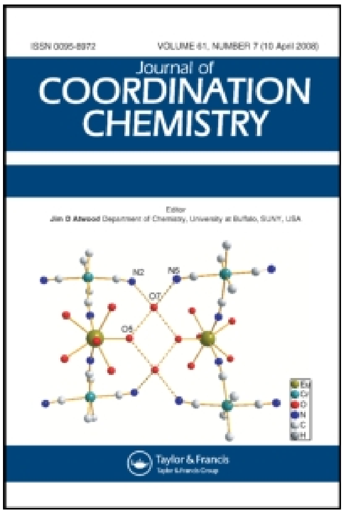

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and magnetochemical studies of dicopper(II) complexes derived from bis(*N*-salicylidene)dicarboxylic acid dihydrazides

Magdi F. Iskander[a]; Laila El-Sayed[a]; Nahed M. H. Salem[a]; Rudiger Werner[b]; Wolfgang Haase[b]
[a] Chemistry Department, Faculty of Science, Alexandria University, Ibrahimia, Alexandria 21321, Egypt [b] Institut fur physikalische Chemie, AG Kondensierte Materie, Fachbereich Chemie, Technische Universitat Darmstadt, Petersenstrasse 20, D-64287 Darmstadt, Germany

To cite this Article Iskander, Magdi F. , El-Sayed, Laila , Salem, Nahed M. H. , Werner, Rudiger and Haase, Wolfgang(2005) 'Synthesis, characterization and magnetochemical studies of dicopper(II) complexes derived from bis(*N*-salicylidene)dicarboxylic acid dihydrazides', Journal of Coordination Chemistry, 58: 2, 125 — 139

To link to this Article: DOI: 10.1080/00958970412331272403

URL: http://dx.doi.org/10.1080/00958970412331272403

Journal of Coordination Chemistry
Vol. 58, No. 2, 20 January 2005, 125–139

Synthesis, characterization and magnetochemical studies of dicopper(II) complexes derived from bis(*N*-salicylidene)dicarboxylic acid dihydrazides

MAGDI F. ISKANDER†*, LAILA EL-SAYED†, NAHED M.H. SALEM†,
RUDIGER WERNER‡ and WOLFGANG HAASE‡

†Chemistry Department, Faculty of Science, Alexandria University, PO Box 426,
Ibrahimia, Alexandria 21321, Egypt
‡Institut fur physikalische Chemie, AG Kondensierte Materie, Fachbereich Chemie,
Technische Universitat Darmstadt, Petersenstrasse 20,
D-64287 Darmstadt, Germany

(Received 24 November 2003; revised 15 November 2003; in final form 1 June 2004)

Two series of dicopper(II) complexes derived from bis(*N*-salicylidine)dicarboxylic acid dihydrazides (H_4L^n) of general formula $[Cu_2(L^n) \cdot xH_2O] \cdot yH_2O$ and $[Cu_2(H_2L^n)Cl_2 \cdot xH_2O] \cdot yH_2O$ have been synthesized and characterized, where n refers to the number of carbon atoms in the aliphatic spacer between the two *N*-salicylideneacylhydrazine units. Magnetic susceptibility measurements for neutral dicopper(II) complexes $[Cu_2(L^n) \cdot xH_2O] \cdot yH_2O$ indicate significant antiferromagnetic coupling between copper(II) centers. The $-2J$ values obtained from the Bleany–Bowers equation are within the range 121–223 cm^{-1}, suggesting association of the coordinated copper(II) units Cu(ONO) via phenoxy bridges. This leads to a polynuclear structure in which the dimeric units are connected with the aliphatic spacer. From the best-fit values of the mole fraction of paramagnetic uncoupled copper(II) centers (ρ), the degree of association in these polynuclear copper(II) complexes has been estimated. The chloro dicopper(II) complexes $[Cu_2(H_2L^n)Cl_2 \cdot xH_2O] \cdot yH_2O$ with $n = 0$, 2 and 3 also show strong antiferromagnetic exchange coupling ($-2J = 215$–$423\,cm^{-1}$), suggesting a polynuclear structure in which the copper(II) is in a distorted square-pyramidal environment, bound in the equatorial plane with a monoanionic ONO tridentate acylhydrazone unit and the μ-phenoxy oxygen and the axial site occupied by a chloride. The dicopper(II) complexes with $n = 1$ and 4 show weak antiferromagnetic exchange coupling ($-2J = 16$–$20\,cm^{-1}$). In these complexes the chloride ion may occupy the fourth equatorial site while the μ-phenoxy is in the apical position.

Keywords: Bis(*N*-salicylidene)dicarboxylic acid dihydrazides; Polynuclear copper(II) complexes; Infrared spectra; Ultraviolet–visible spectra; Magnetic properties

1. Introduction

Bis(*N*-salicylidene)dicarboxylic acid dihydrazides (figure 1a) react with copper(II) salts to give the corresponding dicopper(II) complexes of the type $[Cu_2(H_2L^n)X_2] \cdot yH_2O$ or

---

*Corresponding author. Tel.: +20-3-3911794. E-mail: m.iskander@link.net

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970412331272403

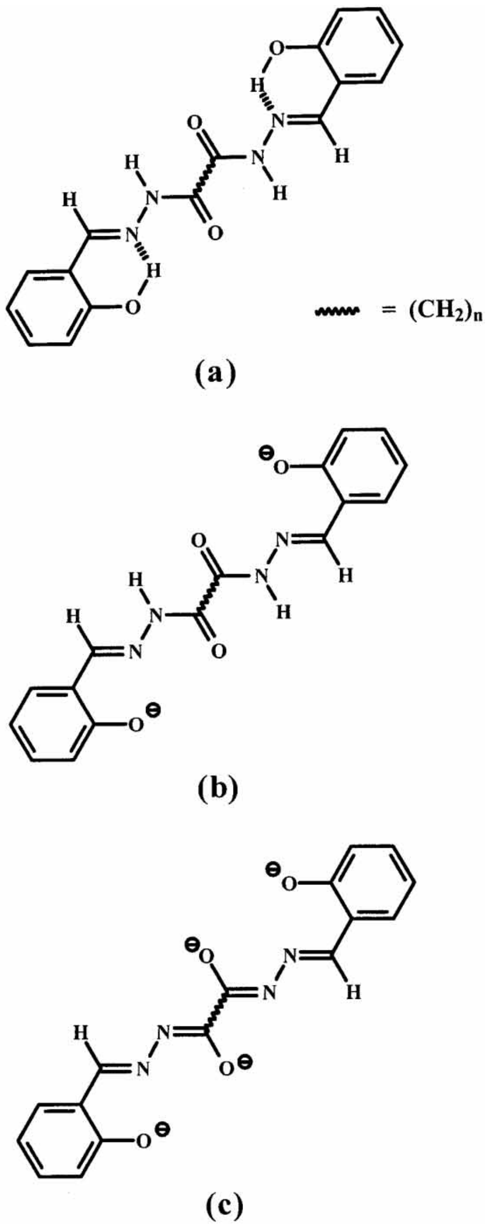

Figure 1. Diagrammatic representations of (a) H_4L, (b) H_2L^{2-} and (c) L^{4-}.

$[Cu_2(H_2L^n)\cdot xH_2O]X_2\cdot yH_2O$ (X = Cl, Br, I, NO_3 or ClO_4) and $[Cu_2(L^n)\cdot xH_2O]\cdot yH_2O$, where H_2L^n and L^n refer respectively to the dinegative (figure 1b) and tetranegative (figure 1c) bishydrazone ligands, while n refers to the number of the carbon atoms in the aliphatic spacer joining the two ONO tridentate acylhydrazone units [1–8]. The degree of ligand deprotonation depends on the copper(II) salt used for the preparation of these dicopper(II) complexes. The X-ray structures of

$[Cu_2(H_2L^1)(H_2O)_2]\cdot(ClO_4)_2\cdot 3H_2O$ and $[\{Cu_2(H_2L^4)(C_2H_5OH)_2\}_m](ClO_4)_{2m}\cdot mC_2H_5OH$ have been reported [8]. The structure of $[Cu_2(H_2L^1)(H_2O)_2]\cdot(ClO_4)_2\cdot 3H_2O$ consists of discrete dicopper molecules with nonsymmetry-related Cu(II) centers. Each copper(II) atom is square-planar coordinated to a tridentate monoanionic ONO acylhydrazone unit with the fourth coordination site occupied by water oxygen [8]. In $[Cu_2(H_2L^1)(H_2O)_2]\cdot(ClO_4)_2\cdot 3H_2O$, each of the symmetry-related copper atoms is in a square-pyramidal environment and is bound in the equatorial plane with the monoanionic ONO acylhydrazone unit and ethanol. The fifth coordination site is occupied by the bridged phenoxy oxygen giving a polymeric structure [8].

At room temperature, most of the reported dicopper(II) complexes of H_4L^n ($n = 0$–4) show low magnetic moments, implying copper(II)–copper(II) antiferromagnetic interactions. The nature and mechanism(s) of these interactions are still uncertain [7,8]. In this paper we report the synthesis and characterization of a number of dicopper(II) complexes of H_4L^n ($n = 0$–4) where the ligands show different degrees of deprotonation. The magnetic properties of these complexes have also been studied. The effect of the length of the aliphatic spacer $-(CH_2)_n-$ between the coordinated ONO tridentate acylhydrazone units on the magnetic behavior of these complexes is discussed.

2. Results and discussion

2.1 *Synthesis*

The reaction of bis(*N*-salicylidene)dicarboxylic acid dihydrazides, H_4L^n (figure 1a; $n = 0$–4), with excess copper(II) acetate in the presence of sodium acetate afforded the neutral dicopper(II) complexes $[Cu_2(L^n)\cdot xH_2O]\cdot yH_2O$ ($n = 0$–4), where L^n refers to the quadruply deprotonated bishydrazone ligand. The isolated copper(II) complexes were insoluble in common solvents but soluble in DMSO or DMF. The reaction of copper(II) chloride, using ($1\,H_4L^n : 2\,CuCl_2$) molar ratio, in ethanol gave the corresponding binuclear chloro copper(II) complexes $[Cu_2(H_2L^n)Cl_2\cdot xH_2O]\cdot yH_2O$ ($n = 0$–4), where each acylhydrazone residue is bonded to Cu(II) as a mononegative ONO tridentate ligand. The isolated chloro complexes were usually contaminated with pale yellow organic crystals, which were readily extracted with benzene leaving the pure copper(II) complexes. Evaporation of the benzene extracts gave pure crystals of salicylaldehydeazine, which was identified by its mp (254°C), IR, UV–visible and ^{1}H NMR spectra. The formation of this compound suggests partial oxidative hydrolysis of the dihydrazone molecule catalyzed by copper(II). Thermogravimetric analyses suggest that the neutral and chloro dicopper(II) complexes contain both lattice and coordinated water molecules. The lattice water evolved at *ca* 100°C, while the loss of the coordinated water started at *ca* 200°C with partial decomposition of the complex. From the weight loss measured on heating the complex at 105°C for 24 h under atmospheric pressure, the number of lattice water molecules was estimated. The isolated dicopper(II) complexes together with their elemental analyses are listed in table 1.

2.2 *Infrared spectra*

The IR spectra of H_4L^n ($n = 0$–4) show a series of bands at *ca* 3200 ± 10, 1665 ± 10, 1600 ± 10, 1568 ± 5, 1530 ± 20 and $1260 \pm 10\,\mathrm{cm^{-1}}$, respectively, due to ν(N–H), amide I [ν(C=O)], ν(C–N), amide II [δ(N–H)] and amide III [ν(C–N)] bands [1,8–11].

Table 1. Elemental analyses of the dicopper(II) complexes $[Cu_2(L^n)\cdot xH_2O]\cdot yH_2O$ and $[Cu_2(H_2L^n)Cl_2\cdot xH_2O]\cdot yH_2O$.

Compound	Yield (%)	Found (Calculated) (%)			
		C	H	N	Cu
$[Cu_2(L^n)\cdot xH_2O]\cdot yH_2O$					
$[Cu_2(L^0)\cdot 1/2H_2O]\cdot H_2O$	87	40.22 (40.34)	2.60 (2.75)	10.90 (11.76)	26.50 (26.68)
$[Cu_2(L^1)\cdot H_2O]\cdot 1/2H_2O$	82	41.96 (41.64)	2.58 (3.08)	11.43 (11.42)	26.10 (25.91)
$[Cu_2(L^2)\cdot 1/2H_2O]\cdot H_2O$	74	43.11 (42.90)	3.09 (3.39)	11.05 (11.11)	25.20 (25.19)
$[Cu_2(L^3)\cdot 1/2H_2O]\cdot 3/2H_2O$	75	43.81 (43.26)	3.43 (3.82)	10.83 (10.62)	25.70 (24.09)
$[Cu_2(L^4)\cdot 1/2H_2O]\cdot 3/2H_2O$	72	44.36 (44.36)	3.76 (4.09)	10.27 (10.35)	22.80 (23.47)
$Cu_2(H_2L^n)Cl_2\cdot xH_2O]\cdot yH_2O$					
$[Cu_2(H_2L^0)Cl_2\cdot 1/2H_2O]\cdot 3/2H_2O$	87	33.79 (34.42)	1.94 (2.89)	9.59 (10.03)	22.62 (22.76)
$[Cu_2(H_2L^1)Cl_2\cdot H_2O]\cdot 2H_2O$	71	34.64 (34.59)	2.69 (3.41)	9.38 (9.49)	22.70 (21.53)
$[Cu_2(H_2L^2)Cl_2\cdot 1/2H_2O]\cdot 3/2H_2O$	68	38.87 (38.04)	2.86 (3.19)	10.03 (9.86)	23.05 (22.36)
$[Cu_2(H_2L^3)Cl_2\cdot H_2O]\cdot H_2O$	68	38.09 (38.01)	3.17 (3.69)	9.10 (9.33)	21.40 (21.68)
$[Cu_2(H_2L^4)Cl_2\cdot H_2O]\cdot 2H_2O$	69	37.48 (37.98)	3.83 (4.14)	8.47 (8.86)	20.63 (20.10)

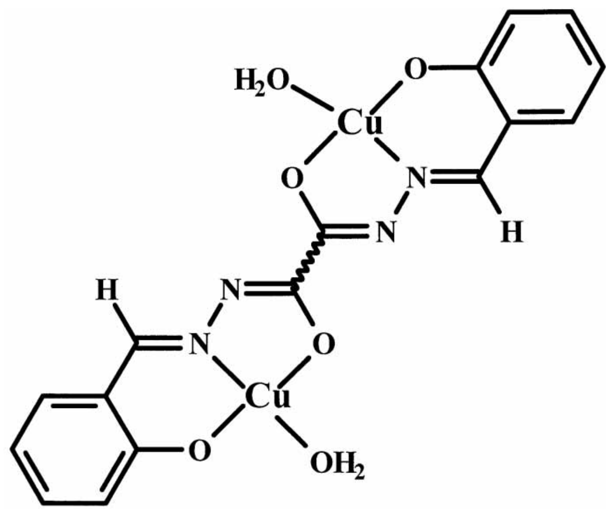

Figure 2. Proposed structure of monomeric dicopper(II) complexes $[Cu_2(L^n)\cdot 2H_2O]$.

The IR spectra of the corresponding dicopper(II) complexes, $[Cu_2(L^n)\cdot xH_2O]\cdot yH_2O$ (figure 2) ($n = 0$–4), lack absorptions due to ν(OH), ν(N–H), amide I [ν(C=O)] and amide II bands, but show a strong band at 1615 cm^{-1} due to ν(C=N–N=C) and the absorption due to the amide III band at 1300 cm^{-1}. The IR data together with the stoichiometry of these complexes suggest complete deprotonation of both phenolic and enolimide groups.

Similar to other copper(II) complexes with dinegative ONO tridentate Schiff bases [12–14], the coordination number 4 of the central copper(II) ion in the isolated dicopper(II) complexes can be achieved either by coordination with one molecule of a neutral monodentate Lewis base (e.g. H_2O), to give $[Cu_2(L^n)\cdot 2H_2O]\cdot yH_2O$ (figure 2), or by dimerization via phenolic oxygen bridges to give the polymeric homonuclear metal complexes $[Cu_2(L^n)\cdot xH_2O]_m\cdot (yH_2O)_m$, as shown in figure 3. The polymerization

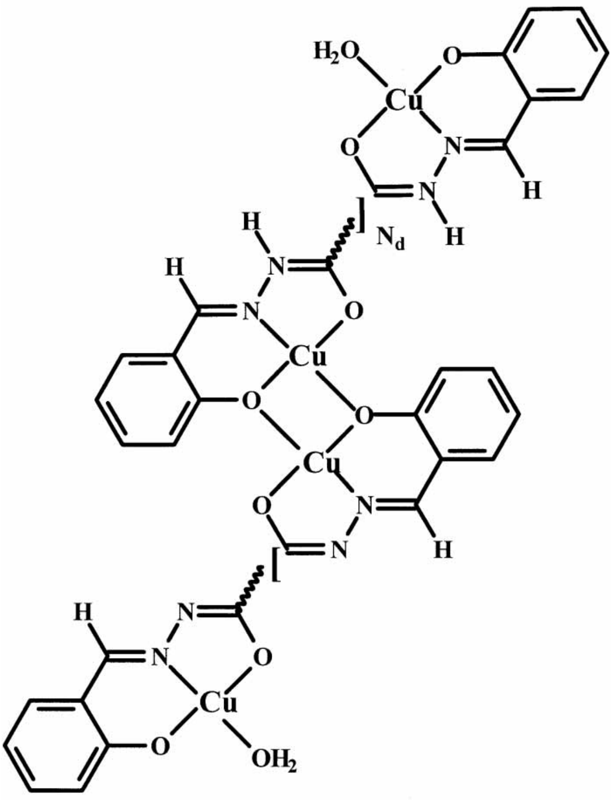

Figure 3. Proposed structure of polymeric copper(II) complexes $[Cu_2(L^{n}) \cdot xH_2O]_m$.

(or oligomerization) in this type of polynuclear metal complex can be terminated by the addition of any available neutral monodentate Lewis base (e.g. H_2O) to the terminal copper(II) ions as given in figure 3. Thus, either binuclear (figure 2) or polynuclear (figure 3) structures may be found for these complexes.

The chloro dicopper(II) complexes $[Cu_2(H_2L^{n})Cl_2 \cdot xH_2O] \cdot yH_2O$ display a set of bands at 3200 ± 70, 1620 ± 5, 1600 ± 5 to 1570 ± 10, 1540 ± 10 and 1310 ± 20 cm^{-1}, respectively, due to ν(N–H), amide I [ν(C=O)], [ν(C=C) + ν(C=N)], amide II [δ(N–H)] and amide III [ν(C–N)]. Both amide I ν(C=O)] and ν(C=N) are shifted to lower frequencies, while the amide III band is shifted to higher frequency relative to those of the corresponding free ligands. In these complexes each acylhydrazone residue acts as a monoanionic ONO tridentate ligand and is bound to the copper(II) via phenoxy oxygen, azomethine nitrogen and ketoamide oxygen, and the fourth coordination site is occupied either by a chloride ion or a solvent molecule. A similar coordination mode was reported for mononuclear copper(II) complexes with *N*-salicylideneacylhydrazines [15,16] as well as the dicopper(II) complex $[Cu_2(H_2L^1)(H_2O)_2] \cdot (ClO_4)_2 \cdot 3H_2O$ [8]. However, association via phenoxy oxygen of the coordinated ONO mononegative acylhydrazone residue is also possible giving a polynuclear structure as shown in figure 4. Similar coordination modes were also found in dimeric copper(II) complexes with *N*-salicylideneacylhydrazines [17–19] as well as polynuclear $[\{Cu_2(H_2L)\ (C_2H_5OH)_2\}_m] \cdot (ClO_4)_{2m} \cdot m(C_2H_5OH)$ [8].

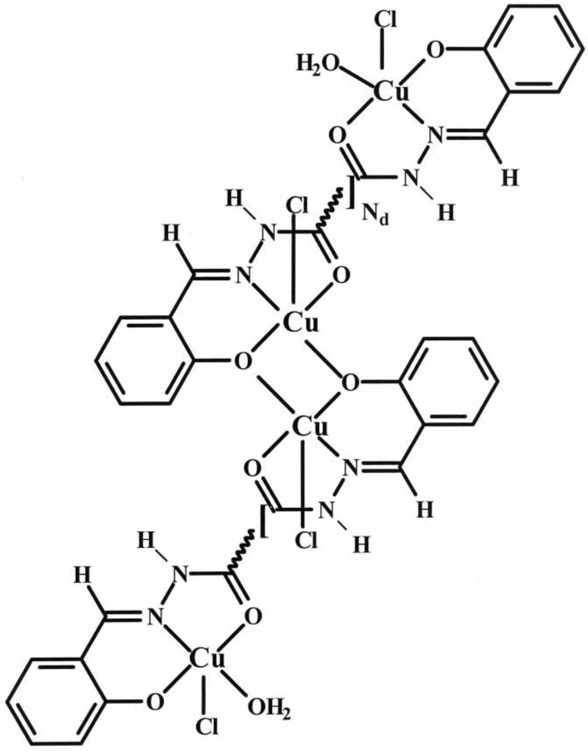

Figure 4. Proposed structure of polymeric chloro copper(II) complexes $[Cu_2(H_2L^n)Cl_2 \cdot xH_2O]_m$, where the chloride ion is in the apical position.

2.3 *Electronic spectra*

Solution electronic absorption spectra of the free ligands H_4L^n ($n = 1$–4) in DMF or DMSO (table 2) are more or less similar. The spectra show two intense absorption bands at *ca* 290 nm (usually as a split band) (band II) and 320 nm (band III) from the π–π^* transitions of the neutral ortho hydroxy azomethine chromophore [20–24]. The spectra also show a broad absorption at *ca* 380 nm (band IV) due to the partial formation of the mononegative anion $(H_3L^n)^{1-}$. The disappearance of band IV on acidification confirms this assignment. The spectrum of H_4L^0 ($n = 0$) shows similar spectral pattern, but the absorption bands II, III and VI undergo a red shift due to extended electron delocalization in the two conjugated acylhydrazone residues.

The spectra of the neutral copper(II) complexes $[Cu_2(L^n) \cdot xH_2O] \cdot yH_2O$ (table 2) show a series of bands within the range 260–330 nm due to different L–L* transitions (bands II and III) of the coordinated ligands, besides a broad intense band at 380 nm (band IV) due to intraligand charge transfer transition of the deprotonated acylhydrazone chromophore. The phenoxide to metal charge transfer band (LMCT transition), which is expected to appear within 370–450 nm [25–28], may be hidden under the intense intraligand charge transfer at *ca* 380 nm. The spectra also display a relatively less intense band at 620–650 nm that arises from the different d–d transitions of copper(II) [29]. The position and intensity of the d–d absorption bands suggest a distorted square-planar or a distorted square-pyramidal environment around the

Table 2. Electronic absorption spectra of H_4L^n and their corresponding copper(II) complexes.

	Absorption maxima (nm) (log ε)		
Compound	L–L[a]	LMCT	d–d
i) H_4L^n			
H_4L^0	295 (426), 305 (4.26), 340 (4.29), 410 (3.30)		
H_4L^1	290 (430), 320 (4.18), 380 (3.05)		
H_4L^2	290 (4.11), 320 (3.75), 380 (3.10)		
H_4L^3	290 (4.23), 320 (4.02), 380 (3.25)		
H_4L^4	290 (4.44), 320 (4.23), 380 (3.31)		
ii) $[Cu_2(L^n)\cdot xH_2O]\cdot yH_2O$			
$[Cu_2(L^1)\cdot H_2O]\cdot 1/2H_2O$	298 (4.46), 313 (4.40), 383 (4.44)		662 (2.50)
$[Cu_2(L^2)\cdot 1/2H_2O]\cdot H_2O$	300 (4.40), 315 (4.00), 380 sh		660 (2.5)
$[Cu_2(L^3)\cdot 1/2H_2O]\cdot 3/2H_2O^a$	300, 313, 378		639
$[Cu_2(L^4)\cdot 2H_2O]\cdot 3/2H_2O$	298 (4.41), 313 (4.36), 378 (4.36)		660 (2.40)
iii) $[Cu_2(H_2L)Cl_2\cdot xH_2O]\cdot yH_2O$			
$[Cu_2(H_2L^1)Cl_2\cdot H_2O]\cdot 2H_2O$	281 (4.73), 313 sh, 384 (4.45)	400 sh	695 (2.54), 810 sh
$[Cu_2(H_2L^2)Cl_2\cdot 1/2H_2O]$	259 sh, 281 (4.75), 318 sh, 384 (4.18)	400 sh	708 (2.37), 810 sh
$3/2H_2O$			
$[Cu_2(H_2L^3)Cl_2\cdot H_2O]\cdot H_2O$	259 (4.68), 278 (4.69) 315 sh, 383 (4.35)	400 sh	711 (2.38), 810 sh
$[Cu_2(H_2L^4)Cl_2\cdot H_2O]\cdot 2H_20$	260 (4.77), 280 (4.67), 315 sh, 383 (4.37)	400 sh	706 (2.50), 810 sh

[a] Saturated solution.

Cu(II) [29]. In DMSO solutions, the phenoxy bridges, if present, may be ruptured and these copper(II) complexes exist as solvated monomeric species $[Cu_2(L^n)(DMSO)_2]$ and/or $[Cu_2(L^n)(DMSO)_4]$ [30].

The spectra of the chloro dicopper(II) complexes $[Cu_2(H_2L^n)Cl_2\cdot xH_2O]\cdot yH_2O$, on the other hand, are more or less similar and exhibit absorptions (bands II, III and IV) due to different L–L* transitions. The phenoxide to metal LMCT transition appears as a prominent shoulder (*ca* 400 nm) at the long wavelength tail of the 380 nm absorption band. The d–d transitions appear as a broad band centered at *ca* 710 nm with a shoulder at *ca* 810 nm, characteristic of a distorted square pyramid [29]. The observed shift to lower frequencies of the d–d bands in the spectra of the chloro complexes relative to those of the neutral complexes suggests the persistence of the copper–chloride bond in the solvated species $[Cu_2(H_2L)Cl_2(DMSO)_2]$.

2.4 *Magnetic measurements*

At room temperature, the neutral dicopper(II) complexes $[Cu_2(L^n)\cdot xH_2O]\cdot yH_2O$ have subnormal magnetic moments within the range 1.55–1.65 μ_β. Variable-temperature magnetic susceptibility data for these complexes were collected over the temperature range 3–300 K, and plots of χ_m versus T for $[Cu_2(L^0)\cdot 1/2H_2O]\cdot H_2O$ and $[Cu_2(L^2)\cdot 1/2H_2O]\cdot H_2O$ are shown in figures 5 and 6, respectively. The data were fit to the revised Bleaney–Bowers equation [31], using the isotropic exchange Hamiltonian ($H = -2JS_1S_2$) for two interacting $S = 1/2$ centers:

$$\chi_m = (1-\rho)\frac{2N_L\mu_\beta^2 g^2 \exp(2J/kT)}{k(T-\theta)(1+3\exp(2J/kT))} + \rho\frac{2N_L\mu_\beta^2 g^2}{4kT} + 2N_\alpha \qquad (1)$$

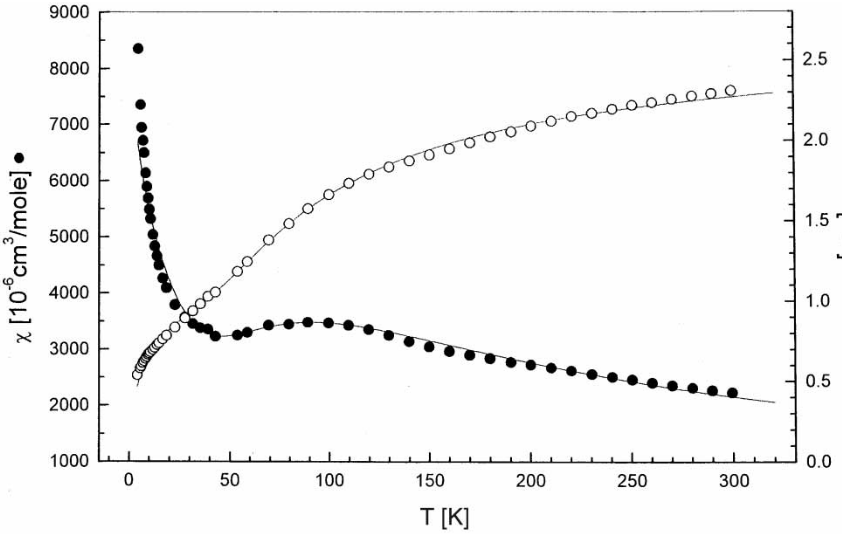

Figure 5. Magnetic susceptibilities χ_m (•) and magnetic moments (o) *vs* temperature for $[Cu_2(L^0)\cdot 1/2H_2O]\cdot H_2O$. Solid lines represent the best least-squares fit to Equation (1), with $2J=-121$, $g=2.06$, $\theta=-50$ and $\rho=23\%$.

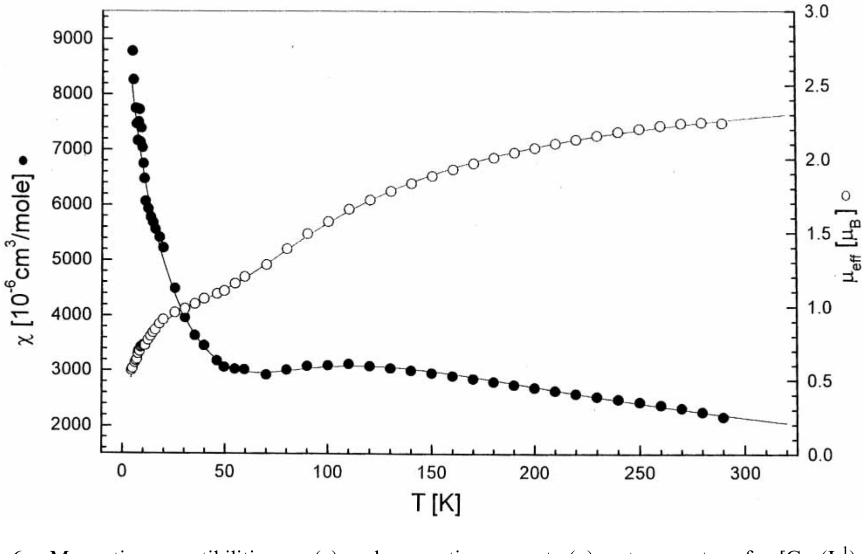

Figure 6. Magnetic susceptibilities χ_m (•) and magnetic moments (o) *vs* temperature for $[Cu_2(L^1)\cdot H_2O]\cdot 1/2H_2O$. Solid lines represent the best least-squares fit to Equation (1), with $2J=-322$, $g=2.05$, $\theta=-14$ and $\rho=49\%$.

where χ_m is the magnetic susceptibility per two copper atoms, N_α is the temperature-independent paramagnetism [$60\times10^{-6}\,cm^3\,mol^{-1}$ per Cu(II)], ρ is the mole fraction of uncoupled copper(II) ions and θ is the corrective term to account for interdimer interactions [32,33]. A nonlinear regression analysis was carried out with g, ρ, θ and J as floating parameters. The best-fit magnetic parameters obtained are listed in table 3.

Table 3. Magnetic parameters and number of dimeric units of $[Cu_2(L^n) \cdot xH_2O] \cdot yH_2O$ and $[Cu_2(H_2L^n)Cl_2 \cdot xH_2O] \cdot yH_2O$ complexes.

Complex	μ_{eff} (298 K)	g	θ	ρ	N_d	$-2J$ (cm^{-1})
$[Cu_2(L^n) \cdot xH_2O] \cdot yH_2O$						
$[Cu_2(L^0) \cdot 1/2H_2O] \cdot H_2O$	1.64	2.06	−50	0.23	3	121
$[Cu_2(L^1) \cdot H_2O] \cdot 1/2H_2O$	1.55	2.05	−14	0.49	1	322
$[Cu_2(L^2) \cdot 1/2H_2O] \cdot H_2O$	1.59	2.05	−10	0.25	3	179
$[Cu_2(L^3) \cdot 1/2H_2O] \cdot 3/2H_2O$	1.64	2.05	−12	0.34	2	209
$[Cu_2(L^4) \cdot 1/2H_2O] \cdot 3/2H_2O$	1.59	2.05	−12	0.33	2	223
$[Cu_2(H_2L^n)Cl_2 \cdot xH_2O] \cdot yH_2O$						
$[Cu_2(H_2L^0)Cl_2 \cdot 1/2H_2O] \cdot 3/2H_2O$	1.65	2.13	−28	0.32	2	215
$[Cu_2(H_2L^1)Cl_2 \cdot H_2O] \cdot 2H_2O$	1.90	2.21	−4	0.47	1	20
$[Cu_2(H_2L^2)Cl_2 \cdot 1/2H_2O] \cdot 3/2H_2O$	1.58	2.21	−10	0.35	2	382
$[Cu_2(H_2L^3)Cl_2 \cdot H_2O] \cdot H_2O$	1.66	2.18	−8	0.57	1	423
$[Cu_2(H_2L^4)Cl_2 \cdot H_2O] \cdot 2H_2O$	1.86	2.06	−5	0.32	2	16

The values of $-2J\,(cm^{-1})$ obtained for the neutral dicopper(II) complexes (table 3) are within the range reported for antiferromagnetic bis-μ-phenoxy bridged dicopper(II) complexes [12–14,34–40]. In these complexes association of the coordinated copper(II) units Cu(ONO) via phenoxy bridges will lead to a polynuclear structure (figure 3), where the dimeric units are connected by an aliphatic spacer of different carbon chain lengths ($n = 0$–4). The propagation of the dimeric units is terminated by coordination of solvent molecules (water) to the terminal copper(II) units. In each dimer, the copper(II) is square planar, coordinated to the dinegative ONO tridentate acylhydrazone unit, with the fourth coordination site occupied by the symmetry-related phenoxy oxygen of another molecule. The antiferromagnetic exchange coupling is mediated through these μ-phenoxy oxygens. Magnetochemical studies [13,14] on related dimeric complexes indicate that the magnitude of singlet–triplet separation ($-2J\,cm^{-1}$) in the Cu–O–Cu bridge depends mainly on the dihedral angle τ between the Cu_2O_2 plane and the plane of the remaining ligand and, to a lesser extent, the Cu–O–Cu angle. The ($-2J$) values estimated for $[Cu_2(L^n) \cdot xH_2O] \cdot yH_2O$ complexes suggest a more or less planar structure with small τ angle, permitting efficient overlap between the $d_{x^2-y^2}$ copper(II) orbitals and sp^2 hybridized orbitals of the phenoxy oxygen. Moreover, the dimeric units in the polynuclear copper(II) complexes $[Cu_2(L^n) \cdot xH_2O] \cdot yH_2O$ with $n = 1$–4 are magnetically isolated by the aliphatic spacer and no interdimer exchange coupling is expected. In $[Cu_2(L^0)1/2H_2O] \cdot H_2O$, however, the two conjugated acylhydrazone units can mediate interdimer interaction between the two copper(II) ions. This is evident from the high θ value of this polynuclear complex with $n = 0$ relative to those of the other complexes with $n = 1$–4.

The propagation of the antiferromagnetic dimeric units in $[Cu_2(L^n) \cdot xH_2O] \cdot yH_2O$ is terminated by coordination of solvent molecules (water) to the two terminal paramagnetic copper(II) units. The relatively high mole fraction of paramagnetic copper(II) (ρ) relative to the mole fraction of antiferromagnetic copper(II) ($1 - \rho$) is in agreement with the presence of terminal paramagnetic copper(II). The extent of association in the resulting polynuclear copper(II) complexes can be evaluated from the corresponding best-fit value of ρ [mole fraction of the uncoupled copper(II) centers in equation (1)]. Taking the number of the uncoupled copper(II) centers [terminal copper(II) centers] as 2, the number of coupled copper(II) centers (N_c) can be estimated from equation (2):

$$N_c = 2(1 - \rho)/\rho \tag{2}$$

and hence the number of dimeric units (N_d) in the polynuclear chain ($N_d = N_c/2$) can be obtained.

It is of interest to note that in this model, the number of dimeric units (N_d) is the statistical average of the number of dimers in different polynuclear chains randomly distributed in the bulk of the complex. Furthermore, from the N_d values estimated for the different neutral complexes (table 3), there is no apparent correlation between the extent of association and the number of carbon atoms in the spacer aliphatic chain.

The room temperature magnetic moments of the chloro dicopper(II) complexes (table 3) were found to depend on the number of carbon atoms in the aliphatic spacer. The magnetic moments of $[Cu_2(H_2L^1)Cl_2 \cdot H_2O] \cdot 2H_2O$ and $[Cu_2(H_2L^4)Cl_2 \cdot 1/2H_2O] \cdot 5/2H_2O$ are within the range reported for uncoupled copper(II) complexes; the chloro complexes with $n = 0$, 2 and 3 exhibit low magnetic moments, suggesting antiferromagnetic coupling between the copper(II) centers. The magnetic susceptibilities of the chloro complexes were also measured within the temperature range 4.5–300 K and the data obtained were fit to equation (1). The best-fit magnetic parameters are included in table 3. The variation of χ_m as a function of temperature for $[Cu_2(H_2L^0)Cl_2 \cdot 1/2H_2O] \cdot 3/2H_2O$ (figure 7) shows an incipient maximum at *ca* 125 K followed by a sharp rise at 70 K indicating antiferromagnetic exchange coupling with a high mole fraction of paramagnetic uncoupled copper(II) centers. Similar behavior was also observed for $[Cu_2(H_2L^2)Cl_2 \cdot 1/2H_2O] \cdot 3/2H_2O$ and $[Cu_2(H_2L^3)Cl_2 \cdot H_2O] \cdot H_2O$. The $-2J$ values obtained for the chloro complexes with $n = 0$, 2 and 3

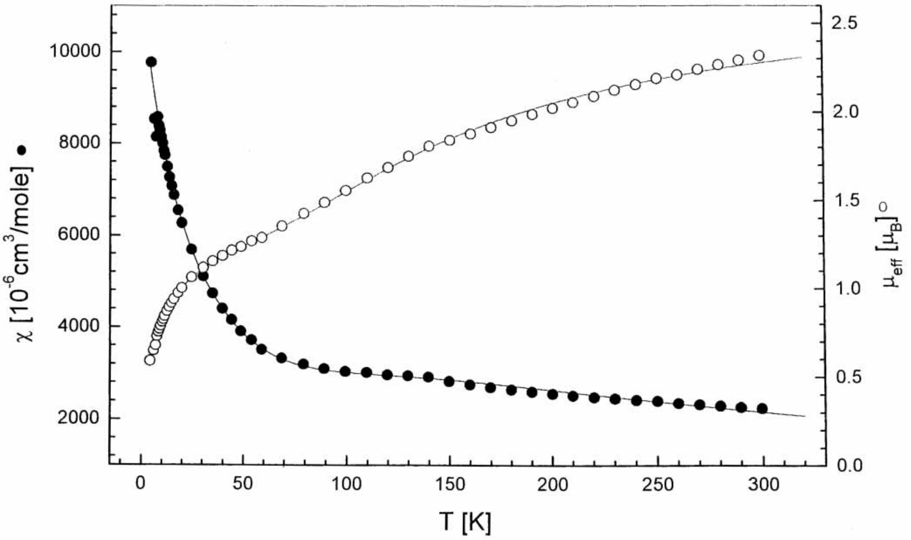

Figure 7. Magnetic susceptibilities χ_m (•) and magnetic moments (o) *vs* temperature for $[Cu_2(H_2L^0)Cl_2 \cdot 1/2H_2O] \cdot 3/2H_2O$. Solid lines represent the best least-squares fit to equation (1), with $2J = -215$, $g = 2.13$, $\theta = -28$ and $\rho = 32\%$.

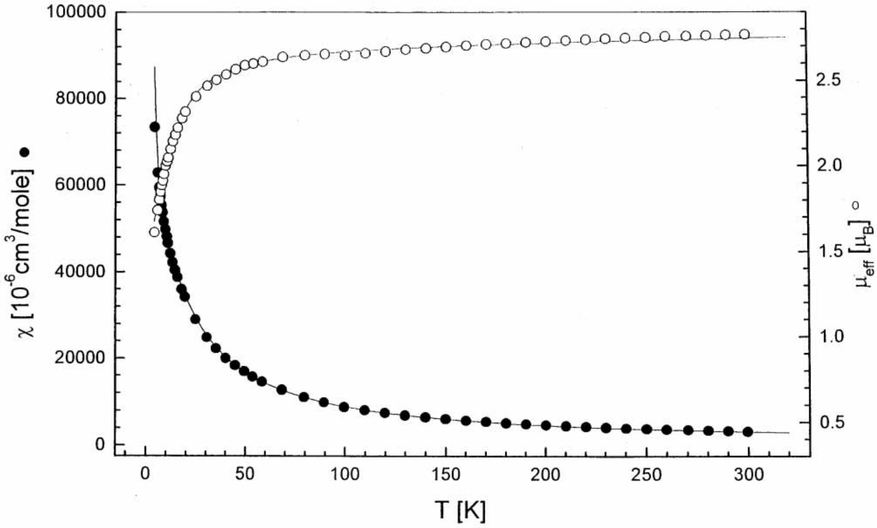

Figure 8. Magnetic susceptibilities χ_m (•) and magnetic moments (o) *vs* temperature for $[Cu_2(H_2L^1)Cl_2 \cdot H_2O] \cdot 2H_2O$. Solid lines represent the best least-squares fit to equation (1), with $2J = -20$, $g = 2.21$, $\theta = -4$ and $\rho = 47\%$.

(table 3) suggest strong antiferromagnetic exchange coupling via phenoxy oxygens. The high θ value recorded for $[Cu_2(H_2L^0)Cl_2 \cdot 1/2H_2O] \cdot 3/2H_2O$ is in agreement with interdimer exchange via the conjugated acylhydrazone residues. A polynuclear structure (figure 4) can be tentatively assigned for these chloro complexes. The Cu(II) in the dimeric units is a distorted square pyramid, bound in the equatorial plane with the monoanionic ONO tridentate acylhydrazone unit and the μ-phenoxy oxygen. The fifth coordination site (axial) is occupied by a chloride ion. A similar structure was also reported for dimeric copper(II) complexes with monoanionic *N*-salicylideneacylhydrazone ligands [16–19].

Variable-temperature magnetic susceptibility data recorded for chloro complexes $[Cu_2(H_2L^1)Cl_2 \cdot H_2O] \cdot 2H_2O$ and $[Cu_2(H_2L^4)Cl_2 \cdot H_2O] \cdot 2H_2O$ (figures 8 and 9) are similar and reveal weak antiferromagnetic exchange coupling ($-2J = 14$–$21\,cm^{-1}$) as compared to those recorded for other chloro complexes with $n = 0$, 2 and 3 ($-2J = 215$–$425\,cm^{-1}$). To account for the weak antiferromagnetic exchange coupling in chloro dicopper(II) complexes with $n = 1$ and 4, a different dimerization mode of the coordinated Cu(ONO) units is proposed. In these complexes, the chloride ion may occupy an equatorial site while the μ-phenoxy oxygen is in the apical position as shown in figure 10. This would effectively result in less or no spin exchange between the $d_{x^2-y^2}$ ground state of copper(II) centers via phenoxy oxygens and hence reduced $-2J$ values are expected. The X-ray structure of the perchlorate complex $[\{Cu_2(H_2L^4)(C_2H_5OH)_2\}_m] \cdot (ClO_4)_{2m}$ shows a similar dimerization mode, where the copper(II) is coordinated in the equatorial plane by the monoanionic tridentate acylhydrazone residue and ethanol oxygen. The μ-phenoxy oxygen occupies the fifth axial coordination site [8].

The N_d values recorded for the polynuclear complexes shown in figure 4 ($n = 0$, 2 and 4) (table 3) reveal that this type of complex probably consists of two dimeric

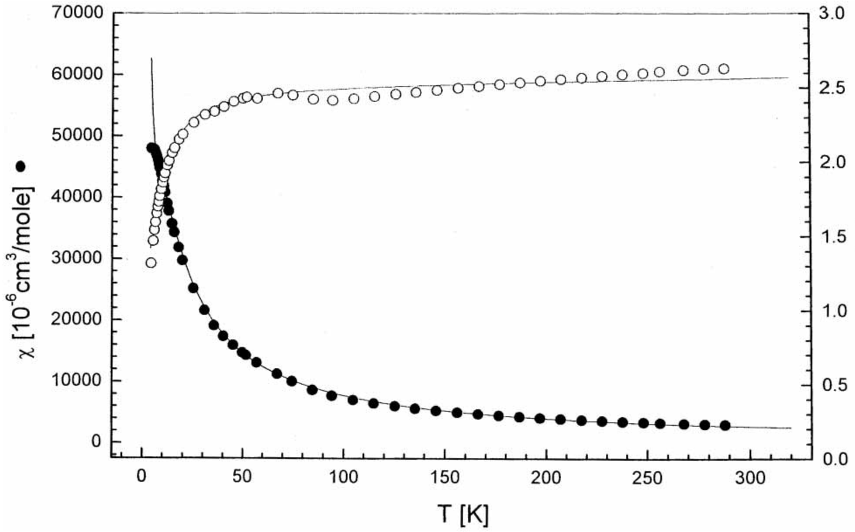

Figure 9. Magnetic susceptibilities χ_m (●) and magnetic moments (o) *vs* temperature for $[Cu_2(H_2L^4)Cl_2 \cdot H_2O] \cdot 2H_2O$. Solid lines represent the best least-squares fit to equation (1), with $2J = -16$, $g = 2.06$, $\theta = -5$ and $\rho = 32\%$.

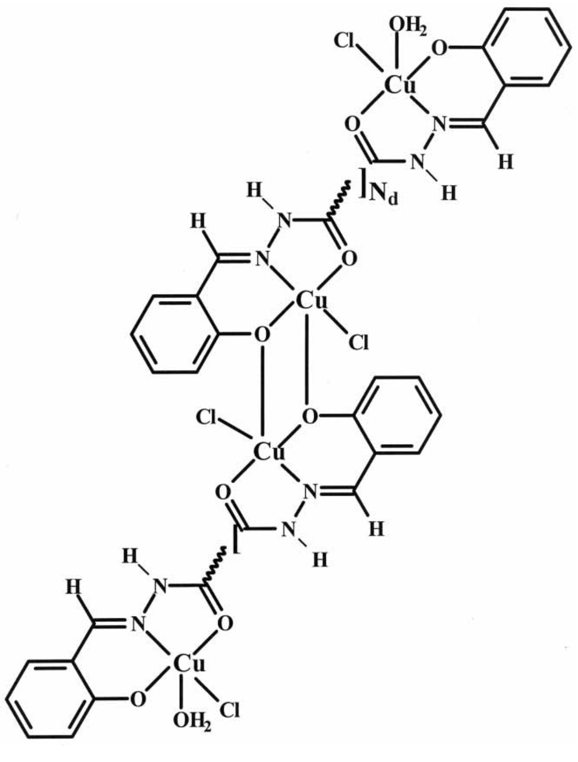

Figure 10. Proposed structure of polymeric chloro copper(II) complexes $[Cu_2(H_2L'')Cl_2 \cdot xH_2O]_m$, where the chloride ion is in the equatorial plane.

units with two terminal copper(II) atoms coordinated to both chloride and water oxygen. Accordingly, these complexes can be formulated as $[Cu_6(H_2L^n)_3Cl_6 \cdot 2H_2O] \cdot yH_2O$ ($y = 1$ or 2). The polynuclear copper(II) complexes (figure 10), on the other hand, can be described best as $[Cu_4(H_2L)_2Cl_4 \cdot 2H_2O] \cdot H_2O$, where two terminal $\{Cu(ONO)Cl \cdot H_2O\}$ units attach to one dimeric unit. Formulations of the neutral polynuclear copper(II) complexes are given in figure 3.

3. Experimental

3.1 *Materials*

Diethyl esters of oxalic, malonic, succinic, glutaric and adipic acids (Aldrich), salicylaldehyde (Prolabo), hydrazine hydrate (99%) (BDH), copper(II) dichloride dihydrate (Fluka) and copper(II) acetate dihydrate (Fluka) were used without further purification. Dicarboxylic acid hydrazides were prepared from the reaction of the dicarboxylic acid diethyl esters with hydrazine hydrate, as described previously [1]. Bis(*N*-salicylidene)dicarboxylic acid hydrazides (figure 1a) ($n = 0$–4) were prepared as described previously [1], from the condensation of salicylaldehyde with dicarboxylic acid dihydrazide in ethanol, and were crystallized from dimethylformamide/water mixture. The purity of the isolated bisacylhydrazones was checked by elemental analysis, EI mass spectrometry and ^{1}H NMR spectroscopy.

3.2 *Preparation of the neutral dicopper(II) complexes $[Cu_2(L^n) \cdot xH_2O] \cdot yH_2O$*

To a hot suspension of bis(*N*-salicylidene)dicarboxylic acid hydrazide H_4L ($n = 1$, 2, 3 or 4) (0.01 mol) in methanol (40 ml), a hot solution of copper(II) acetate dihydrate (0.022 mol) in methanol (60 ml) was added dropwise with constant stirring. The reaction mixture was then boiled under reflux with constant stirring for 3 h. The neutral dicopper complex formed was filtered while hot, washed successively with boiling methanol and diethylether and then dried in air.

3.3 *Preparation of chloro dicopper(II) complexes $[Cu_2(H_2L^n)Cl \cdot xH_2O] \cdot yH_2O$ ($n = 1$–4)*

A hot solution of copper(II) dichloride dihydrate (0.022 mol) in methanol (30 ml) was added to a stirred suspension of H_4L ($n = 1$, 2, 3 or 4) (0.1 mol) in methanol (40 ml). The resulting reaction mixture was boiled under reflux with constant stirring for 2 h, then filtered while hot. The isolated chloro dicopper complex was usually contaminated with yellow organic side product, which can be extracted by hot benzene. The pure dicopper complex was filtered, washed successively with methanol and diethylether and then dried in air. The benzene extract was concentrated by evaporation. The salicylaldehydeazine that separated out on cooling was filtered and dried in vacuum (mp = 254°C).

3.4 *Physical measurements*

Infrared spectra were recorded on a Perkin Elmer 1430 Data system and/or a Perkin Elmer (FT-IR) Paragon 1000 PC spectrophotometer. Calibrations of frequency were made with polystyrene film. Solid samples were examined as KBr disks. Ultraviolet and visible absorption spectra were recorded on double-beam ratio recording Lambda 4B Perkin Elmer and/or Cary 17 spectrophotometers. Thermogravimetric analyses were performed using a Shimadzu TGA-50H instrument.

Magnetic susceptibilities of powdered dried samples were recorded on a Faraday-type magnetometer using a sensitive, computer-controlled D-200 Cahn RG microbalance in the temperature range 4.2–298 K. The magnetic field applied was 1.5 T. Details of the apparatus have been described elsewhere [41,42]. Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal's constants [31].

Acknowledgments

We thank BMBF/Forschungszentrum, Juelich, OA-IB/Wo WTZ, for supporting this bilateral project.

References

[1] M.F. Iskander, L. El Sayed, A.F.M. Hefny, S.E. Zayan, *J. Inorg. Nucl. Chem.* **38**, 2209 (1976).
[2] K.K. Narang, R.A. Lal, *Trans. Met. Chem.* **1**, 260 (1976).
[3] K.K. Narang, R.A. Lal, *Trans. Met. Chem.* **3**, 272 (1978).
[4] R. Chandra, R.N. Kapoor, *Acta Chim. Hung.* **112**, 11 (1983).
[5] R.A. Lal, K.N. Srivastava, S. Das, *Synth. React. Inorg. Met.-Org. Chem.* **18**, 837 (1988).
[6] M.T. Toshev, V.G. Yusupov, Z.T. Karimov, Kh.B. Dustov, B.B. Umarov, N.A. Parpiev, G.G. Aleksandrov, *Koord. Khim.* **16**, 1092 (1990).
[7] V.F. Shulgin, E.A. Sarnit, G.M. Larin, *Russ. J. Coord. Chem.* **24**, 207 (1998).
[8] J.D. Ranford, J.J. Vittal, Y.M. Wang, *Inorg. Chem.* **37**, 1226 (1998).
[9] M. Mashima, *Bull. Chem. Soc. Jpn* **35**, 202, 210 and 1882 (1962).
[10] L. El Sayed, M.F. Iskander, *J. Inorg. Nucl. Chem.* **33**, 435 (1971).
[11] J.T. Edward, M. Gauthier, F.L. Chulb, P. Ponka, *J. Chem. Eng. Data* **33**, 539 (1988).
[12] V. Casellato, P.A. Vigato, M. Vidali, *Coord. Chem. Rev.* **23**, 31 (1977).
[13] M. Melnik, *Coord. Chem. Rev.* **42**, 259 (1982).
[14] M. Kato, Y. Muto, *Coord. Chem. Rev.* **92**, 45 (1988).
[15] A.A. Aruffo, T.B. Murphy, D.K. Johnson, N.J. Rose, V. Shomaker, *Acta Cryst.* **C40**, 1164 (1984).
[16] W. Haase, K. Griesar, M.F. Iskander, Y. Galyametdinov, *Mot. Mat.* **3**, 115 (1993).
[17] E.W. Ainscough, A.M. Brodie, A.J. Dobbs, J.D. Ranford, *Inorg. Chim. Acta* **267**, 27 (1998).
[18] S.C. Chan, L.L. Koh, P.-H. Leung, J.D. Ranford, K.Y. Sim, *Inorg. Chim. Acta* **236**, 101 (1995).
[19] L.L. Koh, O.L. Kon, K.W. Loh, Y.C. Long, J.D. Ranford, A.L.C. Tan, Y. Tjan, *J. Inorg. Biochem.* **72**, 155 (1998).
[20] M.D. Cohen, S. Flavian, *J. Chem. Soc. B* 317, 321, 329 and 334 (1967).
[21] C.M. Metzler, A. Cahill, D.E. Metzler, *J. Am. Chem. Soc.* **102**, 6075 (1980).
[22] J.W. Lewis, C. Sandorfy, *Can. J. Chem.* **60**, 1727 (1982).
[23] D. Gegiou, E. Lambi, E. Hadjoudis, *J. Phys. Chem.* **100**, 17762 (1996).
[24] T. Kawasaki, T. Kamata, H. Ushjima, M. Kanakuba, S. Murata, F. Mizukami, Y. Fujii, Y. Usui, *J. Chem. Soc.*, *Perkin Trans. 2* 193 (1999).
[25] T.N. Sorrell, D.L. Jameson, C.J. O'Conner, *Inorg. Chem.* **23**, 190 (1984).
[26] T.N. Sorrell, C.J. O'Connor, O.P. Anderson, J.H. Reibenspies, *J. Am. Chem. Soc.* **107**, 4199 (1985).
[27] K.J. Oberhausen, J.F. Richardson, R.M. Bachanan, J.K. McCusker, D.N. Hendrickson, J. Mare Latour, *Inorg. Chem.* **30**, 1357 (1991).
[28] S. Teipel, K Griesa, W. Haase, B. Kerbs, *Inorg. Chem.* **33**, 456 (1994).
[29] B.J. Hathaway, In *Comprehensive Coordination Chemistry*, pp. 594–774, Vol. 5, G.W. Wilkinson, R.D. Gillard, J.A. McLeverty (Eds), Pergamon Press, Oxford, New York (1987).
[30] J.M. Dance, M.T. Do, P. Gambardella, R.H. De A. Santos, E. Medina, F.G. Mantique, M.S. Palacios, *Inorg. Chim. Acta* **162**, 239 (1989).
[31] O. Khan, *Molecular Magnetism*, VCH, New York (1993).

[32] K.T. McGregor, J.A. Barnes, W.E. Hatfield, *J. Am. Chem. Soc.* **95**, 7993 (1973).
[33] S. Sikrav, I. Brouche-Waksman, O. Kahn, *Inorg. Chem.* **23**, 490 (1984).
[34] M.S. Palacios, J.M. Dance, *Polyhedron* **7**, 543 (1988).
[35] V.A. Kogan, V.V. Lukov, *Russ. J. Coord. Chem.* **23**, (1997).
[36] S.I. Levchenkov, I.N. Shcherbakov, V.V. Lukov, V.A. Kogan, *Russ. J. Coord. Chem.* **23**, 293 (1997).
[37] S.I. Levchenkov, V.V. Lukov, V.A. Kogan, *Russ. J. Coord. Chem.* **23**, 346 (1997).
[38] S.I. Levchenkov, V.V. Lukov, I.N. Shcherbakov, V.A. Kogan, *Russ. J. Coord. Chem.* **24**, 322 (1998).
[39] V.V. Lukov, S.I. Levchenkov, V.A. Kogan, *Russ. J. Coord. Chem.* **24**, 887 (1998).
[40] M.F. Iskander, T.E. Khalil, R. Werner, W. Haase, I. Svoboda, H. Fuess, *Polyhedron* **19**, 949 (2000).
[41] L. Merz, W. Haase, *J. Chem. Soc.*, *Dalton Trans.* 875 (1980).
[42] S. Gerhring, P. Fleichhauer, H. Haase, *Inorg. Chem.* **23**, 54 (1993).