2θ in the range between 26.20 and 85.90°; $T = 298$ K, graphite monochromated Cu-K_α radiation, $\lambda = 1.54056$ Å, $Z = 8$, $D_c = 1.894$ Mg m^{-3}, $F(000) = 2096.0$, beige prism with dimensions $0.60 \times 0.15 \times 0.10$ mm, μ(Cu-K_α) = 8.73 mm^{-1}, absorption corrections are made based on ψ_0 scans, the minimum and maximum transmission factors are 0.53648 and 0.997416, respectively; intensity data are collected on a Nonius diffractometer using the 2θ scan mode in the range of $3 < 2\theta < 150°$, $\pm h$, $+k$, $+l$, three standard reflections showed no significant variation in intensity; 4677 reflections measured, 3398 unique ($R_{\text{int}} = 0.036$) which were used in all calculations.

Structure solution and refinement: The structure was solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically, by full-matrix least squares, on F^2 (program NRCVAX [13]). Hydrogen atoms were calculated from ideal geometry with coordinates and temperature factors fixed. Weights based on counting-statistics were used, and the weight modifier K in $KF_{O(2)}$ is 0.000300 (based on $w^{-1} = \sigma^2(F_o) + 0.0003F^2$). The last least-squares cycle was calculated with41 atoms, 237 parameters and 3398 with $I \geqslant 2.5\sigma(F)$ out of 3898 reflections. For significant reflections, $R(F)$ was 0.055, Rw 0.081 with goodness-of-fit 3.30 where R_w is defined by $Rw = [\Sigma(\omega(F_o - F_c))^2/[\Sigma(\omega(F_o)^2]^{1/2}$ and GoF defined by GoF $= [\Sigma(\omega(F_o - F_c))^2/3161]^{1/2}$. For all reflections, $R(F)$ was 0.060, Rw 0.082. The maximum $\Delta/\sigma = 0.000$, the deepest hole is -1.010 e Å^{-3} and the highest peak is 0.880 e Å^{-3}.

Atomic coordinates have been deposited with the Cambridge Crystallographic Data Center.

RESULTS AND DISCUSSION

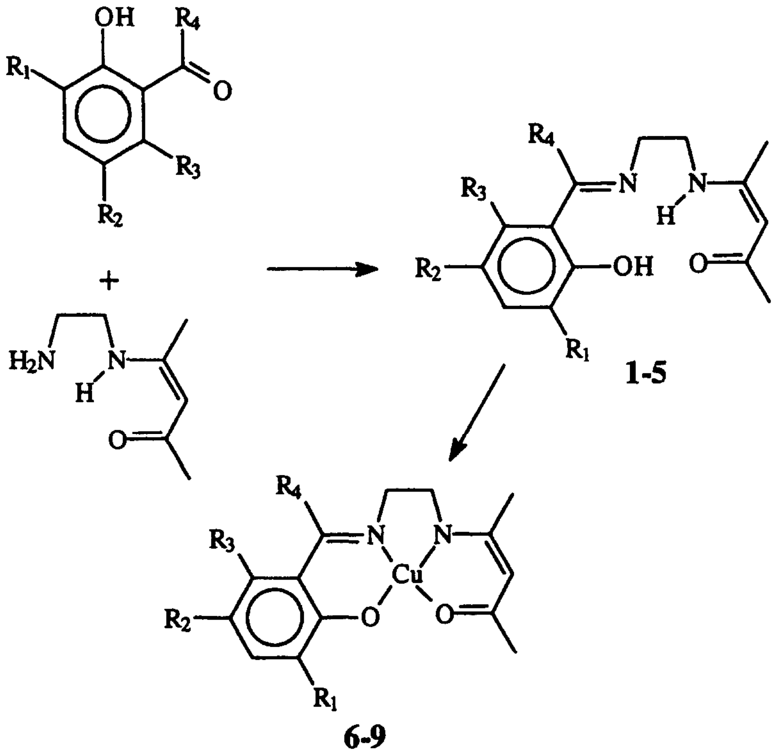
Synthetic study

Five new ligands (**1**–**5**) were prepared through the condensation of salicylaldehyde analogs or 3,5-dibromo-2-hydroxyacetophenone with 7-amino-4-methyl-5-aza-3-heptene-2-one(AMAHO). AMAHO was an intermediate serving as a half unit, prepared from the condensation of ethylenediamine and acetylacetone in chloroform. Several reports have appeared regarding its synthesis, including the condensation of equivalent molar amounts of ethylenediamine and acetylacetone in chloroform [7] or treatment of 3 mol of ethylenediamine and 1 mol of acetylacetone in ethanol [8]. The commonplace method for the separation requires vacuum distillation at relatively high temperature (above 100°C), which easily leads to decomposition of the half unit. We have found a simpler route which avoids the tedious work-up and still gives satisfactory results. The procedure includes the use of appropriate ratio of substrates, control of reaction temperature and separation of the half unit from the starting material in situ. The addition of a chloroform solution of acetylacetone (1 mol) into the diamine (1.5 mol) in chloroform at 0°C leads to the formation of the half unit. Direct removal of unreacted diamine and the solvent at 60°C in vacuum is the key to successfully separate the product from the reactants. Control of the temperature is critical in order for the temperature to be sufficient for removal of reactants, but yet still safe enough for the reactive half unit. The half unit obtained in this fashion is found to be practically pure enough for the preparation of new ligands.

Treatment of the half unit with equimolar amounts of salicylaldehyde derivative leads to the formation of new ligands **1**–**5** *via* the condensation of the free amine of the half unit with the aldehyde. These new ligands are soluble in most common organic solvents. New copper(II) complexes are readily prepared upon reaction of these unsymmetrical ligands with copper(II) chloride or acetate in a mixture of methanol and chloroform. The reaction is found to be unprecedently substituent-dependent, with methyl or bromine substituted ligands yielding "normal" complexes with general formula CuL, where L^{2-} represents a dianionic form of the ligands after deprotonation. Upon reaction with copper(II) ion, ligands **1**–**4** lead to the formation of complexes **6**–**9** in a normal manner (Scheme 1). However, the chlorine-substituted ligand, **5**, undergoes an unusual reaction with copper(II)ions. The reaction of ligand **5** with copper chloride under similar conditions gives the complex **10**, in which the ligand moiety has undergone a partial hydrolyzation which leads to cleavage of an acetylacetone unit (Scheme 2). In order to determine whether this particular ligand is stable under the reaction condition and behaves in such an unusual way toward other metal ions as well, several comparison experiments have been conducted to elucidate the relevance. It is found that the ligand itself is very stable in both methanol and chloroform, as well as in a mixture of methanol–chloroform. It appears to be very stable in the solid state for months at ambient temperature. When used for reactions with other metal ions, the ligand does not lead to the partial hydrolyzation and the cleavage of acetylacetone units, e.g. the reaction with Ni^{II}Cl$_2$ or Ni^{II} acetate gives the corresponding Ni^{II}L [14], the reaction with VO(acac)$_2$ yields the related VOL [15] (Scheme 2). Therefore, we are led to believe that it is a discriminative hydrolysis by Cu^{II} ion of the unsymmetrical ligands of this kind. To the best of our knowledge, this is the first example of such discriminative hydrolysis of the unsymmetrical ligands leading to the cleavage of acetylacetone units.

General characterization

^{1}H NMR data suggest that the new ligands have an enamine structure as shown in Scheme 1. Methyl

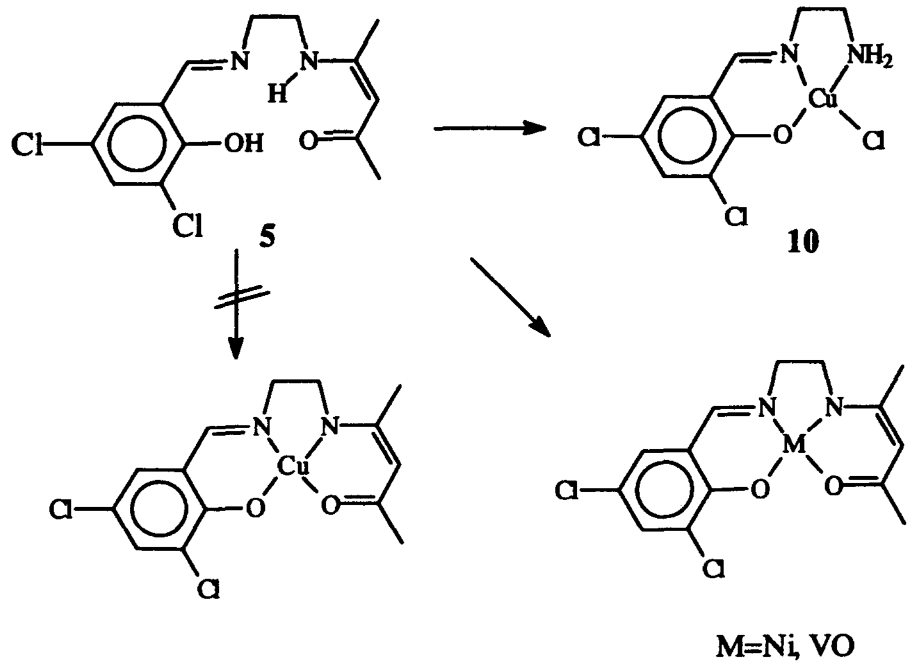


1,6: $R_1=CH_3$, $R_2=R_3=R_4=H$
2,7: $R_1=R_3=CH_3$, $R_2=R_4=H$
3,8: $R_1=R_2=Br$, $R_3=R_4=H$
4,9: $R_1=R_2=Br$, $R_3=H$, $R_4=CH_3$
5: $R_1=R_2=Cl$, $R_3=R_4=H$

Scheme 1. Preparation of new ligands and complexes.

protons on the chelate and aromatic rings are observed at 1.80–2.29 ppm. In the case of ligand **4**, the methyl group bonded to C=N is found at 2.35 ppm. Two methylene protons are found at 3.67–3.90 ppm with irregular multiplets. The vinylic CH and azomethine protons appear at 4.96–5.13 and 8.28–8.81 ppm, respectively. The N—H proton is usually located at 10.8–11 ppm. None of the phenoxylic protons are distinctly detected due to ready H/D exchange, except in **4** and **5** where a broad resonance appears at 16.8 ppm. This unusual downshift for OH is due to intramolecular hydrogen bonding.

The new ligands and their copper(II) complexes exhibit characteristic IR absorptions in which the differences from ligands and complexes correspond to the change of status of donor atoms. For instance, the ligands show a broad band characteristic of OH groups at 3300–3400 cm^{-1} with ν(N—H) band overlapping. Upon complexation, the bands in that region disappear, indicating that both the O—H and N—H groups are deprotonated to give O—Cu and N—Cu bonds. The ligand molecules have two types of intramolecular hydrogen bondings, one of which originates from the interaction between the phenoxyl and imine groups (O—H···N=C) and the other between carbonyl and enamine groups (C=O···H—N). The first one is found to be strongly affected by substituents in the phenyl ring because of its direct conjugation with the phenyl ring. Upon the complexation, the ν(C=N) band shifts correspondingly because of loss of hydrogen bonding and formation of a new chelate ring in which the nitrogen of C=N serves as a donor atom, e.g. the ν(C=N) band which is at 1642 cm^{-1} for ligands **3** is shifted to 1635 cm^{-1} upon complexation in complex **8**. The ν(C=O) band also undergoes to frequency shifts upon complexation. In these complexes, carbonyl, azomethine, enamine and phenoxy groups which are involved in interaction with the metal ion serve a tetradentate ligand which gives a *cis*-N_2O_2 coordination chromophore around the central ion. Complex **10** gives two sharp bands at 3300 and 3250 cm^{-1} corresponding to the amine groups and one strong band at 1642 cm^{-1} due to the azomethine ν(C=N).



Scheme 2. Different reactivity of ligand **5** with different metal ions.

The electronic spectra are measured at room temperature in chloroform for the new copper complexes **6**–**9**, which show a broad *d–d* transition band at 18,000–18,200 cm^{-1}. This *d–d* transition is in the region of that observed for structurally well-characterized complexes of copper(II) *N*-alkylsalicylaldiminates with square-planar geometry [16,17].

Structure study

The general stereochemistry is revealed by an X-ray crystallographic study of one of the complexes, ethylene-*N*-(acetylacetoneiminato)-*N*′-(*ortho*-hydroxy-3,5-dibromoacetophenoneiminato)copper(II) (**9**). The molecular structure with atom numbering is represented in Fig. 2. Selected bond distances and bond angles are listed in Table 1.

The coordination geometry around copper(II) is approximately square planar. Deviations of donor atoms from the mean plane defined by the least square fit indicate it is slightly distorted tetrahedron since one pair of diagonal donor atoms clearly lies below the plane while the other pair is above the plane with the metal ion in the mean plane. Average displacement of the four donor atoms from the mean plane is 0.1359 Å. The dihedral angles between the two planes [N(1)—Cu—O(1) and N(2)—Cu—O(2)] is 11.16°, which compares with 0° for a perfectly square-planar arrangement and 90° for a perfect tetrahedral arrangement. The two diagonal N—Cu—O angles of 171.76° are less than 180° as a result of this tetrahedral distortion. The metal ion, although in the mean plane, is not perfectly centered, and the four bond distances between donor atoms to metal ion are significantly different as shown in Table 1. The mean Cu—N distance of 1.939 Å is slightly longer than that of Cu—O, 1.893 Å, the Cu—N distance in particular is much longer than the Cu—O one in the salicylaldimine residue. Comparison with other copper(II) Schiff base complexes indicates that the mean Cu—O distance appears to be in the normal range while the mean Cu—N distance is a little shorter, e.g. mean distances of Cu—N and Cu—O are 1.985(9) and 1.879(6) Å in bis(*N*-isopropylsalicylaldiminato)copper(II) [18], 1.985(6) and 1.898(6) Å in bis(*N*-*t*-butylsalicylaldiminato)copper(II) [19], 2.01 and 1.97 Å in ethylene-*N*,*N*′-bis(salicylaldiminato)copper(II) [20], 1.99 and 1.90 Å in bis(*N*-methylsalicylaldiminato)copper(II) [21], respectively. However, the mean Cu—N and Cu—O distances are comparable to those of 1.942(9) and 1.891(9) Å, respectively, in bis(*N*-ethylsalicylaldiminato)copper (II) [22].

Incorporation of a metal ion into the ligands has appeared to lead two chelating rings being delocalized. In the first ring containing Cu, N(2), C(6), C(7), C(12) and O(2), the C(6)—C(7) distance of 1.47 Å is much shorter than the normal sp^2–sp^2 C—C single bond (1.51 Å), the C(6)—N(2) distance of 1.30 Å is a little longer than normal imine C═N double bond (1.28 Å) and the C(12)—O(2) bond length of 1.30 Å is shorter than normal sp^2–O C—O single bond (1.34 Å). All these changes in bond length indicate delocalization of the

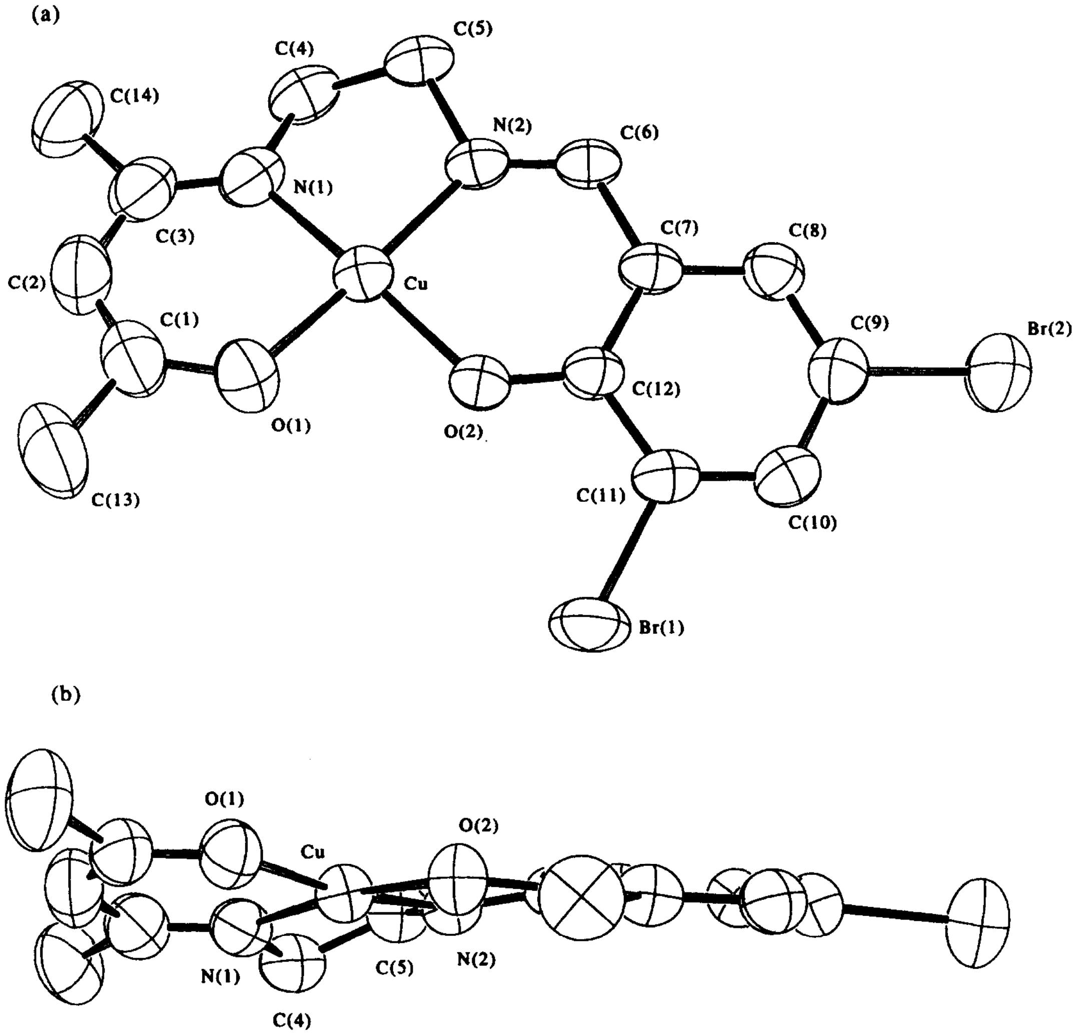


Fig. 2. (a) Molecular structure of complex 9; (b) edge view of the complex showing deviation of N(2) from the mean plane defined by benzene ring and C(6) and O(2).

donating ring of the aromatic Schiff base portion. The same trend in bond lengths can be found in the second ring containing Cu, N(1), C(1), C(2), C(3) and O(1) atoms due to delocalization. Each of these two chelating rings tends to remain planar as a result of this delocalization to form a stable conjugation structure. The deviation from the mean plane in the first ring is insignificant except C(6), which has a maximum deviation of 0.112 Å from the plane. The maximum deviation from the second ring is only 0.051 Å at C(1).

It is interesting to note that the mean plane of the first ring is not coplanar with the benzene plane, the angle between the two planes is 6.93°. A mean plane defined by the benzene ring and O(2) and C(6) indicates that it is a perfect plane with the atoms deviating from the plane by no more than 0.04 Å at O(2). All other deviations are on the order of 0.025 Å or less. The fact that the benzene ring is coplanar with O(2) and C(6), but not with N(2) and Cu suggests the nitrogen atom, instead of the oxygen atom, starts the deviation from the mean plane to adapt to the coordination conformation. It is expected that substantial π-decoupling must occur at N(2) and Cu due to the deviation from the large conjugation including benzene ring and O(2) and C(6).

The two carbons of the ethylene diamine moiety for bridging the two donating groups has almost two identical angles at C(5) and C(4), with <N(2)—C(5)—C(2) of 109.0° and <N(1)—C(4)—C(5) of 109.3°, despite the fact that two donating groups on each side are different. Both C(4) and C(5) deviate from a mean plane defined by Cu, N(1) and N(2). C(4) is 0.234 Å above the plane and C(5) is 0.228 Å below making this ethylene group in *gauche* conformation [Fig. 2(b)] in agreement with results from most of the Schiff base metal complexes containing NCH_2CH_2N moieties.

Table 1. Selected bond distances (Å) and angles (°) of complex **9**

Cu—N(1)	1.923(4)	C(9)—C(10)	1.391(7)	N(1)—C(3)—C(2)	123.2(5)
Cu—N(2)	1.956(4)	C(10)—C(11)	1.369(7)	N(1)—C(3)—C(14)	122.2(6)
Cu—O(1)	1.903(4)	C(11)—C(12)	1.423(6)	C(2)—C(3)—C(14)	114.6(6)
Cu—O(2)	1.882(3)			N(1)—C(4)—C(5)	109.2(4)
Br(1)—C(11)	1.887(4)	N(1)—Cu—N(2)	86.17(18)	N(2)—C(5)—C(4)	109.0(4)
Br(2)—C(9)	1.895(5)	N(1)O—Cu—C(1)	94.60(18)	N(2)—C(6)—C(7)	120.5(4)
N(1)—C(3)	1.287(8)	N(1)—Cu—O(2)	171.87(17)	N(2)—C(6)—C(15)	121.9(4)
N(1)—C(4)	1.446(7)	N(2)—Cu—O(1)	171.62(17)	C(7)—C(6)—C(15)	117.7(4)
N(2)—C(5)	1.479(6)	N(2)—Cu—O(2)	92.49(15)	C(6)—C(7)—C(8)	117.8(4)
N(2)—C(6)	1.299(6)	O(1)—Cu—O(2)	87.90(15)	O(6)—C(7)—C(12)	123.2(4)
O(1)—C(1)	1.281(7)	Cu—N(1)—C(3)	125.6(4)	C(8)—C(7)—C(12)	118.9(4)
O(2)—C(12)	1.301(6)	Cu—N(1)—C(4)	112.5(3)	C(7)—C(8)—C(9)	121.7(4)
C(1)—C(2)	1.354(10)	C(3)—N(1)—C(4)	121.7(5)	Br(2)—C(9)—C(8)	120.5(4)
C(1)—C(13)	1.528(10)	Cu—N(2)—C(5)	110.3(3)	Br(2)—C(9)—C(10)	118.8(4)
C(2)—C(3)	1.446(10)	Cu—N(2)—C(6)	128.0(3)	C(8)—C(9)—C(10)	120.6(5)
C(3)—C(14)	1.518(9)	C(5)—N(2)—C(6)	120.0(4)	C(9)—C(10)—C(11)	118.3(4)
C(4)—C(5)	1.523(8)	Cu—O(1)—C(1)	124.7(4)	Br(1)—C(11)—C(10)	118.2(3)
C(6)—C(7)	1.471(6)	Cu—O(2)—C(12)	127.7(3)	Br(1)—C(11)—C(12)	118.1(3)
C(6)—C(15)	1.505(6)	C(1)—C(1)—C(2)	126.9(6)	C(10)—C(11)—C(12)	123.7(4)
C(7)—C(8)	1.416(7)	O(1)—C(1)—C(13)	113.4(6)	O(2)—C(12)—C(7)	125.2(4)
C(7)—C(12)	1.415(6)	C(2)—C(1)—C(13)	119.6(6)	O(2)—C(12)—C(11)	118.1(4)
C(8)—C(9)	1.368(7)	C(1)—C(2)—C(3)	124.6(5)	C(7)—C(12)—C(11)	116.7(4)

Thermal stability study

Complex **9** has been investigated by means of thermogravimetric analysis (TGA) to determine the general thermal stability of complexes of these unsymmetrical ligands. The representative complex chosen for TGA study has multiple components, including solvated solvent, halogen (bromine atom), methyl groups and a methylene moiety, as well as a core conjugated system associated with a copper ion. The sample is heated up to 1200°C at a rate of 10°C min^{-1} in air, and the TGA is shown in Fig. 3. The complex is very stable up to 258°C exhibiting only the initial loss of solvated solvent (1/2 chloroform) at 137°C. The onset of decomposition of the complex occurs at 259°C due to initial loss of one bromine, which is more readily lost than other components from the aromatic ring. Before the process of losing bromine is completed, two alkyl components of methyl and ethylene start to dissociate at 285°C. A 66.1% weight loss at 430°C indicates a complete loss of one bromine, one methyl and one ethylene. It is followed immediately by the onset of loss of the other bromine. After 438°C this process is further accompanied by the decomposition of other components. A complete loss of the second bromine is estimated at 564°C. The decomposition of the conjugated system including the coordination chromophore is not completed until 720°C. Therefore, while the complex of unsymmetrical ligands is thermally very stable in general, the conjugated system is more stable than the bonds to alkyl groups and these bonds to alkyl groups are more stable than the bonds to halogen. The two different donating moieties, namely salicylaldiminato and acetylacetoneiminato in the complex, exhibit comparable and compatible thermal stability even though the rigidity and conjugation extent of both moieties are different.

Solvent effect and substituent effect study

The ESR spectra of the new copper(II) complexes in chloroform are recorded both at room temperature and at low temperature (120 K). The data are listed in Table 2, where A_0 values are obtained at room temperature and the A_{av} values are the averages of anisotropic tensors in frozen chloroform at low temperature. The A_0 values are satisfactorily matched with A_{av} values in all cases, indicating that the configuration of the complexes in solution at room temperature is the same as in frozen state at low temperature. ESR data of complex **10** listed in Table 2 were obtained in pyridine instead of chloroform because of its poor solubility in chloroform.

Anisotropic g values are observed with $g_{\parallel} > g_{\perp} > 2.0$ ($g_{\parallel} = g_z$, $g_{\perp} = g_x, g_y$) in all the cases, where $g_{\parallel}$ is *ca* 2.10 and $g_{\perp}$ *ca* 2.03. These values are comparable to those found in bis(*N*-salicylidenealkylaminato)copper(II) complexes in which ligands contain an N_2O_2 four-coordinate chromophore [17]. These anisotropic g parameters (Table 2) are characteristic of square-coplanar copper(II) complexes. In addition, the A value is particularly useful for structural information about four-coordinate complexes where two stereochemistries may arise, one having square-planar geometry and the other tetrahedral. The $A_{\parallel}$ value for a tetrahedral CuL_4 chromophore is significantly lower than that of a corresponding square planar chromophore [23]. The

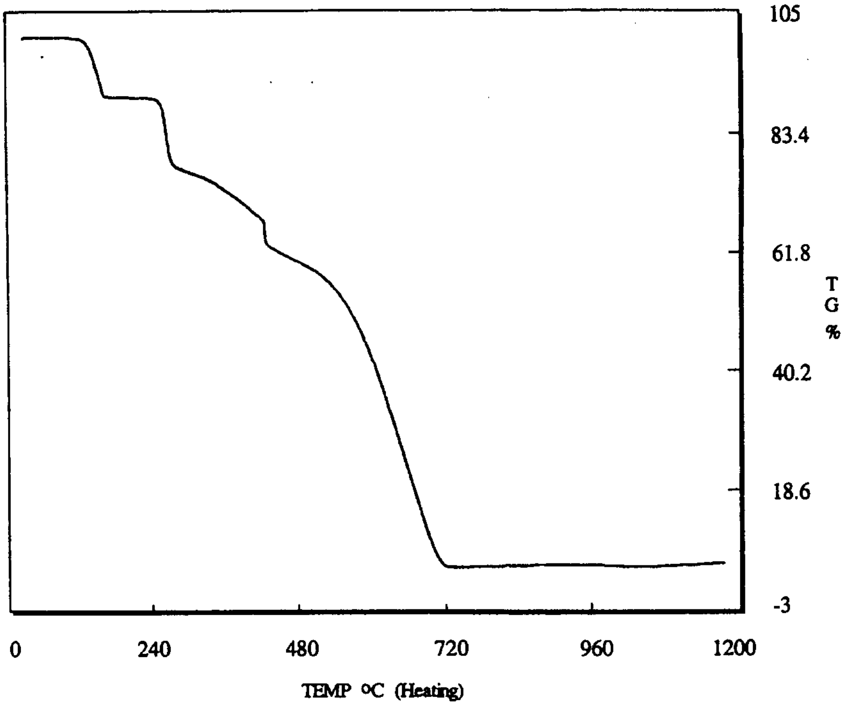


Fig. 3. Thermogravimetric analysis of complex **9**.

Table 2. ESR parameters of complexes

Complex[a]	A_x	A_y	A_z	g_x	g_y	g_z	A_{av}[b]	A_0[c]
6	34.7	33.3	200	2.038	2.028	2.188	89.33	89.05
7	38.89	37.50	210	2.033	2.019	2.178	95.46	94.71
	41.67	40.28						
8	32.00	36.1	200	2.042	2.030	2.184	89.37	89.30
	34.35	38.80						
9	30.56	33.30	200	2.053	2.029	2.190	87.95	87.96
10[d]	24.29	24.29	180.5	2.072	2.072	2.226	76.38	76.38

[a] In chloroform, A_x, A_y, A_z, A_{av} and $A_0 \times 10^{-1}$ mT.
[b] A_{av} is derived from $1/3(A_x + A_y + A_z)$.
[c] A_0 is obtained at room temperature.
[d] In pyridine.

anisotropic A values of the new complexe given an $A_{\parallel}$ of around 200×10^{-4} cm^{-1}, which is in agreement with those of the square-planar complexes having N_2O_2 chromophores [17]. Both g and A values are consistent with those of square-planar complexes, suggesting that these complexes possess primarily the square planar geometry in solution and real distortion is slight, as discussed in the molecular structure of the complex **9**.

The solvent dependence of the A_0 values of complexes **6**, **7** and **9** has been determined by recording the spectra in various solvents. Results in pyridine (Py), tetrahydrofuran (THF), acetonitrile (AN), chloroform and benzene (Ben) are collected in Table 3. The corresponding empirical parameter $D_{I/II}$ for each solvent, defined as the difference between the first and the second absorption d–d bands shifted by the donor solvent [24], is also listed in Table 3 to quantitatively give donating ability of a solvent, e.g. pyridine, a strong donor solvent has $D_{I/II}$ of 4.40 and benzene of weak donor solvent has $D_{I/II}$ of 1.63 here. The isotropic hyperfine coupling constant A_0 obtained at ambient temperature has been used as a simple measure of the interaction of the solvent with square planar copper(II) complexes [25–27]. The solvent can coordinate along the z-axis, which is perpendicular to the chromophore plane, forming an out-of-plane binding. This interaction will cause a decrease in the

Table 3. ESR data in different solvents

		Py[a]	THF[b]	AN[c]	$CHCl_3$	Ben[d]
	$D_{I/II}$	4.40	3.14	2.60	1.98	1.63
6	A_0[e]	80.76	85.27	86.46	87.50	88.88
	g	2.111	2.108	2.106	2.105	2.105
7	A_0	82.85	85.32	86.02	87.49	88.39
	g	2.114	2.108	2.107	2.107	2.105
9	A_0	76.56	81.74	84.09	86.51	88.79
	g	2.117	2.111	2.108	2.107	2.103

[a] Pyridine.
[b] Tetrahydrofuran.
[c] MeCN.
[d] Benzene.
[e] $\times 10^4$ cm^{-1}.

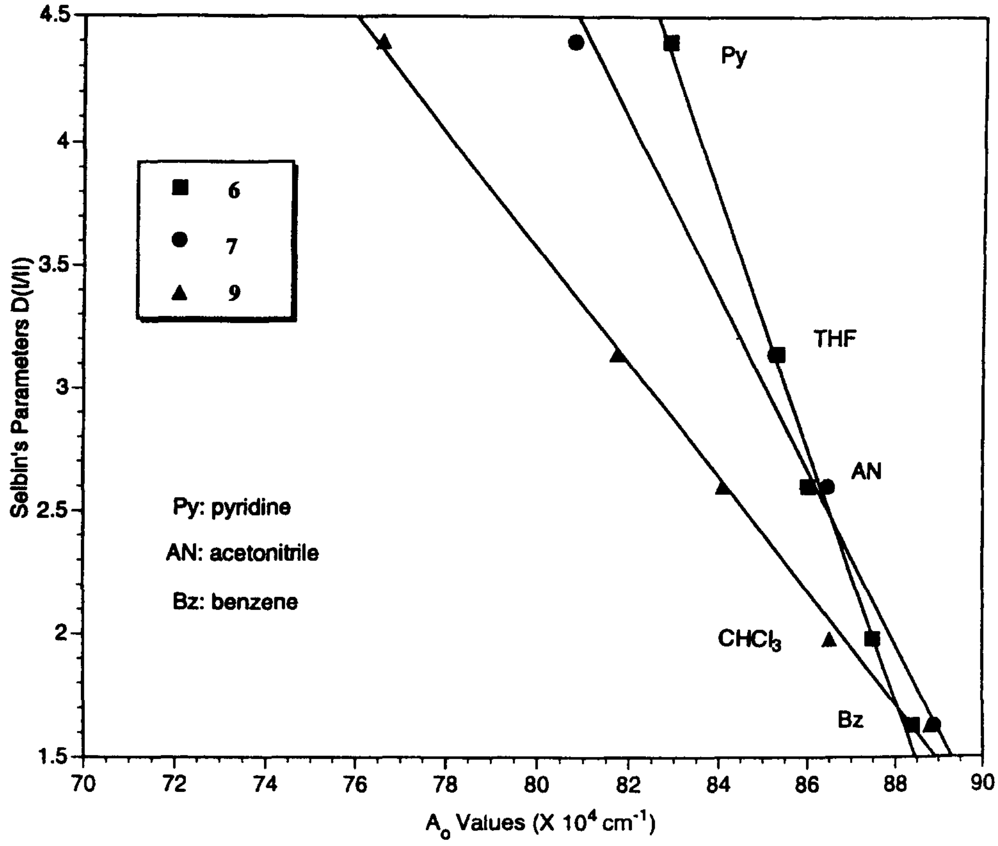


Fig. 4. Correlation between Selbin's parameters (donating ability) and isotropic A_0 values for complexes **6**, **7** and **9**.

in-plane binding. According to Abragam and Pryce, the isotropic term of the hyperfine structure is proportional to the square of the electron's wave function at the nucleus [28]. So, the stronger axial coordination will pull the electron density away from the metal ion leading to the smaller value of unpaired electron wave function at the nucleus.

Inspection of the data in Table 3 clearly indicates that A_0 is strongly solvent-dependent, while g_0 is only slightly changed in various solvents, e.g. the A_0 value of **6** in pyridine is 80.76×10^{-4} cm^{-1} while it is 88.88×10^{-4} cm^{-1} in benzene. The A_0 values of complexes **7** and **9** also have the same tendency to become small going from pyridine, tetrahydrofuran, acetonitrile, chloroform to benzene. A clear and general correlation between A_0 and $D_{I/II}$ for **6**, **7** and **9** is shown in Fig. 4. As discussed above, it is expected that axially strong interactions from strong donating solvents will lead to a decrease of the in-plane interaction of metal ion with the donors from ligands.

The magnitude of the A_0 value change is significantly different for these complexes, e.g. the total change of A_0

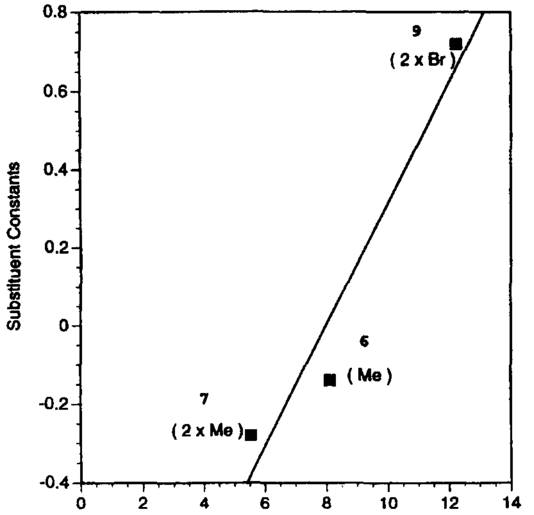


Fig. 5. Magnitude change of A_0 for complexes **6**, **7** and **9**.

is 5.54 units (1 unit = 10^{-4} cm^{-1}) for **7** in solvents on going from pyridine to benzene. This change is 8.12 units for complex **6** and 12.23 units for complex **9**. These changes appear to correspond to substituent effects in the phenyl ring. A correlation of the magnitude of A_0 changes with substituent constant [29] is shown in Fig. 5, where it is found that less donating groups lead to bigger changes of A_0. Since more donating substituents will enhance strength of the in-plane bonding around central metal ions [30], solvent ligation will tend to be weaker in the axial position.

In summary, a series of new copper(II) complexes of unsymmetrical Schiff base ligands have been synthesized and characterized for structural, solvent effect, substituent effect and thermal stability studies. While alkyl- or bromo-substituted ligands react with copper(II) ions to yield normal complexes of CuL, a chloro-substituted ligand reacts with copper(II) ions leading to the partial hydrolysis of the ligand with an acetylacetone moiety cleaved off. The CuL complexes have an approximately square-planar coordination geometry with slight tetrahedron distortion as evidenced by an X-ray crystallographic study of one of the complexes, **9**. The interaction of a solvent with the central metal ion *via* an open axial site(s) of the square-planar complexes has been investigated by ESR, which shows that A_0 values are highly solvent-dependent, with strong donating solvents to yield small A_0. Substituents in the aromatic ring influence the magnitude of A_0 changes, with strong donating substituents leading to small changes of A_0.

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REFERENCES

1. Atkins, R., Brewer, G., Kokot, E., Mockler, G. M. and Sinn, E., *Inorg. Chem.*, 1985, **24**, 127.
2. Liu, H. Y., Schaebert, B. and Holm, R. H., *J. Am. Chem. Soc.*, 1991, **113**, 9529.
3. Calligaris, M. and Randaccio, L., in *Comprehensive Coordination Chemistry*, Vol. 2, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty. Pergamon Press, Oxford, 1987, p. 715.
4. Fenton, D. E., *J. Chem. Soc., Chem. Commun.*, 1979, 39.
5. Saringe, R. P. and Hodgson, D. J., *Inorg. Chem.*, 1976, **15**, 1193.
6. Corazza, F., Floriani, C. and Zehnder, M., *J. Chem. Soc., Dalton Trans.*, 1987, 709.
7. Cros, G. and Coste, J.-P., *Hebd. Seances Acad. Sci., Ser. B*, 1982, **294**, 173.
8. Kwiatkowski, E. and Kwiatkoski, M., *Inorg. Chim. Acta*, 1984, **82**, 101.
9. Kuska, H. A., Farona, M. F., Pappas, P. and Poterton, S., *J. Coord. Chem.*, 1971, **1**, 259.
10. Matsumoto, N., Asakawa, M. and Ohyoshi, A., *J. Chem. Soc., Dalton Trans.*, 1985, 107.
11. Wang, R. X., Meng, Q. J., You, X. Z., Mintz, E. A. and Bu, X. R., *Synth. Commun.*, 1994, **24**, 1757.
12. Buu-Ho, Ng. Ph. and Lavit, D., *J. Chem. Soc.*, 1955, 18.
13. Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. and White, P. S., *J. Appl. Cryst.*, 1989, **22**, 384.
14. Meng, Q. J., Wang, R. X., You, X. Z. and Bu, X. R., *Chem. J. Chin. Univ.*, 1990, 1126.
15. Bu, X. R., Mintz, E. A., You, X. Z., Wang, R. X., Qi, Y., Meng, Q. J., Lu, Y. J. and Van Derveer, D., *Polyhedron*, 1996, **15**, 4585.
16. Sinn, E. and Harris, C. M., *Coord. Chem. Rev.*, 1969, **4**, 391.
17. Yokoi, H., *Bull. Chem. Soc. Jpn*, 1974, **47**, 3037.
18. Orioli, P. L. and Sacconi, L., *J. Am. Chem. Soc.*, 1966, **88**, 277.
19. Cheeseman, T. P., Hall, D. and Waters, T. N., *J. Chem. Soc. A*, 1966, 685.
20. Hall, D. and Waters, T. N., *J. Chem. Soc.*, 1960, 2644.
21. Lingafelter, E. C., Simmons, G. L., Morosin, B., Scheringer, C. and Freiburg, C., *Acta Cryst.*, 1961, **14**, 1222.
22. Baker, E. N., Clark, G. R., Hall, D. and Water, T. N., *J. Chem. Soc. A*, 1967, 251.
23. Hathaway, B. J., in *Comprehensive Coordination Chemistry*, Vol. 5, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty. Pergamon Press, Oxford, 1987, p. 533.
24. Selbin, J., *Chem. Rev.*, 1965, **65**, 168.
25. Adato, I. and Eliezer, I., *J. Chem. Phys.*, 1971, **54**, 1472.
26. Libutti, B. L., Wayland, B. B. and Garito, A. F., *Inorg. Chem.*, 1969, **8**, 1510.
27. Ogata, T., Fujisawa, T., Tanaka, N. and Yokoi, H., *Bull. Chem. Soc. Jpn*, 1976, **49**, 2759.
28. Abragam, A. and Pryce, M. H. L., *Proc. Phys. Soc. London*, 1951, **206**, 164.
29. Stone, R. M. and Pearson, D. E., *J. Org. Chem.*, 1961, **26**, 257; Jaffé, H. H., *Chem. Rev.*, 1953, **53**, 243.
30. Iwaizumi, M., Migita, K. and Isobe, T., *Bull. Chem. Soc. Jpn*, 1976, **49**, 3326.