

Ligand-field Control in the Self-assembly of Polymeric Metal Complexes: Copper(II) Complexes with Quadridentate Schiff-base Ligands involving an Imidazole Moiety†

Takeshi Nozaki,^a Hiroyuki Ushio,^a Genjin Mago,^a Naohide Matsumoto,^{*,a} Hisashi Ōkawa,^a Yukiko Yamakawa,^b Tomoyuki Anno^b and Toshio Nakashima^{*,b}

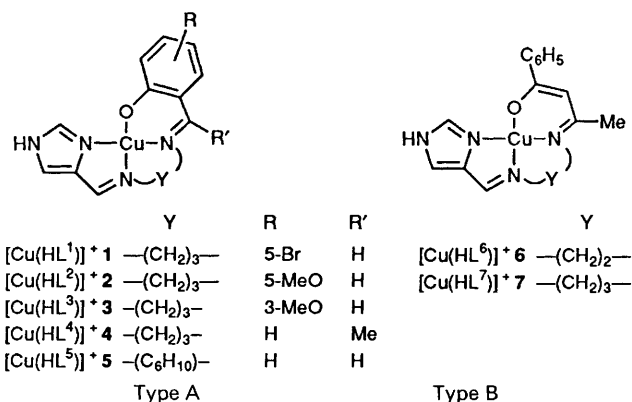
^a Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

^b Faculty of Education, Oita University, Dan-noharu 700, Oita 870-11, Japan

Ligand-field control in the self-assembly of polymeric metal complexes has been studied. A series of seven 'ligand complexes' [Cu(HL)]⁺ containing an imidazole moiety have been prepared, where H₂L are the quadridentate Schiff-base ligands of the 1:1:1 condensation products of 4-formylimidazole, a diamine (ethylenediamine, 1,3-diaminopropane or *trans*-cyclohexane-1,2-diamine), and a salicylaldehyde derivative (salicylaldehyde, 5-bromosalicylaldehyde, 5-methoxysalicylaldehyde, 3-methoxysalicylaldehyde, *o*-hydroxyacetophenone) or benzoylacetone. The single-crystal X-ray analyses of three complexes have confirmed that the co-ordination geometries are essentially square planar. From the deprotonation behaviour of the imidazole proton and the d-d band maxima, the complexes can be classified into two types; type A complexes composed of salicylaldehyde derivatives and type B complexes composed of benzoylacetone. Under alkaline conditions, the type A complexes easily produce a self-assembly process giving insoluble imidazolate-bridged polymeric species and their potentiometric pH titrations are irreversible in the forward and reverse titrations. The variable-temperature magnetic data of the deprotonated type A complexes are well reproduced using the Ising model based on $H = -2\sum J_i S_i S_{i+1}$, and J values of -8.6, -1.8, -5.2, -13.0 and -4.5 cm⁻¹ are obtained. On the other hand, under alkaline conditions, the type B complexes give mononuclear species soluble in common organic solvents and act as good 'ligand complexes'. The potentiometric pH titration curves are almost the same in the forward and reverse titrations, indicating that protonation and deprotonation were reversible. The type A complexes exhibiting weaker ligand-field strength in the equatorial ligand are 'self-assembly complexes' and the type B complexes with stronger fields are 'ligand complexes'.

The design of molecular architecture by self-assembly processes has received much attention.¹ A metal complex can be a useful building unit for the self-assembling process because it contains a variety of structural information to guide the self-assembly reaction.² However, to be a self-assembly molecule, a metal complex should satisfy several conditions. Among metal complexes, a 'ligand complex' can be a possible candidate as a self-assembly molecule.³ If a 'ligand complex' has the ability to receive a donor atom of another 'ligand complex,' a self-assembly reaction will occur. On the other hand, if a 'ligand complex' does not have this ability a self-assembly reaction will not occur, but the complex can be a useful 'ligand complex' for the synthesis of mixed-metal complexes.⁴

In this study, to confirm the above hypothesis, we focused on a family of 'ligand complexes' and examined the controlling factors that determine whether the complex is either a 'self-assembly complex' or a 'ligand complex'. The family of 'ligand complexes' studied is the series of copper(II) complexes 1–7 with quadridentate Schiff-base ligands containing an imidazole moiety derived from the 1:1:1 condensation of 4-formylimidazole, a diamine, and the salicylaldehyde derivative. In general, the copper(II) ion favours a four- or five-co-ordinate geometry. Complexes 1–7 assume a four-co-ordinate square-planar geometry and exist as monomers in the form of the



protonated species under acidic conditions. Under basic conditions, if the complexes have the ability to receive the deprotonated imidazolate nitrogen atom at the axial co-ordination site, the nitrogen atom bared by the deprotonation co-ordinates to another species and thus a self-assembly process might be initiated. Whether the copper(II) ion receives the fifth donor nitrogen atom or not depends on the ligand-field strength and stereochemistry of the equatorial quadridentate ligand. Thus the copper(II) complexes 1–7 with equatorial ligands of various ligand-field strengths were prepared and their deprotonation behaviour investigated.

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Experimental

CAUTION: Perchlorate salts are potentially explosive and should only be handled in small quantities.

Materials.—All chemicals and solvents used for the synthesis were reagent grade. Reagents used for the physical measurements were of spectroscopic grade. 4-Formylimidazole was prepared according to the literature method.⁵

Complexes 1–4.—Complexes 1–4 were prepared as their perchlorate salts using a similar synthetic procedure. The synthesis of $[\text{Cu}(\text{HL}^1)]\text{ClO}_4$ 1 is described as an example.

Bis(*N*-5-bromosalicylidenetrimethylenediaminato)nickel(II) was prepared by the method of Elder.⁶ The nickel(II) complex (5 mmol) and two equivalents of dimethylglyoxime (10 mmol) were mixed in methanol (50 cm³) and refluxed for 2 h. After cooling to room temperature, the precipitated bis(dimethylglyoximate)nickel(II) was filtered off. To the resulting filtrate was added a solution of 4-formylimidazole (0.96 g, 10 mmol) in methanol (20 cm³). The mixture was warmed in a water-bath at 50 °C for 30 min and then cooled to room temperature. A solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (3.71 g, 10 mmol) in methanol (30 cm³) was added. After standing for several hours, a microcrystalline deposit precipitated which was collected by filtration, washed with methanol and diethyl ether and then dried *in vacuo*. Recrystallization was carried out from the minimum amount of dimethylformamide (dmf) and methanol at room temperature.

Complexes 5–7.—Complexes 5–7 were prepared in a similar manner. Complexes 1–3 can be also prepared by this method. The synthesis of $[\text{Cu}(\text{HL}^5)]\text{ClO}_4$ 5 is described as an example.

To a solution of *trans*-cyclohexane-1,2-diamine (1.12 g, 10 mmol) in chloroform (100 cm³) was added dropwise salicylaldehyde (1.22 g, 10 mmol) in chloroform (50 cm³). The resulting solution was kept for *ca.* 1 week at room temperature and then the volume reduced to give an oily material. This was dissolved in methanol (20 cm³) and the solution mixed with 4-formylimidazole (0.96 g, 10 mmol) in methanol (20 cm³). The mixture was warmed on a water-bath at 50 °C for 30 min and then cooled to room temperature. A solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (3.71 g, 10 mmol) in methanol (30 cm³) was added, immediately precipitating microcrystalline material. The crystals were filtered off, washed with methanol and diethyl ether, and then dried *in vacuo*. Recrystallization was carried out from dmf–methanol at room temperature.

Deprotonated Complexes 1'–5'.—Complex 1 (10 mmol) was dissolved in dmf (20 cm³) and then filtered. To the filtrate was added a dmf solution of triethylamine (1.50 g, 15 mmol). After leaving the solution for several hours green microcrystals precipitated which were collected by filtration, washed with methanol and dried. The deprotonated complexes 2'–5' were prepared similarly and are insoluble in common organic solvents including dmf and dimethyl sulfoxide(dmsO).

Deprotonated Complexes 6' and 7'.—The deprotonated complexes 6' and 7' did not crystallize by the procedure adopted for the isolation of 1'–5' since they are very soluble in common organic solvents. The following procedure was therefore adopted. Complex 6 (500 mg) was suspended in chloroform (100 cm³) and NaH (*ca.* 60% in oil) added slowly under stirring at room temperature. During the addition the complex gradually dissolved and hydrogen gas was evolved. After stirring the solution for 1 h it was filtered and the filtrate evaporated to dryness under reduced pressure at room temperature. The resulting green crystals were suspended in diethyl ether, filtered under reduced pressure and washed with a small amount of diethyl ether. Complexes 6' and 7' are soluble in MeOH, CHCl_3 , CH_2Cl_2 , dmf and dmsO.

Physical Measurements.—Elemental analyses for C, H and N were performed at the Elemental Analysis Service Center of Kyushu University. Copper analyses were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Infrared spectra were measured on KBr discs with a JASCO IR-810 spectrophotometer. Electrical conductivity measurements were carried out on a Denki Kagaku Keiki AOL-10 digital conductometer in *ca.* 1×10^{-3} mol dm⁻³ solutions. Electronic spectra were measured on a Shimadzu MPS-2000 multipurpose recording spectrophotometer. Magnetic susceptibilities were measured with a Faraday balance in the temperature range 80–300 K. The Faraday balance calibration was made with $[\text{Ni}(\text{en})_3][\text{S}_2\text{O}_3]$ (en = ethane-1,2-diamine).⁷ Diamagnetic corrections were made with Pascal's constants.⁸ Effective magnetic moments were calculated using the equation $\mu_{\text{eff}} = 2.828(\chi_A T)^{1/2}$, where χ_A is the magnetic susceptibility per copper.

Titration.—All titrations were carried out on a thermostatted bath at 25 °C and dmsO–water (1 : 1) used as the solvent. The pH combination electrode was of type GS-5011s (TOA Co.) and a TOA potentiometer was used. The water used was of extra pure grade, where its resistivity was more than 18.0 MΩ. The standard electrode potential E° of the pH electrode was determined by Gran's plot method in dmsO–water (1 : 1) containing 0.1 mol dm⁻³ LiCl.⁹ The activity coefficient of the proton in aqueous solution can be included in the E° term under the ionic strength constant and therefore the proton concentration can be calculated. First, a 0.1 mol dm⁻³ LiCl solution (solution A), a 0.08 mol dm⁻³ LiCl and 0.02 mol dm⁻³ HCl mixture (solution B) and a 0.08 mol dm⁻³ LiCl and 0.02 mol dm⁻³ LiOH mixture (solution C) were prepared. In non-aqueous solvent the proton and hydroxide concentrations cannot be determined simultaneously since the ionic products of water are unknown. Here a modified Gran's plot method was applied. The solution, which contained 50 cm³ of solution A and 10 cm³ of solution B, was titrated with 0.5 cm³ portions of solution C until neutralization was achieved and $E(\text{mV})$ was then measured. Since $[\text{OH}^-]$ can be calculated stoichiometrically, E° in the acidic region can be determined using the equation $E(\text{mV}) = E^\circ(\text{mV}) + 59.15 \log [\text{H}^+]$. As E° can be calculated from this equation in each titration, an average value was taken to be the final E° . In the basic region, E° was determined similarly by titrating solutions A (50 cm³) and C (10 cm³) with solution B. The value of E° in the basic region was determined using the equation $E(\text{mV}) = E^\circ(\text{mV}) - 59.15 \log [\text{OH}^-]$. Using E° thus determined in acidic and basic solvents, a solution containing the copper complex was titrated with 0.08 mol dm⁻³ LiOH solution (forward titration). Immediately after the forward titration, the solution was re-titrated with solution B (reverse titration). The sample solubilities were as low as *ca.* 3×10^{-3} mol dm⁻³ in dmsO and accordingly the volume of the initial solution was 40 cm³ (dmsO–water) and the final volume after the reverse titration was 50 cm³. The number of dissociated and associated protons, which were obtained from the forward and reverse titrations, respectively, were calculated by Bjerrum's method.¹⁰

X-Ray Crystallographic Studies.—Single crystals of 1, 5 and 6 suitable for X-ray analysis were obtained from dmf–methanol at room temperature. The crystals were mounted on a glass fibre and coated with epoxy resin. X-Ray data were collected using a Rigaku Denki AFC-5 four-circle automated diffractometer with graphite-monochromatized Mo-K α radiation at ambient temperature. The unit-cell parameters were determined by 25 reflections in the range of $20 \leq 2\theta \leq 30^\circ$. Three standard reflections were monitored every 100 reflections and showed good stability. Intensity data were corrected for Lorentz and polarization effects but no absorption correction was applied. The details of data collection, crystallographic data and data reduction are summarized in Table 1. In the

Table 1 Crystallographic data for [Cu(HL¹)]ClO₄ **1**, [Cu(HL⁵)]ClO₄ **5** and [Cu(HL⁶)]ClO₄ **6***

	1	5	6
Formula	C ₁₄ H ₁₄ BrClCuN ₄ O ₅	C ₁₇ H ₁₉ ClCuN ₄ O ₅	C ₃₂ H ₃₄ Cl ₂ Cu ₂ N ₈ O ₁₀
<i>M</i>	497.190	458.361	888.668
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	12.516(2)	19.119(5)	11.745(3)
<i>b</i> /Å	12.122(3)	9.207(3)	28.877(11)
<i>c</i> /Å	12.437(2)	11.310(3)	11.625(3)
α /°	90	90	90
β /°	108.77(1)	111.58(2)	116.22(2)
γ /°	90	90	90
<i>U</i> /Å ³	1786.5(6)	1851.4(1)	3537.0(2)
<i>Z</i>	4	4	4
<i>D</i> _c /g cm ⁻³	1.849	1.644	1.653
<i>D</i> _m /g cm ⁻³	1.85	1.64	1.67
<i>F</i> (000)	1324	1348	2584
μ (Mo-K α)/cm ⁻¹	36.24	13.63	14.25
Crystal size/mm	0.2 × 0.3 × 0.3	0.2 × 0.3 × 0.3	0.4 × 0.4 × 0.3
No. of data used [$ F_o > 3\sigma(F_o)$]	1828	2724	3483
<i>R</i>	0.065	0.057	0.065
<i>R'</i>	0.039	0.047	0.056

* Densities were measured by the flotation method in 1,2-dibromoethane and benzene for **1** and in tetrachloromethane and benzene for **5** and **6**.

Table 2 Atomic coordinates ($\times 10^4$) of [Cu(HL¹)]ClO₄ **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cu	1 012(1)	4 218(1)	6 038(1)
Br	3 939(1)	9 145(1)	4 985(1)
Cl	644(2)	10 681(2)	2 449(2)
O(1)	821(4)	5 771(5)	5 911(4)
O(2)	-273(5)	10 478(5)	2 826(6)
O(3)	1 570(6)	10 425(12)	3 206(8)
O(4)	601(8)	10 191(10)	1 534(8)
O(5)	806(9)	11 723(7)	2 302(10)
N(1)	-1 476(5)	4 235(7)	7 570(5)
N(2)	-108(5)	4 156(6)	6 861(5)
N(3)	1 030(5)	2 564(5)	6 333(5)
N(4)	2 234(5)	4 174(6)	5 405(5)
C(1)	-774(7)	4 811(7)	7 175(6)
C(2)	-1 233(7)	3 146(8)	7 516(7)
C(3)	-364(7)	3 096(7)	7 085(6)
C(4)	311(7)	2 267(7)	6 806(7)
C(5)	1 736(8)	1 736(7)	6 032(7)
C(6)	2 827(7)	2 235(7)	5 973(7)
C(7)	2 634(7)	3 111(7)	5 070(7)
C(8)	2 780(6)	5 039(7)	5 270(6)
C(9)	2 517(6)	6 167(6)	5 441(6)
C(10)	1 569(7)	6 485(7)	5 744(6)
C(11)	1 395(6)	7 627(7)	5 875(6)
C(12)	2 102(7)	8 398(7)	5 654(7)
C(13)	2 994(7)	8 068(7)	5 331(7)
C(14)	3 236(6)	6 981(7)	5 240(6)

Table 3 Atomic coordinates ($\times 10^4$) of [Cu(HL⁵)]ClO₄ **5**

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cu	725(0)	1021(1)	4167(1)
Cl	3672(1)	-1987(2)	7951(1)
O(1)	1236(2)	1866(4)	5767(3)
O(2)	3797(2)	-1958(4)	6775(3)
O(3)	3195(2)	-3187(5)	7923(4)
O(4)	3309(3)	-675(5)	8064(4)
O(5)	4366(2)	-2145(5)	8987(4)
N(1)	2380(2)	-1908(5)	4036(4)
N(2)	1504(2)	-449(5)	4124(4)
N(3)	130(2)	25(5)	2600(4)
N(4)	-207(2)	2125(5)	3825(4)
C(1)	2199(3)	-871(7)	4700(5)
C(2)	1771(3)	-2178(6)	2963(5)
C(3)	1219(3)	-1262(6)	3018(5)
C(4)	447(3)	-972(6)	2204(5)
C(5)	-666(3)	471(6)	2057(5)
C(6)	-1054(3)	247(6)	640(5)
C(7)	-1866(3)	798(7)	234(6)
C(8)	-1928(3)	2273(7)	688(5)
C(9)	-1513(3)	2466(6)	2105(5)
C(10)	-698(3)	2009(7)	2465(5)
C(11)	-339(3)	2942(6)	4587(5)
C(12)	170(3)	3224(6)	5883(5)
C(13)	-105(3)	4067(6)	6656(5)
C(14)	321(3)	4349(6)	7908(5)
C(15)	1049(3)	3814(6)	8399(5)
C(16)	1343(3)	3028(6)	7671(5)
C(17)	913(3)	2680(6)	6393(5)

structure of complex **6** there are two molecular units in the asymmetric unit cell.

The structures were solved by the standard heavy-atom method and refined by block-diagonal least squares. Reliability factors were defined as $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and the function minimized was $R' = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$, where in the final least-squares calculation, the weighting scheme $w = 1/\sigma(F)$ was used. Neutral atomic scattering factors were taken from the literature.¹¹ The hydrogen atoms were inserted at the calculated positions. The hydrogen atoms of **5** and **6** were refined with isotropic thermal parameters, but those of **1** were not refined. Final Fourier difference syntheses were featureless. The computation was carried out on a FACOM V-100 computer at the Computer Center of Kyushu University using the UNICS III program system.¹² Positional parameters of the non-hydrogen atoms of **1**, **5** and **6** are given in Tables 2–4, respectively.

Additional material available from the Cambridge Crystallo-

graphic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

If a 'ligand complex' has the ability to receive a donor atom of another 'ligand complex' at the axial co-ordination site, a self-assembly reaction will occur. If the 'ligand complex' has no such ability a self-assembly reaction will not occur. The ability to receive the donor atom of the 'ligand complex' depends on the ligand-field strength of the equatorial quadridentate ligand, because it is expected that the strength of the axial co-ordination increases as the ligand-field strength of the equatorial ligand decreases. In order to confirm this hypothesis it is necessary to vary the ligand-field strength of the equatorial

ligand, which is possible by substituting the components of the ligand derived from the 1:1:1 condensation reaction of 4-formylimidazole, diamine and the salicylaldehyde or β -diketone. For example, it is known that the ligand composed of benzoylacetone gives a stronger ligand-field strength than that of the salicylaldehyde derivative, based on the investigation of the spin states of the iron(III) complexes with the 1:2 Schiff-base ligands of ethylenediamine and various salicylaldehydes or benzoylacetone.^{13,14}

The copper(II) complexes of the unsymmetrical quadridentate ligands, **1–7**, were isolated as perchlorate salts and characterized (Table 5). The IR spectra of complexes **1–7** showed the characteristic bands due to the counter ClO_4^- anion and the imidazole NH stretching vibration at *ca.* 3200 cm^{-1} . The molar electrical conductivities of **1–7** measured in acetonitrile were

in the range 100–170 $\text{S cm}^2 \text{mol}^{-1}$, consistent with a 1:1 electrolyte.¹⁵

From the deprotonation behaviour of the imidazole proton, complexes **1–7** can be classified into two types, type A complexes **1–5** and type B complexes **6** and **7**. When the imidazole proton is deprotonated under alkaline conditions, type A complexes give insoluble complexes **1'–5'**, while type B complexes give species soluble in common organic solvents. Type B complexes **6'** and **7'** can be only solidified as the solvated crystals by reducing the volume of the solution, using non-aprotic solvents such as chloroform and dichloromethane, to near dryness. The IR bands observed in **1–7** due to the counter anion and the imidazole NH stretching vibration are absent in the deprotonated complexes **1'–7'**. The molar electrical conductivities of type B **6'** and **7'** measured in dichloromethane are nearly zero, consistent with a non-electrolyte.

Potentiometric pH titration was carried out in dmso–water (1:1) at 25 °C. The imidazole proton did not dissociate when the compounds were dissolved in a 1:1 mixture (*ca.* $1 \times 10^{-3} \text{ mol dm}^{-3}$) as the electrode potentials were almost constant. Fig. 1 shows the forward and reverse titrations of complexes **3** (type A) and **6** (type B), where the number of hydroxide ions consumed per copper (\bar{n}_H) is shown as a function of $-\log[\text{OH}^-]$. From these titrations the hydrolysis constants $\text{p}K_\text{h} = \log\{[\text{CuL}]/[\text{Cu}(\text{HL})][\text{OH}^-]\}$ were also determined and values of 6.8, 5.4, 5.8, 7.4 and 5.5 are obtained for **1** and **3–6** respectively. In the forward titration, the type A complex **3** began to give a green precipitate at $\bar{n}_\text{H} = 0.5$ shown by a break in the curve, while the type B complex **6** showed no precipitation in the range of the titration. The reverse titration curve of **3** differed from the forward one, the precipitate finally redissolving in the reverse titration. The \bar{n}_H vs. $-\log[\text{OH}^-]$ curves for the type B complex **6** are almost the same in the forward and reverse titrations, indicating that deprotonation and protonation were reversible.

The electronic spectra were measured both in the solid state and in solution, and the d–d band maxima are given in Table 5. The maxima are indicative of the co-ordination geometry and the ligand-field strength. If a square-planar co-ordination geometry is preserved, the d–d band maxima shifts to lower wavelength as the ligand-field strength increases.¹⁶ When the co-ordination geometry changes from square planar to square pyramidal, the d–d band maxima shifts to higher wavelength.¹⁷ The reflectance spectra of the powdered samples of **1–7** showed a broad maxima assignable to the d–d transition at 530–573 nm and those of the corresponding deprotonated complexes **1'–7'** showed the band at higher wavelengths (610–667 nm). The red shift of the d–d band is ascribed to the change in the co-ordination geometry from four-co-ordinate square planar to five-co-ordinate square pyramidal, as confirmed previously from the structures and d–d band maxima of the complexes $[\text{Cu}(\text{HL})]\text{ClO}_4$ and $[(\text{CuL})_n](\text{H}_2\text{L}) = 1:1:1$ condensation product of 4-formylimidazole, propane-1,3-diamine and

Table 4 Atomic coordinates ($\times 10^4$) of $[\text{Cu}(\text{HL}^6)]\text{ClO}_4$

Atom	x	y	z
Cu(a)	1 255(1)	790(1)	11 135(1)
Cu(b)	517(1)	1 749(1)	8 822(1)
O(1a)	370(7)	712(3)	9 335(7)
N(1a)	4 899(10)	902(4)	11 373(10)
N(2a)	2 994(9)	818(3)	11 304(8)
N(3a)	2 150(9)	922(3)	12 983(8)
N(4a)	–153(9)	660(3)	11 492(8)
C(1a)	3 647(12)	819(5)	10 620(12)
C(2a)	5 076(13)	969(5)	12 641(12)
C(3a)	3 894(11)	906(4)	12 582(11)
C(4a)	3 323(11)	945(4)	13 469(10)
C(5a)	1 299(12)	979(5)	13 605(11)
C(6a)	104(12)	691(4)	12 890(10)
C(7a)	–2 232(12)	306(5)	11 036(12)
C(8a)	–1 204(11)	477(4)	10 680(10)
C(9a)	–1 541(12)	424(4)	9 348(11)
C(10a)	–747(11)	539(4)	8 794(10)
C(11a)	–1 203(12)	474(4)	7 341(11)
C(12a)	–2 411(13)	325(4)	6 542(11)
C(13a)	–2 762(13)	249(5)	5 238(11)
C(14a)	–1 893(15)	346(5)	4 756(13)
C(15a)	–661(13)	500(5)	5 538(12)
C(16a)	–302(13)	567(4)	6 863(11)
O(1b)	1 425(7)	1 806(3)	10 624(7)
N(1b)	–3 041(10)	1 476(4)	8 665(9)
N(2b)	–1 203(9)	1 650(3)	8 724(8)
N(3b)	–490(10)	1 736(4)	6 941(9)
N(4b)	1 941(9)	1 804(4)	8 438(8)
C(1b)	–1 813(13)	1 573(4)	9 392(11)
C(2b)	–3 292(12)	1 495(5)	7 393(12)
C(3b)	–2 141(12)	1 602(4)	7 433(11)
C(4b)	–1 657(11)	1 663(5)	6 507(12)
C(5b)	285(12)	1 824(5)	6 237(11)
C(6b)	1 670(12)	1 699(5)	7 104(11)
C(7b)	4 160(13)	2 003(5)	8 912(12)
C(8b)	3 067(12)	1 938(5)	9 248(11)
C(9b)	3 391(12)	2 038(4)	10 618(11)
C(10b)	2 565(12)	1 962(5)	11 148(11)
C(11b)	3 042(12)	2 072(4)	12 601(10)
C(12b)	4 332(12)	2 104(4)	13 422(11)
C(13b)	4 711(13)	2 206(4)	14 722(11)
C(14b)	3 789(14)	2 274(5)	15 166(12)
C(15b)	2 515(14)	2 252(5)	14 350(12)
C(16b)	2 086(13)	2 143(4)	13 015(12)
Cl(a)	–2 378(3)	1 744(1)	12 373(3)
O(2a)	–2 367(14)	1 529(5)	13 411(10)
O(3a)	–3 061(12)	2 147(4)	12 026(13)
O(4a)	–2 989(9)	1 422(3)	11 339(9)
O(5a)	–1 126(8)	1 837(4)	12 588(9)
Cl(b)	4 295(3)	642(1)	7 653(3)
O(2b)	5 046(9)	893(3)	8 833(8)
O(3b)	4 196(12)	930(5)	6 669(10)
O(4b)	4 906(13)	254(5)	7 649(12)
O(5b)	3 077(9)	551(4)	7 504(10)

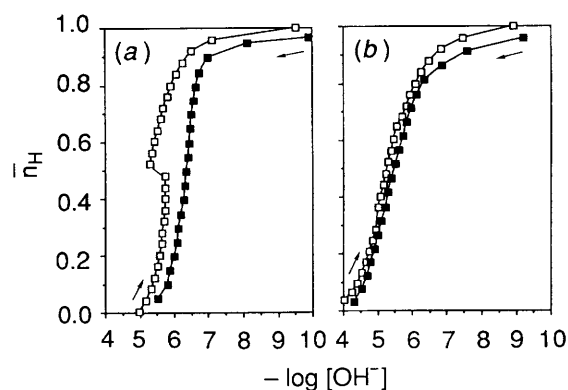
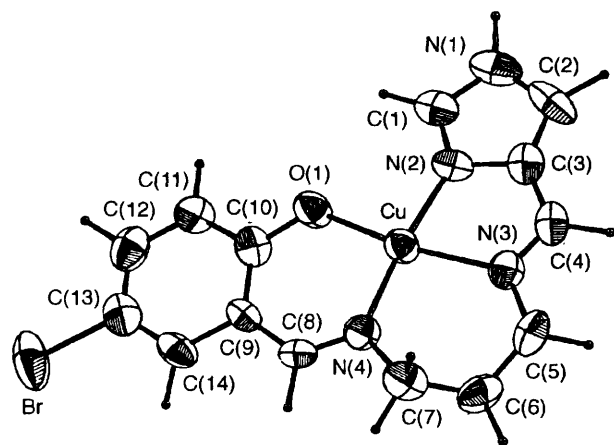


Fig. 1 The forward (\square) and reverse (\blacksquare) titrations of (a) complex **3** (type A) and (b) complex **6** (type B), where the number of hydroxide ions consumed per one copper (\bar{n}_H) is shown as the function of $-\log[\text{OH}^-]$

Complex	Analysis ^a (%)			M.p./°C	Λ_m^b / S cm ² mol ⁻¹	λ_{\max}/nm ($\epsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1}$)				
	C	H	N			dmf	MeCN	MeOH	CHCl ₃	Solid state
1	33.55 (33.80)	2.90 (2.85)	11.00 (11.25)	> 300	100	599 (130)	574 (190)	595 (190)	—	573
2	40.10 (40.20)	3.85 (3.80)	12.70 (12.50)	286–288	130	592 (150)	569 (130)	590(sh) (120)	—	566
3	39.95 (40.20)	3.85 (3.80)	12.35 (12.50)	299–305	110	604 (150)	606 (120)	593 (100)	—	573
4 ·0.5dmf	42.10 (42.25)	4.45 (4.40)	13.20 (13.45)	> 280 (decomp.)	170	584 (130)	564 (120)	585 (90)	—	570(sh)
5	44.95 (44.55)	4.35 (4.20)	12.10 (12.20)	220–225	130	582 (220)	570 (240)	590 (190)	—	561
6	43.20 (43.25)	3.85 (3.85)	12.85 (12.60)	270–275	120	551 (90)	542 (90)	560 (130)	—	530
7	44.35 (44.55)	4.20 (4.20)	12.30 (12.20)	271–273	160	580 (80)	560 (70)	584 (80)	—	530
1'	42.15 (42.40)	3.45 (3.30)	13.90 (14.10)	> 280 (decomp.)	<i>c</i>					667
2' ·0.5MeOH	51.45 (51.15)	4.70 (5.00)	15.65 (15.40)	> 280 (decomp.)	<i>c</i>					648
3'	51.20 (51.80)	4.65 (4.65)	15.85 (16.10)	> 290 (decomp.)	<i>c</i>					643
4'	51.70 (51.50)	5.10 (5.20)	15.85 (16.00)	> 280 (decomp.)	<i>c</i>					648
5' ·0.5H ₂ O	55.65 (55.65)	4.95 (5.20)	15.00 (15.25)	> 280 (decomp.)	<i>c</i>					655
6' ·0.2CHCl ₃	53.25 (52.90)	4.60 (4.45)	14.90 (15.25)	161–166	0.2	538 (280)	535 (150)	549 (190)	537 (240)	610
7' ·0.5MeOH	56.65 (56.35)	5.45 (5.15)	15.25 (15.00)	155–160	0.4	556 (90)	540 (80)	568 (70)	530(sh) (80)	632

Fig. 2 An ORTEP drawing of $[\text{Cu}(\text{HL}^1)]^+ \mathbf{1}$ showing the atom-numbering scheme (thermal ellipsoids at 50% probability level)



The copper ions essentially assume a square-planar co-

salicylaldehyde).^{3a} The d–d band maxima of the type A complexes **1–5** (561–573 nm) are higher in wavelength than those of the type B complexes **6** and **7** (530 nm), indicating that the ligand-field strengths of the equatorial plane of the type A complexes are weaker than those of type B. The deprotonated type B complexes **6'** and **7'** are green in the solid state (λ_{\max} 610 and 632 nm) and red in chloroform (λ_{\max} 537 and 530 nm), indicating that the copper(II) ion assumes a five-co-ordinate geometry in the solid state and a four-co-ordinate geometry in solution. In other words, a polynuclear structure produced by self-assembly is preserved in the solid but destruction to the mononuclear structure occurs in solution. It should be also noted that the d–d band maxima depend on the solvent used. For example, the d–d band maxima of **7'** are at 530, 540, 556 and 568 nm in chloroform, MeCN, dmf and MeOH,

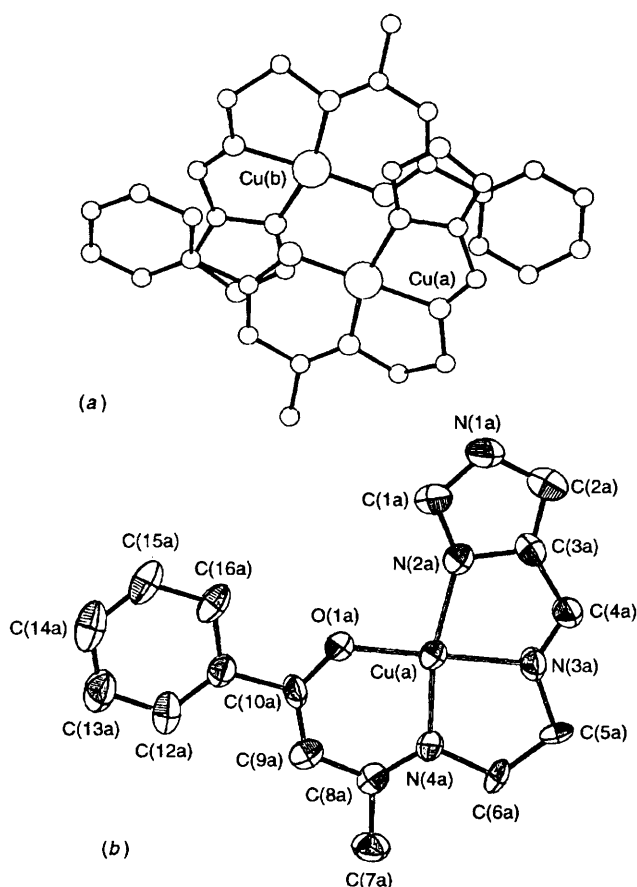


Fig. 4 (a) A unique unit of $[\text{Cu}(\text{HL}^6)]_2^{2+}$ showing parallel packing of two planar complex molecules of **6** and (b) an ORTEP drawing of molecule A of $[\text{Cu}(\text{HL}^6)]^+$ **6** with the atom numbering scheme (thermal ellipsoids at 50% probability level)

Table 6 Selected bond distances (Å) and angles (°) for $[\text{Cu}(\text{HL}^1)]\text{ClO}_4$ **1**, $[\text{Cu}(\text{HL}^5)]\text{ClO}_4$ **5** and $[\text{Cu}(\text{HL}^6)]\text{ClO}_4$ **6***

	1	5	6	
			a	b
Cu—O(1)	1.897(6)	1.880(3)	1.895(7)	1.892(7)
Cu—N(2)	1.984(7)	2.026(5)	1.965(12)	1.994(12)
Cu—N(3)	2.036(7)	1.948(5)	1.967(8)	1.973(9)
Cu—N(4)	1.934(7)	1.962(4)	1.912(12)	1.918(12)
O(1)—Cu—N(2)	89.4(3)	100.0(2)	98.9(4)	97.8(4)
N(2)—Cu—N(3)	80.7(3)	81.5(2)	81.5(4)	80.7(5)
N(3)—Cu—N(4)	94.7(3)	83.1(2)	84.1(4)	84.4(4)
N(4)—Cu—O(1)	95.0(3)	95.0(2)	96.4(4)	97.4(4)
Cu...O(1)	2.749(4)	4.619(4)	3.017(9)	3.073(9)
Cu...Cu	3.531(1)	4.313(1)		3.687(2)

* The structure of **6** consists of two $[\text{Cu}(\text{HL}^6)]\text{ClO}_4$ molecules a and b as a unique unit.

ordination geometry with the N_3O donor atoms of the quadridentate Schiff-base ligands. However, in complexes **1** and **6**, a dimeric structure is formed by parallel packing of the two planar complex molecules, where the axial site of the copper(II) ion is occupied by a phenol oxygen of an adjacent dimeric unit with distances of 2.749(4) Å for **1**, 3.017(9) (molecule A) and 3.073(9) Å (molecule B) for **6**. These distances seem to be too long for axial co-ordination. On the other hand, complex **5** is definitely a monomer with an intermolecular

Cu—O distance of 4.619(4) Å. The cyclohexane part of **5** adopts a chair conformation, where atoms C(6) and C(9) deviate by -0.64 and 0.67 Å from the plane defined by C(5), C(7), C(8) and C(10). The atoms N(3) and N(4) adopt a *trans* conformation and deviate -0.48 and 0.48 Å respectively from the same plane.

The average bond distance for Cu to each of the four N_3O donor atoms for **1**, **5** and **6** is 1.963(7), 1.954(4) and 1.940(10) Å [average of 1.935(10) (molecule A) and 1.944(10) Å (molecule B)], respectively, indicating that the type B complex **6** with the shortest distance has a stronger ligand field than the type A complexes **1** and **5**.

Magnetic Susceptibility Studies of Complexes 1'–5'.—Type A complexes **1–5** give the insoluble deprotonated complexes **1'–5'** when they are treated under alkaline conditions. The temperature dependence of the magnetic susceptibilities of **1'–5'**, together with that of **6'** were measured. Since their magnetic behaviours are similar that of **1'** is described as an example. The plot of $1/\chi_A$ vs. T is linear and obeys the Curie–Weiss law $[1/\chi_A = (T - \theta)/C]$ with a Weiss constant of $\theta = -9.9$ K, suggesting a weak antiferromagnetic interaction. The μ_{eff} is $1.85 \mu_B$ at 290 K which is compatible with the spin-only value of $1.73 \mu_B$ for $S = \frac{1}{2}$. As the temperature is lowered, the μ_{eff} value gradually decreases from $1.85 \mu_B$ at 290 K to $1.80 \mu_B$ at 90 K. The magnetic susceptibility data were analysed on the basis of the Ising model for a one-dimensional infinite chain structure,¹⁹ equation (1), where the spin Hamiltonian in the

$$\chi_A = \frac{Ng^2\beta^2}{12kT} \times \frac{e^{4K} + (2 + K^{-1})e^{2K} - K^{-1}e^{-2K} + 5}{e^{2K} + e^{-2K} + 2} + N\alpha \quad (1)$$

form $H = -\sum J_{ij}S_iS_j$ is used and $K = J/kT$. The symbols have their usual meanings, $N\alpha$ denoting the temperature-independent paramagnetism. The observed susceptibility data were fitted by a least-squares method, where the disagreement factor $R = [\sum(\mu_{\text{obs}} - \mu_{\text{calc}})^2 / \sum \mu_{\text{obs}}^2]^{\frac{1}{2}}$ was minimized and $N\alpha$ was fixed at $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. The best-fit parameters, $J = -8.6 \text{ cm}^{-1}$, $g = 2.15$ and $R = 0.020$ were obtained. The variable-temperature magnetic data of the other deprotonated type A complexes are well reproduced using the Ising model based on $H = -\sum J_{ij}S_iS_j$, where the J values of **2–5** are -1.8 , -5.2 , -13.0 and -4.5 cm^{-1} , respectively. The present J value is compatible with those of imidazolate-bridged zigzag-chain ($J = -1.8 \text{ cm}^{-1}$)^{2a} and helical-chain ($J = -15 \text{ cm}^{-1}$) structures.^{3a} The J values observed (-1.8 to -13.0 cm^{-1}) are consistent with the imidazolate group bridging two adjacent copper(II) ions in an axial fashion, since a relatively strong antiferromagnetic interaction (*ca.* $2J = -40$ to -100 cm^{-1}) has been observed when an imidazolate group bridges two copper(II) ions in an equatorial manner.²⁰

Conclusion

Ligand-field control in the self-assembly of polymeric metal complexes has been investigated. Copper(II) complexes with quadridentate Schiff-base ligands involving an imidazole moiety have a donor atom that can potentially co-ordinate to other metal ions. Complexes can be classified into two types by the d–d band maxima, the average bond distances in the coordination sphere, and their deprotonation behaviour. Under alkaline conditions, the type A complexes self assemble and give insoluble imidazolate-bridged polymeric species whereas the type B complexes give mononuclear species soluble in common organic solvents. Depending on the ligand-field strength of the planar quadridentate ligand, whether the complex is either a 'self-assembly molecule' or a 'ligand complex' can be controlled.

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