

Synthesis, characterization and properties of ternary copper(II) complexes containing reduced Schiff base *N*-(2-hydroxybenzyl)- α -amino acids and 1,10-phenanthroline †

Chang-Tong Yang,^a Boujemaa Moubaraki,^b Keith S. Murray^{*b} and Jagadese J. Vittal^{*a}

^a Department of Chemistry, National University of Singapore, Singapore 117543.

E-mail: chmjiv@nus.edu.sg

^b School of Chemistry, Monash University, PO Box 23, Victoria, 3800, Australia.

E-mail: k.murray@sci.monash.edu.au

Received 20th November 2002, Accepted 16th December 2002

First published as an Advance Article on the web 28th January 2003

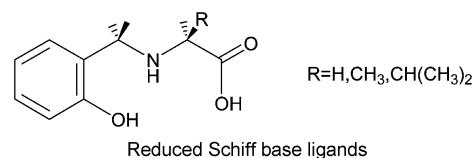
Ternary copper(II) complexes containing reduced Schiff base ligands (*N*-(2-hydroxybenzyl)- α -amino acid, where α -amino acid = glycine (H₂sgly), L-alanine (H₂sala) and L-valine (H₂sval)) and 1,10-phenanthroline (phen) have been synthesized and characterized. The neutral mononuclear Cu^{II} complexes [Cu(L)(phen)] \cdot *x*H₂O (L = sgly (**1**), sala (**2**), sval (**3**)) have been prepared from Cu(OAc)₂ \cdot H₂O, H₂L, phen, LiOH in the ratio 1 : 1 : 1 : 2 in H₂O–MeOH. The monodeprotonated Cu^{II} complexes [Cu(HL)(phen)](ClO₄) \cdot *x*H₂O (L = Hsgly (**4**), Hsala (**5**), Hsval (**6**)) have been obtained from Cu(ClO₄)₂ \cdot 6H₂O, H₂L, phen, LiOH in the ratio 1 : 1 : 1 : 1 in H₂O–MeOH. The dinuclear Cu^{II} complexes [Cu₂(L)(phen)₃](ClO₄)₂ \cdot *x*H₂O (L = sgly (**7**), sala (**8**), sval (**9**)) were the only product isolated instead of **1–3** when Cu(ClO₄)₂ \cdot 6H₂O was used in the place of Cu(OAc)₂ \cdot H₂O. The electronic spectral titration experiments indicate that the neutral mononuclear compounds could be converted to protonated **4–6** but not *vice versa*. The protonated phenolic oxygen is involved in medium to weak interaction with Cu^{II}–OH distances, 2.446(3) Å in **4**, and 2.73(4) and 2.79(4) Å in **5**. Compound **4** is a mononuclear cation while **5** is a helical coordination polymer in the solid state with the carboxylate group in *anti–anti* bridging mode. The structures of **1**, **4**, **5** and **7** have been determined by X-ray crystallography. Variable temperature magnetic measurements of the helical polymer **5** showed very weak ferromagnetic coupling with μ_{eff} per Cu remaining constant at 1.80 BM between 300 and 30 K, then a rapid increase to 2.07 BM at 4 K. Fitting to a Heisenberg $S = \frac{1}{2}$ chain model gave a J value of 1.2 cm⁻¹.

Introduction

The physical and chemical properties of metal complexes are greatly influenced by their structures and the coordination geometries at the metal centers. Hence chemists have long standing interest in the understanding of the factors that determine the coordination geometry and in the control of complex structure by ligand design.^{1–6} For the given ligand with flexible conformation, the conversion from one structure to another is possible by changing pH, anion, solvent, *etc.*, and hence the physical and chemical properties.^{1–3,7–16} In this respect we have been interested in the structures of metal complexes containing reduced Schiff base ligands formed between amino acids and salicylaldehyde.^{17–20} The influence of thermal dehydration on the three-dimensional architectures have been demonstrated for Cu^{II} and Zn^{II} complexes containing *N*-(2-hydroxybenzyl)-L-alanine. Recently we observed that the protonation of the neutral monomer, [Cu(Sbal)(phen)] (H₂Sbal = *N*-(2-hydroxybenzyl)- β -alanine), leads to the isolation of two types of 1D coordination polymers.²¹ In order to understand the influence of the side arms of the ligand on the structure, we have now prepared similar reduced Schiff base ligands of salicylaldehyde with glycine (H₂sgly), alanine (H₂sala) and valine (H₂sval). Ternary Cu^{II} complexes of H₂sgly, H₂sala and H₂sval with phen have been isolated and characterized. Further the single crystal X-ray structures of [Cu(sgly)(phen)] \cdot 2.75H₂O, [Cu(Hsgly)(phen)](ClO₄) \cdot 1.5H₂O and [(phen)Cu(μ -sgly)Cu(phen)₂](ClO₄)₂ \cdot 3H₂O and [Cu(Hsala)(phen)](ClO₄) \cdot 0.625H₂O have been determined. The results of our investigations are discussed in detail in this paper.

An interesting Cu^{II} complex containing an axial Cu^{II}–O(phenol) bond has been put forward to explain the nature of substrate binding at the active site of tyrosinase which is a

copper containing monooxygenase that catalyses the hydroxylation of phenols to catechols and the two electron oxidation of catechols to *o*-quinones.²² Our present investigation involved protonation of mononuclear Cu^{II} complexes which might lead to such Cu–phenol interactions in the solid state and hence might provide more insight into the Cu^{II}–phenol bonding.



Experimental

All reagents were commercially available and were used as received. Reagents used for the physical measurements were of spectroscopic grade. The yields are reported with respect to the metal salts. All the syntheses were carried out at room temperature in air.

The ¹H NMR spectrum was recorded on a Bruker ACF 300FT-NMR spectrometer using TMS as an internal reference at 25 °C in DMSO and the infrared spectra (KBr pellet) were recorded using a FTS165 Bio-Rad FTIR spectrophotometer in the range 4000–450 cm⁻¹. The electronic transmittance spectra were recorded on a Shimadzu UV-2501/PC UV-vis spectrophotometer in nujol mull and MeOH solution. The pH-dependent electronic absorption spectral titrations were carried out at room temperature upon sequential and reverse procedures. MeOH–H₂O solutions (1 : 1 v/v) of 0.1 mmol of the complexes were used. Conductance measurements were made using a Kyoto Electronics CM-115 conductivity meter using 1 mM solutions. ESI-MS spectra were recorded on a Finnigan MAT LCQ Mass Spectrometer. The elemental analyses were performed in the microanalytical laboratory, chemistry

† Electronic supplementary information (ESI) available: ESI-MS and UV titration data. See <http://www.rsc.org/suppdata/dt/b211496h/>

department, National University of Singapore. Water present in the compounds was determined using a SDT 2980 TGA Thermal Analyzer with a heating rate of 10 °C min⁻¹ in a N₂ atmosphere using a sample size of 5–10 mg per run. Room temperature magnetic susceptibility measurements were carried out on a Johnson-Matthey Magnetic Susceptibility balance with Hg[Co(SCN)₄] as standard for 1–9. Corrections for diamagnetism were made using Pascal's constants. The reported magnetic moments are per Cu^{II} ion. Variable temperature magnetic measurements were made for 5 using a Quantum Design MPMS5 SQUID magnetometer in the 4.2–300 K temperature range operating in an applied field of 1 T.

Caution! Perchlorate salts are potentially explosive and should be handled in small quantities, although we worked with these ClO₄⁻ salts without any incident. H₂sgly, H₂sala were synthesized as reported in ref. [17]. The synthesis of the H₂sval ligand is described below.

Ligand, *N*-(2-hydroxybenzyl)-L- α -valine (H₂sval)

To a solution of the L-valine (1.17 g, 10 mmol) in 10 mL of H₂O containing NaOH (0.40 g, 10 mmol) was added salicylaldehyde (1.22 g, 10 mmol) in EtOH (10 mL). The yellow solution was stirred for 30 min at room temperature prior to cooling in an ice bath. The intermediate Schiff base solution was carefully adjusted to pH = 6.0–7.0 with HCl, then excess NaBH₄ (0.46 g, 12 mmol) was added in portions with gentle stirring while the yellow color slowly discharged. After 15 min the solution was acidified to pH = 3.0–5.0 with concentrated HCl, left to stand for 1 h. The resulting solid was filtered off, washed with MeOH and Et₂O, dried and then recrystallized from H₂O–EtOH (1 : 1). Yield: 1.23 g (55%). mp 228–229 °C. Anal. Calc. for C₁₂H₁₇N₁O₃: C, 64.6; H, 7.6; N, 6.3. Found: C, 64.5; H, 7.7; N, 6.4%. ¹H NMR (DMSO-*d*₆): δ 0.89 (d, 6H, *J* = 8.8 Hz), 2.02 (m, 1H, *J* = 7.2 Hz), 2.98 (d, 1H, *J* = 4.8 Hz), 3.79 and 3.92 (AB system, 2H, *J*_{AB} = 13.5 Hz), 6.74–6.79 (m, 2H), 7.11–7.20 (m, 2H). IR (KBr, cm⁻¹): ν (OH) 3446, ν (NH) 3175, $\nu_{\text{as}}(\text{COO}^-)$ 1607, $\nu_{\text{s}}(\text{COO}^-)$ 1364, $\nu(\text{C}-\text{O})$ (phenolic) 1265.

[Cu(sgly)(phen)]·2.75H₂O, 1

To the royal blue solution formed from Cu(OAc)₂·H₂O (0.200 g, 1.00 mmol) in MeOH (15 mL) and phen (0.180 g, 1.00 mmol) in MeOH (10 mL) was added a filtered solution of H₂sgly (0.186 g, 1.00 mmol) in H₂O (20 mL) with LiOH (0.048 g, 2 mmol). The resulting green solution was stirred for about 2 h and then filtered, and left for several days. The yellow green crystals formed were isolated by filtration and air-dried. Yield: 0.335 g (71%). Anal. Calc. for C₂₁H_{22.50}N₃O_{5.75}Cu: C, 53.3; H, 4.7; N, 8.9; H₂O, 10.5. Found: C, 53.6; H, 4.8; N, 9.1; H₂O, 10.2%. IR (KBr, cm⁻¹): ν (OH) 3405, ν (NH) 2919, $\nu_{\text{as}}(\text{COO}^-)$ 1609, $\nu_{\text{s}}(\text{COO}^-)$ 1387, $\nu(\text{C}-\text{O})$ (phenolic) 1282.

[Cu(sala)(phen)]·3H₂O, 2. This complex was obtained as yellow green crystals by a similar method described for 1. Yield: 57%. Anal. Calc. for C₂₂H₂₅N₃O₆Cu: C, 53.8; H, 5.1; N, 8.6; H₂O, 11.0. Found: C, 53.5; H, 5.2; N, 8.4; H₂O, 11.1%. IR (KBr, cm⁻¹): ν (OH) 3425, ν (NH) 2931, $\nu_{\text{as}}(\text{COO}^-)$ 1631, $\nu_{\text{s}}(\text{COO}^-)$ 1384, $\nu(\text{C}-\text{O})$ (phenolic) 1290.

[Cu(sval)(phen)]·2H₂O, 3. This complex was prepared as yellow green crystals using a procedure identical to that of 1 except that H₂sval was used in the place of H₂sgly. Yield: 75%. Anal. Calc. for C₂₄H₂₇N₃O₅Cu: C, 57.7; H, 5.5; N, 8.3; H₂O, 7.2. Found: C, 57.5; H, 5.4; N, 8.4; H₂O, 6.9%. IR (KBr, cm⁻¹): ν (OH) 3420, ν (NH) 2960, $\nu_{\text{as}}(\text{COO}^-)$ 1630, $\nu_{\text{s}}(\text{COO}^-)$ 1384, $\nu(\text{C}-\text{O})$ (phenolic) 1321.

[Cu(Hsgly)(phen)](ClO₄)·1.5H₂O, 4. To the green solution formed from Cu(ClO₄)₂·6H₂O (0.371 g, 1.00 mmol) in MeOH (15 mL) and phen (0.180 g, 1.00 mmol) in MeOH (10 mL) was

added a filtered solution of H₂sgly (0.186 g, 1.00 mmol) in H₂O (20 mL) with LiOH (0.024 g, 1 mmol). The resulting blue solution was stirred for about 2 h, filtered, and left for several days to provide blue prism-like crystals, which were isolated by filtration and air-dried. Yield: 0.423 g (77%). Anal. Calc. for C₂₂H₂₂N₃O_{8.5}ClCu: C, 46.0; H, 3.9; N, 7.7; H₂O, 4.9. Found: C, 45.8; H, 3.8; N, 7.7; H₂O, 4.7%. IR (KBr, cm⁻¹): ν (OH) 3457, ν (NH) 2943, $\nu_{\text{as}}(\text{COO}^-)$ 1604, $\nu_{\text{s}}(\text{COO}^-)$ 1383, $\nu(\text{C}-\text{O})$ (phenolic) 1260, $\nu(\text{Cl}-\text{O})$ 1144 and 1090.

[Cu(Hsala)(phen)](ClO₄)·0.625H₂O, 5. This complex was obtained as blue prism-like crystals. Yield: 67%. Anal. Calc. for C₂₂H_{21.25}N₃O_{7.625}ClCu: C, 48.2; H, 3.9; N, 7.7; H₂O, 2.1. Found: C, 48.4; H, 3.7; N, 7.4; H₂O, 1.9%. IR (KBr, cm⁻¹): ν (OH) 3363, ν (NH) 2947, $\nu_{\text{as}}(\text{COO}^-)$ 1600, $\nu_{\text{s}}(\text{COO}^-)$ 1431, $\nu(\text{C}-\text{O})$ (phenolic) 1262, $\nu(\text{Cl}-\text{O})$ 1146 and 1089.

[Cu(Hsval)(phen)](ClO₄)·1.5H₂O, 6. Blue crystals of 6 were obtained by following the procedure described for 4 but using H₂sval instead of H₂sgly. Yield: 69%. Anal. Calc. for C₂₄H₂₇N₃O_{8.5}ClCu: C, 48.6; H, 4.6; N, 7.0; H₂O, 4.6. Found: C, 48.3; H, 4.4; N, 6.8; H₂O, 4.5%. IR (KBr, cm⁻¹): ν (OH) 3424, ν (NH) 2943, $\nu_{\text{as}}(\text{COO}^-)$ 1624, $\nu_{\text{s}}(\text{COO}^-)$ 1374, $\nu(\text{C}-\text{O})$ (phenolic) 1256, $\nu(\text{Cl}-\text{O})$ 1146 and 1090.

Alternatively, 4–6 have also been obtained quantitatively from the reaction between an aqueous solution of HClO₄ and 1–3 respectively in MeOH.

[(phen)Cu(μ -sgly)Cu(phen)]₂(ClO₄)₂·3H₂O, 7. To the green solution formed from Cu(ClO₄)₂·6H₂O (0.371 g, 1.00 mmol) in MeOH (15 mL) and phen (0.270 g, 1.50 mmol) in MeOH (10 mL) was added a filtered solution of H₂sgly (0.093 g, 0.50 mmol) in H₂O (20 mL) with LiOH (0.024 mg, 1 mmol). The resulting deep green solution was stirred for about 2 h, filtered, and then left for several days to furnish green crystals, which were isolated by filtration. Yield: 0.335 g (61%). Anal. Calc. for C₄₅H₃₉N₇O₁₄Cl₂Cu₂: C, 49.1; H, 3.6; N, 8.9; H₂O, 4.9. Found: C, 48.9; H, 3.5; N, 8.7; H₂O, 4.8%. IR (KBr, cm⁻¹): ν (OH) 3420, ν (NH) 3064, $\nu_{\text{as}}(\text{COO}^-)$ 1597, $\nu_{\text{s}}(\text{COO}^-)$ 1427, $\nu(\text{C}-\text{O})$ (phenolic) 1277, $\nu(\text{Cl}-\text{O})$ 1145 and 1090.

[Cu₂(sala)(phen)]₃(ClO₄)₂·2.5H₂O, 8. Deep green crystals of 8 were obtained by following the procedure described for 7 using H₂sala instead of H₂sgly. Yield: 68%. Anal. Calc. for C₄₆H₄₀N₇O_{13.5}Cl₂Cu₂: C, 50.0; H, 3.6; N, 8.9; H₂O, 4.1. Found: C, 49.7; H, 3.6; N, 9.0; H₂O, 4.3%. IR (KBr, cm⁻¹): ν (OH) 3423, ν (NH) 3033, $\nu_{\text{as}}(\text{COO}^-)$ 1596, $\nu_{\text{s}}(\text{COO}^-)$ 1426, $\nu(\text{C}-\text{O})$ (phenolic) 1267, $\nu(\text{Cl}-\text{O})$ 1145 and 1090.

[Cu₂(sval)(phen)]₃(ClO₄)₂·3H₂O, 9. This complex was obtained as deep green crystals by a procedure similar to that described for 7 using H₂sval instead of H₂sgly. Yield: 71%. Anal. Calc. for C₄₈H₄₅N₇O₁₄Cl₂Cu₂: C, 50.4; H, 3.9; N, 8.6; H₂O, 3.7. Found: C, 50.1; H, 3.8; N, 8.8; H₂O, 4.0%. IR (KBr, cm⁻¹): ν (OH) 3421, ν (NH) 3045, $\nu_{\text{as}}(\text{COO}^-)$ 1601, $\nu_{\text{s}}(\text{COO}^-)$ 1430, $\nu(\text{C}-\text{O})$ (phenolic) 1273, $\nu(\text{Cl}-\text{O})$ 1145 and 1090.

When the synthesis was repeated with Cu(ClO₄)₂·6H₂O (instead of Cu(OAc)₂ as described for 1–3), H₂L, phen, and LiOH in the ratio of 1 : 1 : 1 : 2 in H₂O–MeOH, 7–9 were the only products isolated in low yields. Further, 1–3 when reacted with NaClO₄ in the ratio of 1 : 1 in H₂O–MeOH, 7–9 were again the only products isolated.

X-Ray crystallography

The diffraction experiments were carried out on a Bruker AXS SMART CCD diffractometer. The program SMART²³ was used for collecting the intensity data, for reflections indexing and for the determination of lattice parameters, SAINT²³ was used for integration of the intensity of reflections and scaling,

Table 1 Crystallographic data and structure refinement details

Complex	1	4	5	7
Formula	C ₂₁ H _{22.50} CuN ₃ O _{5.75}	C ₂₁ H ₂₁ N ₃ O _{8.5} ClCu	C ₂₂ H _{21.25} ClN ₃ O _{7.625} Cu	C ₄₅ H ₃₉ N ₇ O ₁₄ Cl ₂ Cu ₂
<i>M</i>	472.5	550.4	548.7	1099.8
<i>T</i> /K	223(2)	253(2)	223(2)	293(2)
Wavelength, λ/Å	0.71073			
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>Cc</i> ^c	<i>P</i> $\bar{1}$	<i>P</i> 1 ^c	<i>P</i> $\bar{1}$
<i>a</i> /Å	22.825(3)	7.8954(5)	7.8926(5)	10.9601(5)
<i>b</i> /Å	5.2237(7)	9.7201(6)	10.1888(7)	13.9862(6)
<i>c</i> /Å	20.459(3)	14.9638(9)	14.0856(9)	16.3650(7)
<i>a</i> /deg	90	96.463(1)	96.655(1)	81.260(1)
<i>β</i> /deg	121.990(2)	95.979(1)	97.344(2)	72.151(1)
<i>γ</i> /deg	90	93.234(1)	90.346(1)	70.315(1)
<i>V</i> /Å ³	2068.9(5)	1132.2(1)	1115.6(1)	2245.0(2)
<i>Z</i>	4	2	2	2
ρ_{calc} /g cm ⁻³	1.517	1.615	1.633	1.627
μ /mm ⁻¹	1.098	1.139	1.153	1.145
Reflns collected	5569	11075	9355	11198
Independent reflns	2767	3993	7609	7460
Reflns (<i>I</i> > 2σ(<i>I</i>))	2475	3380	6543	5140
<i>R</i> _{int}	0.0433	0.0222	0.0419	0.0300
Goof	1.117	1.057	0.997	1.024
Final <i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0531	0.0581	0.0435	0.0586
Final <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>)) ^b	0.1368	0.1667	0.0869	0.1169

^a $R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|)$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. ^c The absolute structure parameter (Flack) was refined to 0.005(30) for **1** and 0.04(13) for **5**.

SADABS²⁴ was used for absorption correction and SHELXTL²⁵ for space group and structure determination, least-squares refinements on F^2 . Of the six disordered positions of water molecules found in the lattice of **1**, five have an occupancy of 0.5 and one has an occupancy of 0.25, and no hydrogen atom was added to these disordered oxygen atoms. The oxygen atoms of the ClO₄⁻ ions in **4** were found to be disordered. Two disorder models with occupancy of 0.5 each were resolved. There were two oxygen atom positions of lattice water molecules found in **4**, one of them only has an occupancy of 0.5. In this compound, all the hydrogen atoms were located and refined in the model along with common isotropic thermal parameters. In **5** two water molecules were present of which one has an occupancy of 0.25. No hydrogen atom was included for this oxygen atom for which only the isotropic thermal parameter was refined. However, the positional parameters were refined for the hydrogen atoms of the other water molecule with full occupancy of the O atom. Of the four positions of the O atoms of the lattice water in **7**, two have fractional occupancies (0.65 and 0.35). Only isotropic thermal parameters were refined for these two oxygen atoms. All the hydrogen atom positions were located and their positional parameters were refined in the least-squares cycles. Some of the crystals have lattice water, the presence of which was supported by TG and IR data. The fractional lattice water may be due to partial loss of lattice water at room temperature. Selected crystallographic data and refinement details are displayed in Table 1.

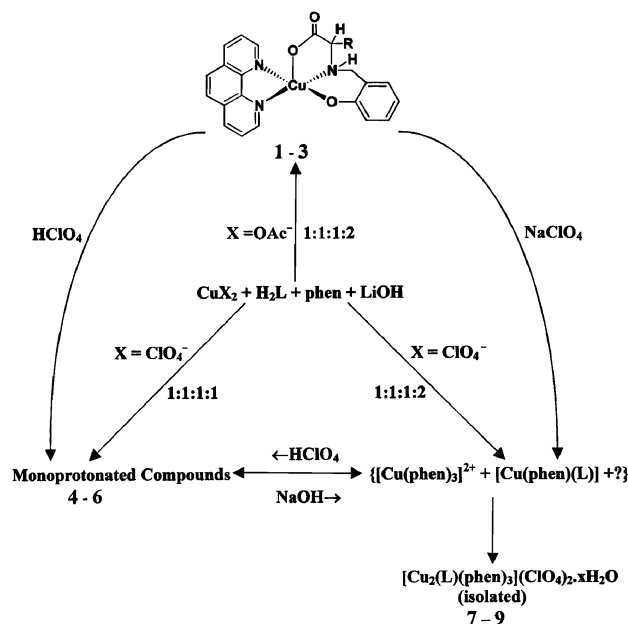
CCDC reference numbers 191976–191979.

See <http://www.rsc.org/suppdata/dt/b2/b211496h/> for crystallographic data in CIF or other electronic format.

Results and discussion

The neutral mononuclear Cu^{II} complexes **1–3** have been prepared in moderate yield from equimolar amounts of Cu(OAc)₂·H₂O, H₂L and phen, and two molar equivalents of LiOH in H₂O–MeOH mixture (pH ≈ 7). Further, the monoprotonated Cu^{II} complexes **4–6** have been synthesized just by decreasing the ratio of the base by half in the above reaction (pH ≈ 5), but Cu(ClO₄)₂·6H₂O was used instead of Cu(OAc)₂·H₂O. The same compounds **4–6** have also been synthesized in a quantitative yield by the addition of equimolar HClO₄ solution to **1–3**.

However, the neutral monomeric complexes **1–3** did not result when the synthesis was repeated with Cu(ClO₄)₂·6H₂O instead of Cu(OAc)₂·H₂O. On the other hand, the dinuclear complexes **7–9** have been isolated from the mixture of Cu(ClO₄)₂·6H₂O, H₂L, phen, and LiOH in the ratio of 1 : 1 : 1 : 2 in H₂O–MeOH (pH ≈ 6.5). Compounds **7–9** were also isolated when equimolar NaClO₄ was added to the solution of **1–3** (Scheme 1). The influence of the pH on the structure has been investigated in detail below.



Scheme 1

Physicochemical studies

All the compounds contain lattice water and the IR absorption bands in the range 3200–3500 cm⁻¹ confirm their presence.²⁶ This is further supported by the weight loss observed in TG (see Experimental). The sharp band observed in the region 2920–3064 cm⁻¹ is assigned to $\nu(\text{NH})$.²⁷ The $\nu(\text{N–H})$ bands have been

Table 2 Magnetic data, electronic absorption and conductivity data for 1–9

Complex	Absorption bands/nm ^a		Molar conductivity		Magnetic moment
	CT	d–d	S/cm ² mol ⁻¹		μ_B , BM
1	432 (499)	708 (116) ^b	2 ^d	14 ^e	1.76
	444 sh	706 br ^c			
2	425 (583)	696 (195)	4	28	1.79
	434 sh	705 br			
3	438 (523)	656 (240)	17	42	1.77
	437 sh	713 br			
4	415 (121)	648 (68)	52	93	1.78
	408 sh	614 br			
5	411 (183)	637 (118)	62	114	1.79
	401 sh	646 br			
6	403 (229)	605 (198)	75	124	1.74
	395 sh	602 br			
7	420 (326)	686 (129)	113	183	1.48
	449 sh	701 br			
8	418 (396)	692 (137)	127	202	1.50
	429 sh	676 br			
9	417 (373)	687 (145)	134	217	1.51
	424 sh	665 br			

^a $\lambda_{\max}(\epsilon)$. ^b In MeOH. ^c As Nujol mull transmittance. ^d In DMSO. ^e In CH₃OH.

shifted from 3110–3175 cm⁻¹ for the free ligands to 2920–3064 cm⁻¹ for all the Cu^{II} complexes indicating the complex formation. The asymmetric [$\nu_{\text{as}}(\text{COO}^-)$] and the symmetric stretching vibrations [$\nu_{\text{sym}}(\text{COO}^-)$] fall in the region 1596–1631 and 1374–1431 cm⁻¹, respectively. For **1**, **2**, **3**, **4** and **6** the difference between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ stretching frequencies is >200 cm⁻¹, thus suggesting a terminal coordination mode for the carboxylate group.^{28–30} Complexes **5**, **7–9** exhibit smaller values indicating a bridging coordination mode of the carboxylate group. These observations were confirmed by the X-ray crystal structures of **1**, **4**, **5** and **7** (see below). Two typical bands in the region *ca.* 1145 and *ca.* 1090 cm⁻¹ have been assigned to $\nu(\text{C}=\text{O})$ of the anion.²⁷

Electronic spectral data in MeOH solution and as Nujol mulls are given in Table 2 along with molar conductivity and room temperature magnetic data. The UV absorption bands observed in Nujol mull exhibit a charge transfer transition (CT) band in the range 395–450 nm, which may be assigned to the ligand to Cu^{II} transition. The d–d transitions generally fall around 700 nm and are more consistent with the square pyramidal and the square planar geometries at Cu^{II} as seen for **1–9** and related complexes.³¹ The transmittance spectra for **1–9** in MeOH exhibit essentially two bands, and the assignment of the electronic transitions is similar to those discussed above. It appears that the coordination geometry is not affected much in solution. The changes in the numerical values observed in MeOH solution may be attributed to solvent effects. The molar conductance values in MeOH and DMSO indicate that the complexes **4–6** are 1 : 1 electrolytes (Table 2). The complexes **7–9** are 1 : 2 electrolytes.³² The neutral mononuclear compounds **1–3** are nonelectrolytes.

Description of crystal structures

[Cu(sgly)(phen)]·2.75H₂O, **1**. An ORTEP view of the coordination environment at **1** is shown in Fig. 1. The crystal structure of **1** consists of monomeric units in which the Cu^{II} ion has highly distorted square pyramidal geometry with N₃O₂ donor set. The angular structural parameter, $\tau = 0.34$ supports the distortion.^{33–35} The four basal positions are occupied by two N atoms of the phen ligand, and the phenolic O and amine N atoms of the sgly ligand. The coordination sphere at the apical position is completed by carboxylate O of the ligand. Selected bond distances and angles are listed in Table 3. It should be noted that the coordination environment in **1** is similar to that of [Cu(Sbal)(phen)]·2H₂O,²¹ while they are different from those

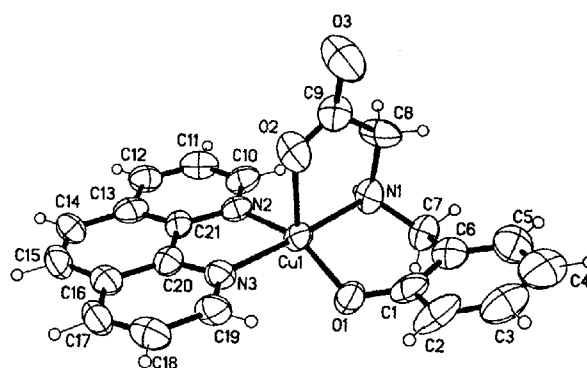


Fig. 1 A thermal ellipsoid plot with 50% probability of displacement, showing a perspective view of **1**.

containing a salicylate derivative in which each N atom of the phen ligand occupies both the axial and equatorial positions.¹⁷ The axial Cu–O bond length [Cu(1)–O(2) 2.127(6) Å] in **1** agrees well with those reported Cu^{II} complexes containing square pyramidal geometry.^{21,36,37}

The mononuclear units are held together by intermolecular hydrogen bonds involving the N–H protons and O(2) to form 1D hydrogen bonded polymer along the *b* axis as shown in Fig. 2. The hydrogen bonding parameters are as follows: N(1)–H(1), 0.92 Å; H(1) ··· O(2), 2.01 Å; N(1)–H(1) ··· O(2), 153°; N(1) ··· O(2), 2.010 Å. The water molecules present in the

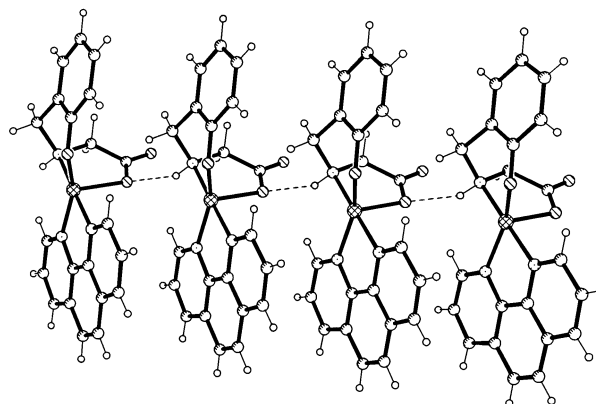


Fig. 2 A view of the packing of the 1-D hydrogen bonded polymer in **1**.

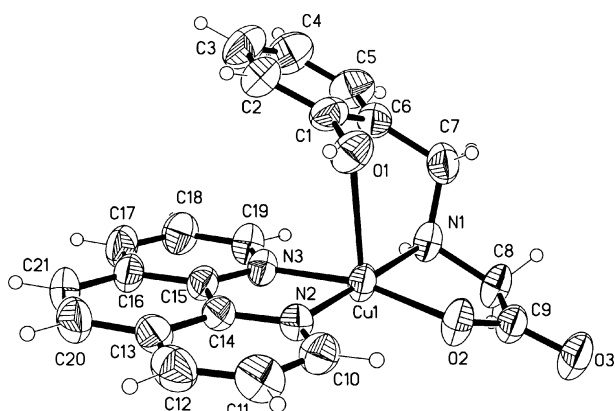
Table 3 Selected bond distances [Å] and angles [deg] for **1**

Cu(1)–O(1)	1.919(6)	O(3)–C(9)	1.217(1)
Cu(1)–N(1)	1.992(6)	N(1)–C(7)	1.459(1)
Cu(1)–N(3)	2.004(6)	N(1)–C(8)	1.510(1)
Cu(1)–N(2)	2.071(7)	N(2)–C(10)	1.322(1)
Cu(1)–O(2)	2.127(6)	N(2)–C(21)	1.375(1)
O(1)–C(1)	1.304(1)	N(3)–C(19)	1.321(1)
O(2)–C(9)	1.249(1)	N(3)–C(20)	1.369(1)
O(1)–Cu(1)–N(1)	93.5(3)	C(7)–N(1)–C(8)	113.1(7)
O(1)–Cu(1)–N(3)	89.8(3)	C(7)–N(1)–Cu(1)	114.1(6)
N(1)–Cu(1)–N(3)	176.3(3)	C(8)–N(1)–Cu(1)	110.5(5)
O(1)–Cu(1)–N(2)	155.8(3)	C(10)–N(2)–C(21)	115.6(7)
N(1)–Cu(1)–N(2)	96.6(3)	C(10)–N(2)–Cu(1)	132.8(6)
N(3)–Cu(1)–N(2)	81.2(3)	C(21)–N(2)–Cu(1)	111.6(6)
O(1)–Cu(1)–O(2)	108.0(3)	C(19)–N(3)–C(20)	118.6(7)
N(1)–Cu(1)–O(2)	83.0(3)	C(19)–N(3)–Cu(1)	127.4(6)
N(3)–Cu(1)–O(2)	94.3(3)	C(20)–N(3)–Cu(1)	114.0(6)
N(2)–Cu(1)–O(2)	95.1(3)	O(1)–C(1)–C(6)	122.8(9)
C(1)–O(1)–Cu(1)	124.4(6)	O(1)–C(1)–C(2)	120.7(1)
C(9)–O(2)–Cu(1)	113.7(5)		

lattice were severely disordered indicating that they are not tightly bound, but to fill in the hydrophobic packets of the crystal lattice.

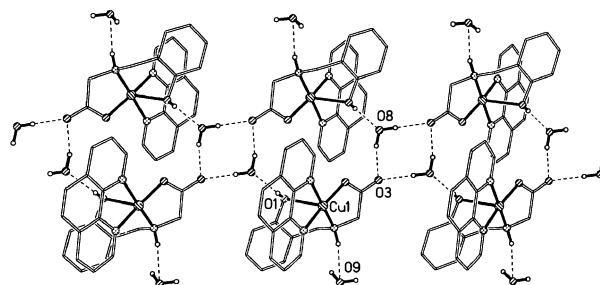
[Cu(Hsgly)(phen)](ClO₄)·1.5H₂O, **4.** Monoprotonation of **1** has changed the coordination environment and the conformation of the ligand at the Cu^{II} in **4**. Fig. 3 shows a perspective view of the [Cu(Hsgly)(phen)]⁺ cation in **4** that consists of a Cu^{II}, a monoprotonated Hsgly and a bidentate phen ligand. The Cu^{II} atom assumes an approximate square pyramidal geometry with N₃O₂ donor set. The square pyramidal geometry is less distorted than that in **1** as indicated by the τ parameter, 0.13.^{33–35} All the nitrogen atoms occupy the equatorial positions as in **1**, but protonated phenolic oxygen occupies the axial position in **4**. Selected bond distances and angles are listed in Table 4. This is the second structurally characterized compound with a Cu^{II}–OH (phenolic) bond. The distance in **4** is much shorter than the 2.601(4) Å found in [Cu(Tyr-His)] (Tyr-His = L-tyrosyl-L-histidine).²² The shorter distance between Cu(1) and the phenolic O may be attributed to the $\pi \cdots \pi$ interactions between the phenolic ring and phen ligand. This phenolic ring of Hsgly is approximately parallel to the square plane with an interplanar angle of 24.6° and the closest distance, 3.1486 Å, is between C(2) and N(2) whilst the farthest C \cdots C distance, 3.732 Å, is between C(3) and C(11). While C(6)–C(7)–N(1) angles in **1** and **4** are comparable, a significant deviation of nitrogen N(1) from the coordination plane N(1)N(3)N(2)O(2) towards the phenolic ring occurs, perhaps as a consequence of $\pi \cdots \pi$ interactions. Further to these ring stacking interactions, a moderately strong Cu(1)–O(1) bond contributes to the structure stabilization.

Hydrogen bond distances and angles in **4** are shown in Table 5. The O–H proton of the phenolic group is involved in

**Fig. 3** An ORTEP diagram of the cation in **4**.**Table 4** Selected bond distances [Å] and angles [deg] for **4**

Cu(1)–O(2)	1.931(3)	O(3)–C(9)	1.235(6)
Cu(1)–N(3)	1.998(4)	N(1)–C(7)	1.481(7)
Cu(1)–N(1)	2.011(4)	N(1)–C(8)	1.493(6)
Cu(1)–N(2)	2.015(4)	N(2)–C(10)	1.326(6)
Cu(1)–O(1)	2.446(3)	N(2)–C(14)	1.360(6)
O(1)–C(1)	1.376(6)	N(3)–C(15)	1.347(6)
O(2)–C(9)	1.273(6)	N(3)–C(19)	1.334(6)
O(2)–Cu(1)–N(3)	92.4(2)	C(7)–N(1)–C(8)	111.9(4)
O(2)–Cu(1)–N(1)	84.4(2)	C(7)–N(1)–Cu(1)	113.0(3)
N(3)–Cu(1)–N(1)	174.7(2)	C(8)–N(1)–Cu(1)	106.2(3)
O(2)–Cu(1)–N(2)	167.2(2)	C(10)–N(2)–C(14)	117.7(4)
N(3)–Cu(1)–N(2)	82.4(2)	C(10)–N(2)–Cu(1)	130.8(3)
N(1)–Cu(1)–N(2)	101.6(2)	C(14)–N(2)–Cu(1)	111.5(3)
C(9)–O(2)–Cu(1)	114.8(3)	C(19)–N(3)–C(15)	118.6(4)
O(1)–C(1)–C(6)	116.1(4)	C(19)–N(3)–Cu(1)	128.6(3)
O(1)–C(1)–C(2)	122.2(5)	C(15)–N(3)–Cu(1)	112.7(3)
C(6)–C(7)–N(1)	111.5(4)		

strong hydrogen bonding to O(8) of the lattice water. All the atoms attached to O(8) participate in strong O–H \cdots O hydrogen bonding. These protons are hydrogen bonded to the two neighboring carboxylate oxygen O(3) to form eight member rings. The 1D hydrogen bonded polymer runs along the [110] direction as shown in Fig. 4. The N–H protons are involved in strong hydrogen bonding to water molecules O(9) with partial occupancy, 0.5 and involved in weak hydrogen bonding to the disordered perchlorate anion through O(7).

**Fig. 4** A portion of the hydrogen bonded 1D polymer in **4**.

[Cu(Hsala)(phen)](ClO₄)·0.625H₂O, **5.** There are two crystallographically independent Cu^{II} atoms in **5** in which Cu(1) and Cu(2) assume very similar coordination geometry of an approximate square pyramid as depicted in Fig. 5. Selected bond distances and angles are listed in Table 6. The coordination sphere at the square plane is similar to that observed in **4**. The structure also exhibits intramolecular stacking between coordinated phen and phenolic ring of ligand as in **4**. The phenolic ring is approximately parallel to the square plane with the interplanar angle of 23.7° in Cu(1) and 19.4° in Cu(2), respectively. The closest distances, 3.062 and 3.116 Å are between C(1) and N(2), and between C(23) and N(5) respect-

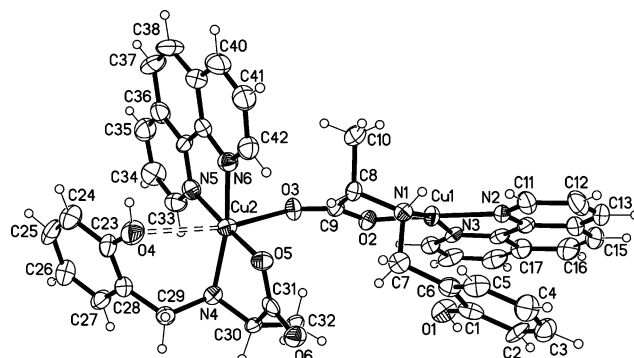
**Fig. 5** An ORTEP view of the cation in the asymmetric unit of **5**.

Table 5 Hydrogen bonds distances [\AA] and angles [deg] in **4**

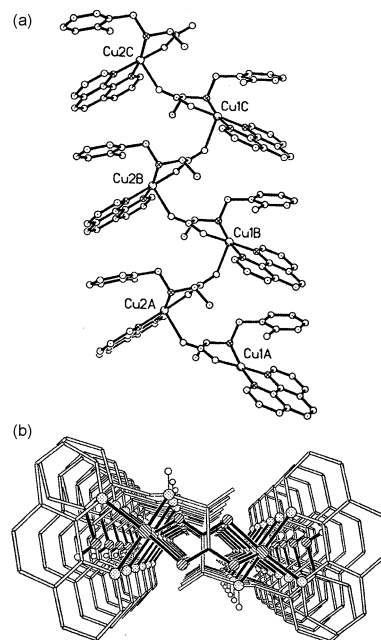
D–H	$d(\text{D–H})$	$d(\text{H} \cdots \text{A})$	$\angle \text{DHA}$	$d(\text{D} \cdots \text{A})$	A	Symmetry
O1–H1A	0.56	2.07	176	2.624(5)	O8	$[-x, -y, -z]$
N1–H1	0.91	2.13	151	2.953(5)	O9	
O8–H8A	0.90	1.89	162	2.757(5)	O3	
O8–H8B	0.90	1.95	176	2.844(5)	O3	$[-x, -y-1, -z]$

Table 6 Selected bond lengths [\AA] and angles [deg] for **5**

Cu(1)–O(2)	1.92(4)	Cu(2)–O(5)	1.94(4)
Cu(1)–N(3)	2.00(4)	Cu(2)–N(6)	2.00(5)
Cu(1)–N(2)	2.02(5)	Cu(2)–N(5)	2.00(5)
Cu(1)–N(1)	2.02(4)	Cu(2)–N(4)	2.03(5)
Cu(1)–O(6) ^a	2.41(4)	Cu(2)–O(4)	2.79(4)
Cu(1)–O(1)	2.73(4)	O(4)–C(23)	1.37(7)
O(1)–C(1)	1.37(7)	O(5)–C(31)	1.28(7)
O(2)–C(9)	1.29(6)	O(6)–C(31)	1.26(7)
O(3)–C(9)	1.23(7)	Cu(2)–O(3)	2.35(4)
O(3)–Cu(2)	2.35(4)	N(4)–C(30)	1.47(7)
N(1)–C(8)	1.49(7)	N(4)–C(29)	1.51(7)
N(1)–C(7)	1.51(7)	N(5)–C(33)	1.32(7)
N(2)–C(11)	1.31(7)	N(5)–C(44)	1.36(7)
N(2)–C(22)	1.35(7)	N(6)–C(42)	1.33(7)
N(3)–C(20)	1.31(7)	N(6)–C(43)	1.35(7)
N(3)–C(21)	1.36(7)		
O(2)–Cu(1)–N(3)	92.8(2)	O(5)–Cu(2)–N(6)	92.6(2)
O(2)–Cu(1)–N(2)	175.4(2)	O(5)–Cu(2)–N(5)	174.5(2)
N(3)–Cu(1)–N(2)	82.6(2)	N(6)–Cu(2)–N(5)	82(2)
O(2)–Cu(1)–N(1)	83.7(2)	O(5)–Cu(2)–N(4)	83.0(2)
N(3)–Cu(1)–N(1)	166.6(2)	N(6)–Cu(2)–N(4)	164.9(2)
N(1)–Cu(1)–N(1)	100.6(2)	N(5)–Cu(2)–N(4)	101.6(2)
O(2)–Cu(1)–O(6) ^a	98.9(2)	O(5)–Cu(2)–O(3)	97.3(2)
N(3)–Cu(1)–O(6) ^a	92.4(2)	N(6)–Cu(2)–O(3)	93.6(2)
N(2)–Cu(1)–O(6) ^a	81.8(2)	N(5)–Cu(2)–O(3)	84.8(2)
N(1)–Cu(1)–O(6) ^a	101.0(2)	N(4)–Cu(2)–O(3)	101.2(2)
O(2)–Cu(1)–O(1)	96.1(2)	O(5)–Cu(2)–O(4)	94.7(2)
N(3)–Cu(1)–O(1)	80.7(2)	N(6)–Cu(2)–O(4)	81.1(2)
N(2)–Cu(1)–O(1)	82.8(2)	N(5)–Cu(2)–O(4)	82.9(2)
N(1)–Cu(1)–O(1)	86.8(2)	N(4)–Cu(2)–O(4)	84.9(2)
O(6) ^a –Cu(1)–O(1)	163.8(1)	O(3)–Cu(2)–O(4)	167.1(1)
C(1)–O(1)–Cu(1)	99(3)	C(23)–O(4)–Cu(2)	98(3)
C(9)–O(2)–Cu(1)	116(4)	C(31)–O(5)–Cu(2)	114(4)
C(9)–O(3)–Cu(2)	130(4)	C(31)–O(6)–Cu(1) ^b	126(4)
C(8)–N(1)–C(7)	110(4)	C(30)–N(4)–C(29)	110(4)
C(8)–N(1)–Cu(1)	106(3)	C(30)–N(4)–Cu(2)	105(3)
C(7)–N(1)–Cu(1)	112(3)	C(29)–N(4)–Cu(2)	113(3)
C(11)–N(2)–C(22)	119(5)	C(33)–N(5)–C(44)	117(5)
C(11)–N(2)–Cu(1)	130(4)	C(33)–N(5)–Cu(2)	131(4)
C(22)–N(2)–Cu(1)	111(4)	C(44)–N(5)–Cu(2)	112(4)
C(20)–N(3)–C(21)	118(5)	C(42)–N(6)–C(43)	117(5)
C(20)–N(3)–Cu(1)	130(4)	C(42)–N(6)–Cu(2)	130(4)
C(21)–N(3)–Cu(1)	112(4)	C(43)–N(6)–Cu(2)	113(4)

Symmetry operators: ^a $x - 1, y, z$; ^b $x + 1, y, z$.

ively, whilst the farthest C \cdots C distances, 3.741 and 3.780 \AA are at the peripheral between C(3) and C(12), and C(25) and C(34), respectively. Further, one of the axial positions is occupied by the O atom from the carboxylate group of an adjacent cation. The Cu(1)–O(6a) and Cu(2)–O(3) bond lengths 2.41(4) and 2.35(4) \AA , respectively, are much longer than the Cu^{II}–O(=C) bonds.²¹ In the polymeric complexes containing bridging carboxylate groups having μ_2 – η_1, η_1 bonding mode, three conformations are possible, namely, *syn*–*syn*, *anti*–*anti* and *syn*–*anti*.³⁸ It should be noted that carboxylate groups bridging the Cu^{II} ions have an *anti*–*anti* conformation similar to both a two-dimensional³⁹ and a zigzag polymeric chain Cu^{II} complex³⁸ reported in the literature. Interestingly, these Cu \cdots O interactions lead to a helical coordination polymer with a 2_1 screw axis as shown in Fig. 6. The polymer strands are arranged parallel to the [101] direction with a pitch of 7.89 \AA . Weak interactions between Cu(1) and O(1) [2.73(4) \AA], and between Cu(2) and O(4) [2.79(4) \AA] at the axial direction are due to the phenol group coordinated to Cu^{II}, as observed in **4**. These weak

**Fig. 6** (a) A segment of the helical polymer **5**. (b) Top view of the polymer **5** showing the helicity.

axial interactions provide distorted octahedral geometry at the Cu^{II} centers.

The N–H protons are involved in weak hydrogen bonding to the O atoms [O(10) and O(13)] of the perchlorate anion. The O–H protons of phenolic group are also involved in strong hydrogen bonding to O atoms [O(8) and O(11)] of the perchlorate anion. One of the H atoms of the water molecules participates in weak hydrogen bonding to carboxylate oxygen O(6). Hydrogen bond parameters for **5** are given in Table 7. Unlike the monodeprotonated compound **4**, the oxygen atoms of the perchlorate anions were not disordered due to strong O–H \cdots O and N–H \cdots O hydrogen bonds to phenolic and N–H protons.

[(phen)Cu(μ -sgly)Cu(phen)]₂(ClO₄)₂·3H₂O, **7. A perspective view of the coordination environment of Cu^{II} atoms in **7** is shown in Fig. 7. The geometric parameters are listed in Table 8. Compound **7** contains a dinuclear cation in which the**

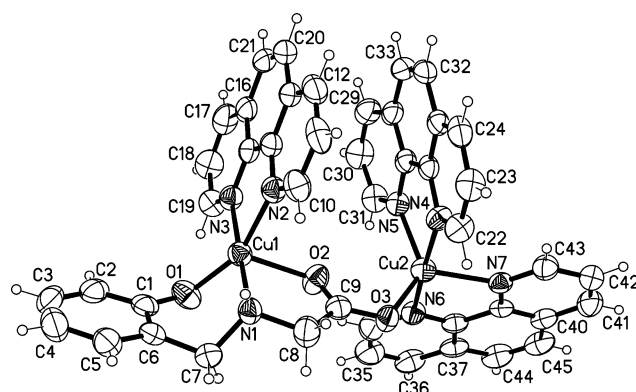
**Fig. 7** A thermal ellipsoid diagram showing the coordination environment of the cation in **7**.

Table 7 Hydrogen bonds distances [\AA] and angles [deg] in **5**

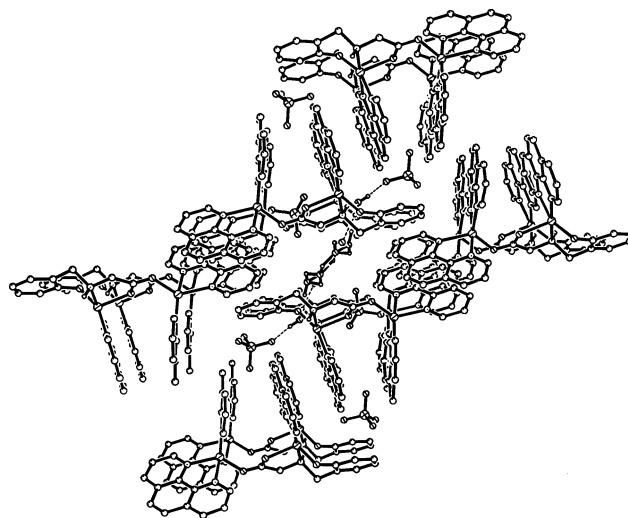
D–H	$d(\text{D–H})$	$d(\text{H} \cdots \text{A})$	$\angle\text{DHA}$	$d(\text{D} \cdots \text{A})$	A	Symmetry
N1–H1	0.91	2.22	165	3.110(7)	O10	$[x, y-1, z]$
O1–H1A	0.82	1.99	158	2.766(7)	O8	
O4–H4A	0.82	1.94	156	2.708(7)	O11	$[x, y-1, z]$
N4–H4	0.91	2.21	163	3.087(7)	O13	
O15–H15B	0.94	2.00	165	2.918(7)	O6	

Table 8 Selected bond lengths [\AA] and angles [deg] for **7**

Cu(1)–O(1)	1.943(3)	Cu(2)–O(3)	2.028(4)
Cu(1)–N(3)	2.000(4)	Cu(2)–N(5)	2.111(4)
Cu(1)–N(1)	2.032(4)	Cu(2)–N(7)	2.128(4)
Cu(1)–N(2)	2.108(4)	O(1)–C(1)	1.332(6)
Cu(1)–O(2)	2.143(4)	C(9)–O(2)	1.251(6)
Cu(2)–N(6)	1.981(4)	C(9)–O(3)	1.266(6)
Cu(2)–N(4)	1.988(4)		
O(1)–Cu(1)–N(3)	91.1(2)	N(4)–Cu(2)–O(3)	90.5(2)
O(1)–Cu(1)–N(1)	92.0(2)	N(6)–Cu(2)–N(5)	95.5(2)
N(3)–Cu(1)–N(1)	175.7(2)	N(4)–Cu(2)–N(5)	80.5(2)
O(1)–Cu(1)–N(2)	157.4(2)	O(3)–Cu(2)–N(5)	130.2(2)
N(3)–Cu(1)–N(2)	80.7(2)	N(6)–Cu(2)–N(7)	80.9(2)
N(1)–Cu(1)–N(2)	95.3(2)	N(4)–Cu(2)–N(7)	95.4(2)
O(1)–Cu(1)–O(2)	111.5(2)	O(3)–Cu(2)–N(7)	120.0(1)
N(3)–Cu(1)–O(2)	99.1(2)	N(5)–Cu(2)–N(7)	109.6(1)
N(1)–Cu(1)–O(2)	82.6(2)	C(1)–O(1)–Cu(1)	112.0(3)
N(2)–Cu(1)–O(2)	90.7(2)	O(1)–C(1)–C(2)	122.8(5)
N(6)–Cu(2)–N(4)	173.4(2)	C(9)–O(2)–Cu(1)	111.8(3)
N(6)–Cu(2)–O(3)	96.1(2)	C(9)–O(3)–Cu(2)	111.4(3)

[Cu(sgly)phen] fragment is bonded to the $[\text{Cu}(\text{phen})_2]^{2+}$ cation through an oxygen atom of the CO_2^- group in a sgly ligand. The [Cu(sgly)phen] moiety has square pyramidal geometry which is similar to **1**, but the conformation of the ligand backbone is quite different from **1** in which the phenolic ring is approximately parallel to the phen ligand and perpendicular to carboxylate groups. In contrast both the aromatic rings and the carboxylate groups are approximately perpendicular to each other in **7**. The carboxylate groups bridge the two Cu centers in the *syn-anti* mode. The angular structural parameters, $\tau = 0.30$ and 0.72 indicate that the coordination geometry at Cu(1) and Cu(2) can be regarded as highly distorted square pyramid and trigonal bipyramid, respectively.^{33–35} The equatorial positions at Cu(2) are occupied by the oxygen O(3) of a carboxylate group and one nitrogen atom from each phen ligand [N(5) and N(7)], while N(4) and N(6) occupy the axial positions. The presence of $\pi \cdots \pi$ interactions between the two phen ligands attached to each Cu^{II} atom is evident as they are bent toward each other with an interplanar angle of 17.5° . The closest C \cdots C distance, 3.184 \AA , is between C(20) and C(33), and the Cu \cdots Cu separation is 4.892 \AA . In addition, there are intermolecular $\pi \cdots \pi$ interactions between the two parallel phen ligands from the neighboring molecules as shown in the packing diagram (Fig. 8). The closest distance between the two intermolecular phen ligands is 3.63 \AA . It is evident from the structural similarities with the previously reported $[\text{Cu}_2(\text{Sbal})(\text{phen})_3]^{2+}$ cation²¹ that the $\pi \cdots \pi$ interactions between the phen ligands are responsible for the structural and conformational changes at the Cu^{II} centers and the reduced Schiff base ligands. This $\pi \cdots \pi$ stacking in metal complexes with aromatic nitrogen-containing ligands is important in stabilizing the supramolecular structures in the solid state.^{40–43}

The N–H protons are involved in weak hydrogen bonding to the O(12) atom of the lattice water. One of the H atoms in the O(12) water molecule is strongly hydrogen bonded to the O atom of another lattice water O(13) and the second H atom is hydrogen bonded to the O(7) atom of the perchlorate anion. However, these hydrogen bonds did not lead to any recognizable pattern in the solid state. Hydrogen bond parameters in **7** are given in Table 9.

**Fig. 8** View of packing in **7** along the a axis showing the $\pi \cdots \pi$ interactions.

Magnetic properties

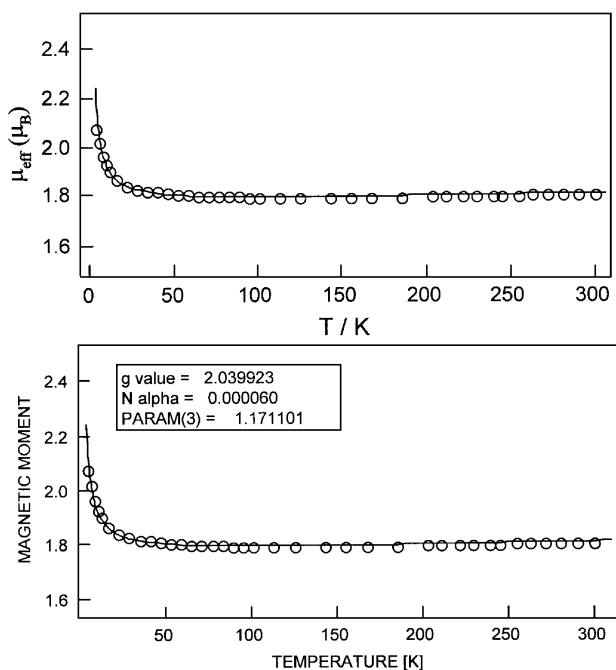
The magnetic moments measured at room temperature for **1–6** showed normal spin-only behavior (Table 2). The room temperature magnetic moments have been found to be lower than expected based on the spin-only formula ($1.48\text{--}1.51 \text{ BM}$ for **7–9** versus 1.732 BM). A lower magnetic moment for **7** in which the two Cu^{II} centers are separated by 4.892 \AA is attributed to weak antiferromagnetic coupling as seen in the related complexes.²⁰ A similar argument may also be valid for **8** and **9** which probably have structures similar to **7**, and the previously reported $[\text{Cu}_2(\text{Sbal})(\text{phen})_3](\text{ClO}_4)_2$.²¹ It is noteworthy that a number of structurally well characterized copper (II) complexes involving the *syn-anti* mode exist in the literature, but the magnetic properties have not been studied for all. Of these magnetically characterized Cu^{II} compounds, weak exchange interactions were observed that can be either ferromagnetic^{44–46} or antiferromagnetic.^{47–49} A variable temperature magnetic moment study of **5** showed that very weak intrachain ferromagnetic coupling occurs with μ_{eff} (per Cu) remaining constant at 1.8 BM between 300 and 30 K , then increasing rapidly to 2.07 BM at 4 K as shown in Fig. 9. The data gave a good fit to a Heisenberg $S = 1/2$ chain model⁵⁰ with $g = 2.04$ and $2J = 2.4 \text{ cm}^{-1}$. The reason for weak ferromagnetic coupling occurring via the *anti-anti* carboxylate bridge is that the adjacent equatorial places are at $\approx 90^\circ$ to each other and through the axial–equatorial pathway.

Behavior of protonated and deprotonated complexes in solution and solid state

ESI mass spectra were recorded for **1–9** to investigate the behavior in solution of these compounds. The positive ion ESI mass spectra show signals for **1–3** predominantly at m/z $[\text{Cu}(\text{L})(\text{phen})+\text{H}]^+$ 422.9 , 436.9 and 464.9 similar to **4–6** at m/z $[\text{Cu}(\text{HL})(\text{phen})]^+$ 422.9 , 436.9 and 464.9 , respectively, as major peaks. Unlike the corresponding complexes of *N*-(2-hydroxybenzyl)- β -alanine ligand,²¹ these cations do not appear to dissociate in MeOH solution. It is evident that **1–6** exist as monomers in solution. On the contrary, the signals for dinuclear complexes **7–9** indicate the presence of various dissociated

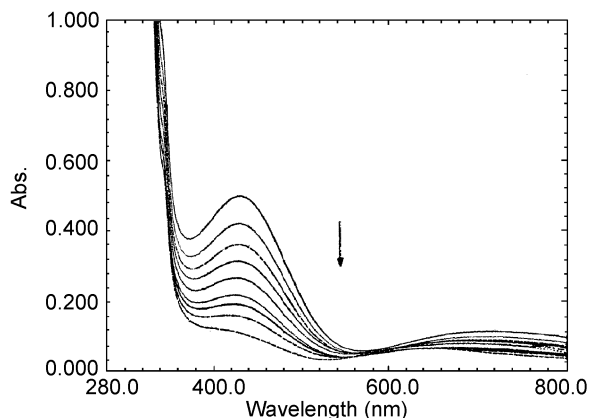
Table 9 Hydrogen bonds distances [\AA] and angles [deg] in **7**

D-H	$d(\text{D-H})$	$d(\text{H} \cdots \text{A})$	$\angle\text{DHA}$	$d(\text{D} \cdots \text{A})$	A	Symmetry
N1-H1	0.91	2.13	153	2.972(4)	O12	
O12-H12A	0.90	1.97	164	2.844(4)	O13	
O12-H12B	0.90	2.09	170	2.976(4)	O7	$[x, y-1, z]$

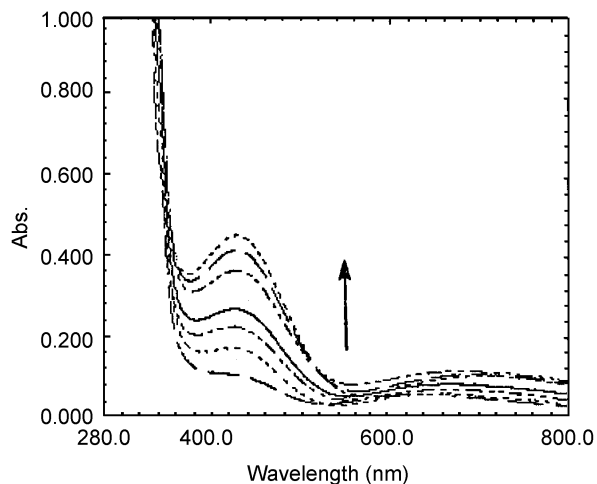
**Fig. 9** Plot of μ_{eff} , per Cu, versus temperature for **5** in a field of 1 T. The solid line is the best fit using a Heisenberg $S = 1/2$ chain model with $g = 2.04$, $2J = +2.4 \text{ cm}^{-1}$.

species in solution, including $[\text{Cu}(\text{L})(\text{phen})+\text{H}]^+$ and $[\text{Cu}(\text{phen})_3]^{2+}$, for these complexes. (see Electronic Supplementary Information †).

The conversions between neutral and protonated compounds have been investigated by UV-visible titration methods. With the addition of an equimolar amount of HClO_4 to **1** in MeOH, the intensity of an absorption band at $\sim 430 \text{ nm}$ decreased drastically and blue shifted to $\sim 415 \text{ nm}$ to form **4** as shown in Fig. 10. The decrease in the intensity of this CT transition may be attributed to LMCT from phenolate and phen to Cu^{II} . This suggests that, due to protonation, the solution structure does not have phenol oxygen bonded to Cu^{II} , unlike the solid-state structure of **4**. Furthermore, the intensity of the d-d transition band decreased and shifted from ~ 710 to $\sim 696 \text{ nm}$. The shift in the absorption and the associated reduction in the intensity may be attributed to a change in the coordination environment but

**Fig. 10** Variation of UV-vis spectra of **1** with addition of aqueous HClO_4 to indicate the formation of **4**.

not in the geometry. A similar behavior was observed for the protonation of **2** and **3** leading to the formation of **5** and **6**, respectively (see Electronic Supplementary Information †). The formation of **4** in the resultant solution was confirmed by comparing this electronic spectra with that of pure **4** in MeOH. Due to the nature of the experiment, the ESI mass spectrum could not be used to distinguish the neutral and the protonated species in solution as both exhibit the same molecular ions in the positive ion mode. However, the formation of the product in each case was confirmed by their isolation and characterization. Further, these conversions were also accompanied by a change in color from green (protonated compounds) to blue (neutral compounds). The deprotonation of **4-6** by a molar equivalent of base is expected to form the neutral mononuclear compounds, **1-3**. Although the UV-visible spectral titration results appear to show that the deprotonation is reversible (Fig. 11), the ESI mass spectra of the resultant solution support non-reversibility of protonation. Further, a comparison of the UV-spectrum of the resultant solution obtained from $\text{Cu}(\text{ClO}_4)_2 + \text{H}_2\text{sgly} + \text{phen} + 2\text{LiOH}$ with **1**, as shown in Fig. 12, would reveal that they are not the same. The ESI-MS spectrum of **4** + NaOH indicated the presence of various species including $[\text{Cu}(\text{phen})\text{L}+\text{H}]$ and $[\text{Cu}(\text{phen})_3]^{2+}$ from which **7** was isolated. On the other hand, the change of UV-vis titration curves by the incremental addition of HClO_4 to $\text{Cu}(\text{ClO}_4)_2 + \text{H}_2\text{sgly} + \text{phen} + 2\text{LiOH}$ shown in Fig. 13 indicate the formation of **4** thereby confirming the reversibility of this reaction. Similar behavior was also observed on addition of a base to **5** and **6** (see Electronic Supplementary Information †). These results demonstrate that the conversion of protonated species **4-6** to neutral compounds **1-3** is not possible (Scheme 1).

**Fig. 11** Variation of UV-vis spectra with the incremental addition of an equimolar amount of NaOH to **4** which is same as the spectra of $[\text{Cu}(\text{ClO}_4)_2 + \text{H}_2\text{sgly} + \text{phen} + 2\text{LiOH}]$ solution but not the spectra of **1**.

ESI mass spectral experiments have been carried out to investigate whether the difference in the reactivity of $\text{Cu}(\text{II})$ salts is due to the effect of the anions or the pH of the solution. The ESI-MS of the solution containing $\text{Cu}(\text{OAc})_2$, H_2sgly , phen and LiOH in 1 : 1 : 1 : 1 ratio shows a prominent peak due to $[\text{Cu}(\text{Hsgly})(\text{phen})(\text{OAc})+\text{H}]^+$. Further, when the solution obtained from $\text{Cu}(\text{ClO}_4)_2$, H_2sgly , phen and LiOH in the ratio of 1 : 1 : 1 : 2 (pH ≈ 6.5) was neutralized with NaOH to pH ≈ 7 , the

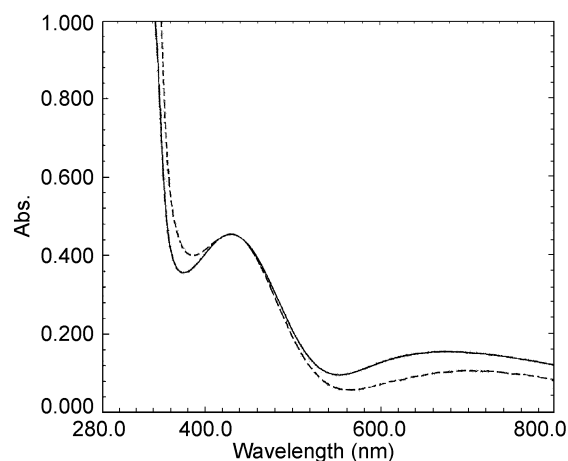


Fig. 12 UV-vis spectra of **1** (—) and mixture of $[\text{Cu}(\text{ClO}_4)_2 + \text{H}_2\text{sgly} + \text{phen} + 2\text{LiOH}]$ (---).

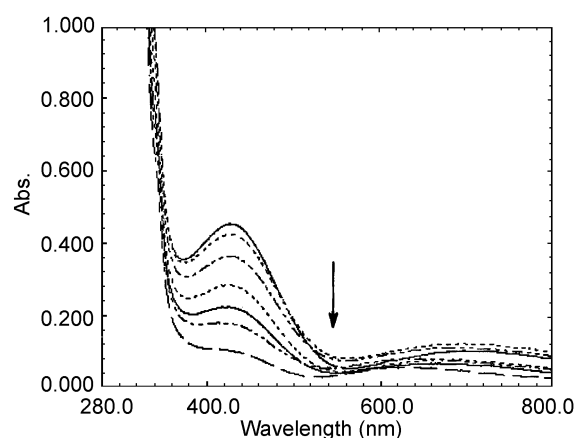
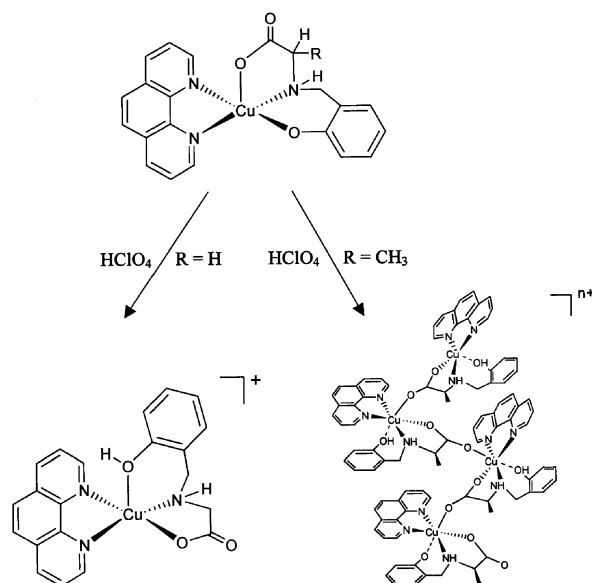


Fig. 13 Variation of UV-vis spectra with the incremental addition of an equimolar amount of HClO_4 to $[\text{Cu}(\text{ClO}_4)_2 + \text{H}_2\text{sgly} + \text{phen} + 2\text{LiOH}]$ which indicates formation of **4**.

ESI-MS exhibited only one peak due to $[\text{Cu}(\text{sgly})(\text{phen}) + \text{H}^+]$. These experiments confirm that the change in the reactivity due to acetate and perchlorate ions is, indeed, due to the change in the pH of the medium.

The most striking difference between **1** and the mononuclear cation in **4** is the change in the coordination environment at the Cu^{II} centers caused by protonation of the phenolic oxygen atom. The changes in the coordination sphere due to exogenous monodentate ligands have been observed before.⁵¹ Although there are several reports on the influence of pH on the structure of Cu^{II} complexes, none of the pH changes resulted in simple protonation of the compound accompanied by change in the coordination sphere at the metal center.^{1-3,7-16} Further, the neutral mononuclear compounds on protonation of the phenolic oxygen by HClO_4 gave two different types of products in the solid state; one is a protonated mononuclear cation **4** and the other is a helical coordination polymer **5** (Scheme 2). The stereochemistry of the sgly ligand is expected to be quite different from those of sala and sval, which have chiral centers at the amino acid portion of the ligand. The origin of the structural diversity is yet to be understood, however the formation of the helical coordination polymeric structure in **5** may be traced to the H_2sala ligand with a chiral center at the backbone. However, the contribution from the packing and/or the different number of lattice waters cannot be ruled out. It is worth mentioning here that the solid-state structures of $[\text{Cu}(\text{sala})(\text{phen})]$ contains one water molecule¹⁷ which is different from **1**. The influence of the acetate ion in the formation of the mononuclear compounds **1-3** appears to be evident (Scheme 1). When $\text{Cu}(\text{ClO}_4)_2$ was used instead of $\text{Cu}(\text{OAc})_2$, the products were not the same.



Scheme 2

Further, addition of NaClO_4 to **1-3** resulted in a mixture of products from which **7-9** could be isolated successfully in the solid state and characterized. The attack on the $\text{Cu}-\text{O}(\text{carboxylate})$ bond by the base may be responsible for the decomposition of the protonated complexes. In all the solid-state structures, the six-membered rings formed by a part of the reduced Schiff bases, $\text{Cu}-\text{O}-\text{C}-\text{C}-\text{N}$ have a highly energetic boat conformation. The $\text{O}(1)\text{C}(1)\text{C}(6)\text{C}(7)$ atoms (torsion angles, 5.5° in **1**, 0.1° in **4**, 0.6 and 1.2° in **5**, and 7.8° in **7**) and $\text{O}(1)\text{Cu}(1)\text{N}(1)\text{C}(7)$ atoms (torsion angles, 20.4° in **1**, 2.4° in **4**, 4.0 and 3.8° in **5**, and 7.2° in **7**) form a plane with interplanar angles of 139.5° in **1**, 116.8° in **4**, 114.4 and 113.9° in **5**, and 122.7° in **7**.

Summary

By changing the metal-ligand ratio, the counterions and the pH of the solution, three types of compounds were synthesized and characterized in the solid state as well as in solution. The details are summarized in Scheme 1 and 2. Protonation of mononuclear compounds causes structural changes at the Cu^{II} center.

Acknowledgements

This research was supported by Grant R-143-000-153-112 to J. J. V. from the National University of Singapore and by an Australian Research Council Large grant to K. S. M. We would like to sincerely thank the referees for their constructive suggestions to improve the quality of the revised manuscript.

References

- 1 C. Wendelstorf and R. Krämer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2791.
- 2 M. Tsaramyrsi, M. Kaliva, A. Salfoglou, C. P. Raptopoulou, A. Terzic, V. Tangoulis and J. Giapintzakis, *Inorg. Chem.*, 2001, **40**, 5772.
- 3 H. Karosaki, H. Yoshida, A. Fujimoto, M. Goto, M. Shionoya, E. Kimura, E. Espinosa, J.-M. Barbe and R. Guillard, *J. Chem. Soc., Dalton Trans.*, 2001, 898.
- 4 D. L. Kepert, *Inorganic Chemistry Concepts*, Vol. 6, Springer-Verlag, Berlin, 1982.
- 5 P. Comba, *Coord. Chem. Rev.*, 1993, **123**, 1.
- 6 A. von Zelesky, *Stereochemistry of Coordination Compounds*, Wiley, Chichester, UK, 1996.
- 7 C. Belle, C. Beguin, I. Gautier-Luneau, S. Hamman, C. Philouze, J. L. Pierre, F. Thomas, S. Torelli, E. Saint-Aman and M. Bonin, *Inorg. Chem.*, 2002, **41**, 479.

- 8 S. Torelli, C. Belle, I. Gautier-Luneau, J. L. Pierre, E. Saint-Aman, J. M. Latour, L. Le Pape and D. Luneau, *Inorg. Chem.*, 2000, **39**, 3526.
- 9 N. Matsumoto, Y. Mizuguchi, G. Mago, S. Eguchi, H. Miyasaka, T. Nakashima and J.-P. Tuchagues, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1860.
- 10 Y. Shii, Y. Motoda, T. Matsuo, F. Kai, T. Nakashima, J.-P. Tuchagues and N. Matsumoto, *Inorg. Chem.*, 1999, **38**, 3513.
- 11 N. Matsumoto, Y. Motoda, T. Matsuo, T. Nakashima, N. Re, F. Dahan and J.-P. Tuchagues, *Inorg. Chem.*, 1999, **38**, 1165.
- 12 V. Amendola, L. Fabbri, L. Linati, C. Mangomo, P. Pallavicini, V. Pedrazzini and M. Zema, *Coord. Chem. Rev.*, 2001, **216–217**, 435.
- 13 V. Amendola, L. Fabbri, L. Gianelli, C. Maggi, C. Mangomo, P. Pallavicini and M. Zema, *Inorg. Chem.*, 2001, **40**, 3579.
- 14 V. Amendola, C. Brusoni, L. Fabbri, C. Mangomo, H. Miller, P. Pallavicini, A. Perotti and A. Taglietti, *J. Chem. Soc., Dalton Trans.*, 2001, 3528.
- 15 V. Amendola, L. Fabbri, M. Licchelli, C. Mangomo, P. Pallavicini, L. Parodi and A. Poggi, *Coord. Chem. Rev.*, 1999, **190–192**, 649.
- 16 L. Fabbri, M. Licchelli, P. Pallavicini and L. Parodi, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 800.
- 17 L. L. Koh, J. D. Ranford, W. T. Robinson, J. O. Svensson, A. L. C. Tan and D. Wu, *Inorg. Chem.*, 1996, **35**, 6466.
- 18 J. D. Ranford, J. J. Vittal and D. Wu, *Angew. Chem., Int. Ed.*, 1998, **37**, 1114.
- 19 J. D. Ranford, J. J. Vittal, X. Yang and D. Wu, *Angew. Chem., Int. Ed.*, 1999, **38**, 1114.
- 20 J. J. Vittal and X. Yang, *Cryst. Growth Des.*, 2002, **2**, 259.
- 21 C. T. Yang, B. Moubaraki, K. S. Murray, J. D. Ranford and J. J. Vittal, *Inorg. Chem.*, 2001, **40**, 5934.
- 22 H. Masuda, A. Odani and O. Yamauchi, *Inorg. Chem.*, 1989, **28**, 624.
- 23 SMART & SAINT Software Reference manuals, Version 5.0, Bruker AXS Inc., Madison, WI, 1998.
- 24 G. M. Sheldrick, SADABS software for empirical absorption correction, University of Göttingen, Germany, 2000.
- 25 SHELXTL Reference Manual, Version 5.1, Bruker AXS Inc., Madison, WI, 1998.
- 26 J. R. Ferraro, *Low-frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York, 1971.
- 27 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, 4th edn., 1986.
- 28 C. Djordjevic, M. Lee and E. Sinn, *Inorg. Chem.*, 1989, **28**, 719.
- 29 G. B. Deacon and R. Philips, *J. Coord. Chem. Rev.*, 1980, **33**, 227.
- 30 M. Tsaramyrsi, M. Kaliva, A. Salifoglou, C. P. Raptopoulou, A. Terzis, V. Tangorlis and J. Giapintzakis, *Inorg. Chem.*, 2001, **40**, 5772.
- 31 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1984.
- 32 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
- 33 A. W. Addison, T. N. Rao, J. Reedijk, J. van Jijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
- 34 G. Murphy, C. O'Sullivan, B. Murphy and B. Hathaway, *Inorg. Chem.*, 1998, **37**, 240.
- 35 C. O'Sullivan, G. Murphy, B. Murphy and B. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1999, 1835.
- 36 P. S. Marlin, M. M. Olmstead and P. K. Mascharak, *Inorg. Chem.*, 2001, **40**, 7003.
- 37 M. Melnik, M. Kabešová, M. Koman, M. Macáškova and C. E. Holloway, *J. Coord. Chem.*, 2000, **50**, 177.
- 38 E. Colacio, J. M. Domínguez-Vera, M. Ghazi, R. Kivekäs, M. Klinga and J. M. Moreno, *Eur. J. Inorg. Chem.*, 1999, 441.
- 39 M. Inoue and M. Kubo, *Inorg. Chem.*, 1970, **9**, 2310.
- 40 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
- 41 P. S. Subramanian, E. Suresh, P. Dastidar, S. Waghmode and D. Srinivas, *Inorg. Chem.*, 2001, **40**, 4291.
- 42 M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645.
- 43 S. Lopez and S. W. Keller, *Inorg. Chem.*, 1999, **38**, 1883.
- 44 E. Calacio, M. Ghazi, R. Kivekäs and J. M. Moreno, *Inorg. Chem.*, 2000, **39**, 2882.
- 45 D. Schulz, T. Weyhermüller, K. Wiegardt, C. Butzlaff and A. X. Tautwein, *Inorg. Chim. Acta*, 1996, **246**, 387.
- 46 E. Calacio, J. M. Domínguez-Vera, R. Kivekäs, J. M. Moreno, A. Romerosa and J. Ruiz, *Inorg. Chim. Acta*, 1993, **212**, 115.
- 47 P. K. Coughlin and S. J. Lippard, *J. Am. Chem. Soc.*, 1984, **106**, 2328.
- 48 R. L. Carlin, K. Kopinga, O. Kahn and M. Verdager, *Inorg. Chem.*, 1986, **25**, 1786.
- 49 F. Sapiña, E. Escrivá, J. V. Folgado, A. Beltrán, D. Beltrán, A. Fuertes and M. Drillon, *Inorg. Chem.*, 1992, **31**, 3851.
- 50 M. E. Fisher, *Am. J. Phys.*, 1964, **32**, 343.
- 51 P. Manikandan, K. R. J. Thomas and P. T. Manoharan, *J. Chem. Soc., Dalton Trans.*, 2000, 2779.