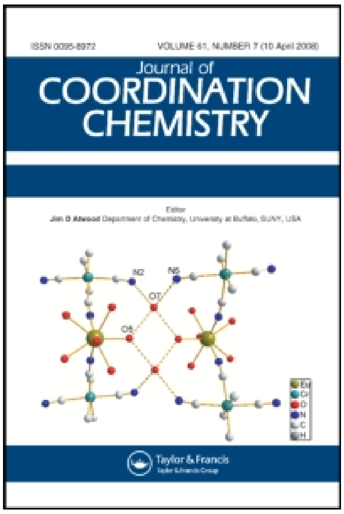

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and magnetochemical studies of some copper(II) complexes derived from 5,5'-methylene bis(*N*-salicylideneacylhydrazines)

Adel W. Nashed[a]; Tamer A. ElBokl[a]; Tarek E. Khalil[b]; Wolfgang Haase[c]; Magdi F. Iskander[b]
[a] Institute of Graduate Studies and Research, Material Science department, Shatby 21526, Alexandria, Egypt [b] Chemistry Department, Faculty of Science, Alexandria University, Ibrahimia, Alexandria 21321, Egypt [c] Institut fur Physikalische Chemie, AG Kondensierte Materie, Fachbereich Chemie, Technische Universitat Darmstadt, Petersenstrasse 20, D-64287 Darmstadt, Germany

To cite this Article Nashed, Adel W. , ElBokl, Tamer A. , Khalil, Tarek E. , Haase, Wolfgang and Iskander, Magdi F.(2005) 'Synthesis, characterization and magnetochemical studies of some copper(II) complexes derived from 5,5'-methylene bis(*N*-salicylideneacylhydrazines)', Journal of Coordination Chemistry, 58: 2, 153 — 163

To link to this Article: DOI: 10.1080/00958970412331295219

URL: http://dx.doi.org/10.1080/00958970412331295219

Journal of Coordination Chemistry
Vol. 58, No. 2, 20 January 2005, 153–163

Taylor & Francis
Taylor & Francis Group

Synthesis, characterization and magnetochemical studies of some copper(II) complexes derived from 5,5′-methylene bis(*N*-salicylideneacylhydrazines)

ADEL W. NASHED†, TAMER A. ELBOKL†, TAREK E. KHALIL‡,
WOLFGANG HAASE§ and MAGDI F. ISKANDER‡*

†Institute of Graduate Studies and Research, Material Science department,
163 horreya Avenue, Shatby 21526, P.O. Box 832, Alexandria, Egypt
‡Chemistry Department, Faculty of Science, Alexandria University,
P.O. 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 7 January 2004; revised 24 May 2004; in final form 28 July 2004)

5,5′-methylene bis(*N*-salicylideneacetylhydrazine) (H_4LMe) and 5,5′-methylene bis(*N*-salicylidenebenzoylhydrazine) (H_4LPh) were prepared and characterized by elemental analysis, IR, Uv-Vis, ^{1}Hnmr and EI mass spectra. These acylhydrazones were found to act as dinucleating bis(tridentate) ligands and a number of copper(II) complexes with formulas: i) $[\{Cu_2(LMe)H_2O\}_x]$ and $[\{Cu_2(LPh)0.5H_2O\}_x]1.5H_2O$, ii) $[\{Cu_2(H_2LMe)Cl_2\}_x]$ and $[\{Cu_2(H_2LPh)Cl_2\}_x]$ iii) $[\{Cu_2(H_2LMe)\}_x]x(NO_3)_2$ and $[\{Cu_2(H_2LPh)\}_x]x(NO_3)_2$ were prepared and characterized. Magnetic susceptibility measurements at different temperatures (4.5–300 K) revealed that both neutral $[\{Cu_2\ (LMe)H_2O\}_x]$ and $[\{Cu_2(LPh)0.5H_2O\}_x]x1.5H_2O$ ($-2J = 197–200\,cm^{-1}$) and nitrate $[\{Cu_2(H_2LMe)\}_x]x(NO_3)_2$ and $[\{Cu_2(H_2LPh)\}_x]x(NO_3)_2$ ($-2J = 199–203\,cm^{-1}$) complexes show strong antiferromagnetic spin–spin coupling, implying association *via* phenoxy oxygens and coplanar Cu_2O_2 bridges with the Cu(II) coordination plane. The chloro complexes, on the other hand, show weak antiferromagnetic exchange coupling ($-2J = 6–9\,cm^{-1}$) implying association but with perpendicular Cu_2O_2 bridges.

Keywords: 5,5′-Methylene bis(*N*-salicylideneacylhydrazines); Copper(II) complexes; Magnetochemical studies

1. Introduction

In their copper(II) complexes, *N*-salicylideneacylhydrazines act as neutral, mono- and dinegative ONO′ tridentate ligands [1–10]. Copper(II) ion coordinated to this type of ONO′ acylhydrazone ligand can achieve coordination number four or five by

---

*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: 10.1080/00958970412331295219

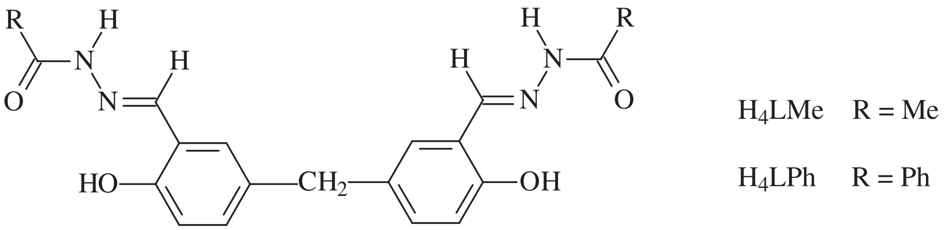

Figure 1. Molecular formula of 5,5′- methylene–bis(N-salicylideneacylhydrazine).

dimerization *via* μ-phenoxy oxygens or by coordination to monodentate ligands available in the reaction medium [1–7]. The dimeric nature of many copper(II) complexes derived from *N*-salicylideneacylhydrazines have been confirmed by X-ray molecular structures [2–6] as well as variable temperature magnetic susceptibility measurements [1,2,6,8–10]. On the other hand, dinucleating ligands such as bis(*N*-salicylidene) dicarboxylic acid hydrazides which contain two *N*-salicylidene acylhydrazine residues separated by an aliphatic spacer, were found to react with copper(II) salts giving either dicopper(II) complexes or copper(II) coordination polymers through association via μ-phenoxy oxygens [11–13]. Accordingly, 5,5′-methylene bis(*N*-salicylideneacylhydrazine), figure 1 (structure 1, R = Me and Ph), which contains two *N*-salicylideneacylhydrazine residues capable of coordinating with copper(II) ions, seems to be a good candidate for new copper(II) coordination polymers.

In this paper we wish to report the synthesis and characterization of some new copper(II) coordination polymers based on both 5,5′ methylene bis(*N*-salicylidene acetyl- and benzoylhydrazines), hereafter abbreviated as H_4LMe, (figure 1, R = Me) and H_4LPh (figure 1, R = Ph), respectively. The magnetic properties of the prepared coordination polymers will be discussed in relation to the mode of bridging via μ-phenoxy oxygens.

2. Experimental

2.1 *Materials used*

Acetyl- and benzoylhydrazines were prepared by the hydrazinolysis of the corresponding methyl esters as previously described [14]. 5,5′-methylene bis(salicylaldehyde) was prepared by reaction of salicylaldehyde with trioxan in glacial acetic acid as previously described by Marvel and Tarkoy [15]. Solvents and other reagents were obtained from commercial sources (Aldrich) and used as received.

2.2 *Condensation of 5,5′-methylene bis salicylaldehyde with acyl hydrazines*

A solution of 5,5′-methylene bis(salicylaldehyde) (0.01 mole) in THF ($30\,cm^3$) was added dropwise to a solution of acetyl- or benzoylhydrazine (0.02 mole) in methanol ($50\,cm^3$). The reaction mixture was acidified with glacial acetic acid ($0.5\,cm^3$) then refluxed with constant stirring for two hours. The pale yellow precipitate of 5,5′-methylene bis(*N*-salicylideneacylhydrazine), was filtered, washed several times with hot methanol then dried in vacuo.

2.2.1 H_4LMe (1, R = Me). Yield, 65%; m.p. (decomposed) 325–330°C; Anal. Calcd. For $C_{19}H_{20}N_4O_4$ (%): C, 61.95; H, 5.47; N, 15.21. Found: C, 61.72; H, 5.48; N, 14.95. UV-Vis. (DMF solution, λ_{max}/ nm)(logε): 290 sh; 335 (4.05) . IR (KBr, cm^{-1}): 3207 ν(N-H); 1665 ν(C=O) (amide I); 1625 ν(C=N); 1552 δ(N-H) (amide II); 1272 [δ(N-H) + ν(C-N)] (amide III). ^1H NMR (DMSO-d_6, ppm (number of protons): 11.60 (2H, s, OH); 8.93 (2H, s, CONH); 8.29 and 8.21 (2H, d, HC=N); 7.45 (1H, d, aromatic); 7.35 (1H,d,aromatic); 7.10 (2H, m, aromatic); 6.85 (2H, m, aromatic); 4.00 and 3.79 (2H, CH_2); 2.14 and 1.95 (3H, CO-CH_3); 1.83 and 1.24 (3H, CO–CH_3). EI mass spectrum, m/z (RA %): 368 [M^+] (85.4), 351(2.0), 326 (9.7), 310 (100), 268 (18.7), 251 (33.5), 238 (11.6), 223 (3.2), 210 (5.2), 182 (6.5), 147 (9.0), 132 (14.8), 120 (5.8), 91 (9.3).

2.2.2 H_4LPh (1, R = Ph). Yield, 73%; m.p. (decomposed) 332–338°C; Anal. Calcd. For $C_{29}H_{24}N_4O_4$ (%); C, 70.72; H, 4.91; N, 11.37. Found: C, 70.56; H, 4.87; N, 11.08. Uv-Vis. (saturated DMF solution, λ_{max}/ nm, (log ε): 290, 335 (4.00), 345(sh). IR (KBr/cm^{-1}): 3224 ν(N-H); 1646 ν(C=O)(amide I); 1625 ν(C=N); 1543 δ(N-H) (amide II); 1284 [δ(N-H) + ν(C-N)] (amide III). ^1H NMR (DMSO-d_6), TMS, ppm (number of protons): 12.08(2H,s, -OH); 11.22 (2H, s, CONH); 8.63 (2H, s, CH=N); 7.92 (4H,d, aromatic); 7.52 (10H, m, aromatic); 6.86 (2H, d, aromatic); 3.87 (2H, s, -CH_2-). EI mass spectrum m/z (RA %): 492 (1.2), 372 (22.9), 250 (4.8), 136(4.8), 122 (12.4), 105 (100), 77 (59.1).

2.3 *Preparation of [$Cu_2(LMe)H_2O$ and [$Cu_2(LPh)0.5H_2O]1.5H_2O$*

A hot solution of (H_4LMe) or (H_4LPh) (1.0 mmole) in THF (30 cm^3) was added dropwise to a stirred solution of copper(II) acetate monohydrate (2.2 mmole) in methanol (50 cm^3). This mixture was treated with sodium acetate (2.5 mmole) in methanol (25 cm^3) then refluxed with constant stirring for two hours. The isolated copper(II) complex was filtered, washed with boiling methanol and dried in vacuo.

2.3.1 [$Cu_2(LMe)H_2O$]. Yield, 68%. Anal. Calcd. For $C_{19}H_{18}N_4O_5Cu_2$ (%): C, 44.79; H, 3.56; N, 11.00; Cu, 24.95. Found: C, 44.50; H, 3.60; N, 10.72; Cu, 24.68. Uv-Vis: (saturated DMSO solution, λ_{max}/nm): 290 sh, 330; Nujol mull 386, 620. IR: (KBr/cm^{-1}): 1620 ν(C=N-N=C); 1310 amide III [ν(C-N)]; 992 ν(N-N).

2.3.2 [$Cu_2(LPh)0.5H_2O]1.5H_2O$. Yield, 73%. Anal. Calcd. for $C_{29}H_{24}N_4O_6Cu_2$ (%): C, 53.45; H, 3.71; N, 8.60; Cu, 19.50. Found: C, 53.65; H, 3.65; N, 8.71, Cu, 19.50. Uv-Vis: (saturated DMSO solution, λ_{max}/nm): 281 sh, 330; Nujol mull, 404, 608 sh. IR (KBr/cm^{-1}): 1616, [ν(C=N-N=C)]; 1320, amide III [ν(C-N)]; 995, ν(N-N).

2.4 *Preparation of [$Cu_2(H_2LMe)Cl_2$] and [$Cu_2(H_2LPh)Cl_2$]*

A solution of (H_4LMe) or (H_4LPh) (1.0 mmole) in minimum of THF was added dropwise with constant stirring to a solution of copper(II) chloride dihydrate (2.2 mole) in methanol (20 ml). The reaction mixture was refluxed with constant stirring for two hours. The insoluble copper(II) complex was filtered while hot, washed with methanol several times and then dried in vacuo.

2.4.1 [$Cu_2(H_2LMe)$ Cl_2]. Yield, 60%. Anal. Calcd. For $C_{19}H_{18}N_4O_4Cu_2Cl_2$ (%): C, 40.44; H, 3.21; N, 9.93; Cu, 22.52. Found: C, 40.72; H, 3.30; N; 9.71; Cu, 22.60. Uv-Vis. (saturated DMSO solution, λ_{max}/ nm): 290 sh, 330; Nujol mull 385, 610. IR spectum (KBr/cm^{-1}): 3188 ν(N-H); 1620 ν(C=O) (amide I); 1580 ν(C=N); 1520 δ(N-H) (amide II); 1315 ν(C-N) (amide III); 990 ν(N-N).

2.4.2 [$Cu_2(H_2LPh)$ Cl_2]. Yield, 68 %. Anal. Calcd. For $C_{29}H_{22}N_4O_4Cu_2Cl_2$ (%): C, 50.59; H, 3.22; N, 8.14; Cu, 18.46. Found: C, 50.65; H, 3.47; N, 8.17, Cu, 18.28. Uv-Vis. (saturated DMSO solution, λ_{max}/nm): 330; Nujol mull 385, 616. IR spectum (KBr/cm^{-1}): 3200 ν(N-H); 1620 ν(C=O) (amide I); 1570 ν(C=N); 1520 δ(N-H) (amide II); 1315 ν(C-N) (amide III); 990 ν(N-N).

2.5 *Preparation of [$Cu_2(H_2LMe)$]$(NO_3)_2$ and [$Cu_2(H_2LPh)$]$(NO_3)_2$*

A suspension of (H_4LMe) or (H_4LPh) (1.0 mmole) in methanol (50 ml) was heated with a solution of copper(II) nitrate hexahydrate (2.0 mmole) in methanol (30 ml). The resulting green mixture was refluxed with constant stirring for two hours. The formed copper(II) complex was filtered, washed several times with hot methanol, and then dried in vacuo.

2.5.1 [$Cu_2(H_2LMe)$] $(NO_3)_2$. Yield, 58%. Anal. Calcd. For $C_{19}H_{22}N_6O_{10}Cu_2$ (%): C, 36.96; H, 2.94; N, 13.61; Cu, 20.58. Found: C, 36.62; H, 2.64; N; 13.62; Cu, 20.28. Uv-Vis. (saturated DMSO solution, λ_{max}/nm): 290 sh, 330; Nujol mull 385, 630. IR spectum (KBr/cm^{-1}): 3215 ν(N-H); 1620 ν(C=O) (amide I); 1580 ν(C=N); 1535 δ(N-H) (amide II); 1305 ν(C-N) (amide III); 970 ν(N-N).

2.5.2 [$Cu_2(H_2LPh)$] $(NO_3)_2$. Yield, 63%. Anal. Calcd. for $C_{29}H_{22}N_6O_{10}Cu_2$ (%): C, 46.97; H, 2.99; N, 11.33; Cu, 17.14. Found: C, 46.96; H, 3.09; N, 11.16, Cu, 17.20. Uv-Vis. (saturated DMSO solution, λ_{max}/nm): 290 sh, 330; Nujol mull 395, 644 sh. IR spectum (KBr/cm^{-1}): 3220 ν(N-H); 1620 ν(C=O) (amide I); 1570 ν(C=N); 1520 δ(N-H) (amide II); 1320 ν(C-N) (amide III); 990 ν(N-N).

2.6 *Physical measurements*

Elemental (carbon, hydrogen and nitrogen) analyses were performed at the microanalytical lab, at the Institut für Organische Chemie, Technische Universität, Darmstadt, Germany. The copper(II) content was determined by direct titration with EDTA, using pyridine azonaphthol (PAN) as an indicator [16]. Infrared spectra were recorded on a Perkin Elmer 1430 Data system infrared spectrophotometer. ^{1}Hnmr Spectra were recorded on a Brucker WM 300 (300 MHz) instrument. All chemical shifts are reported in parts per million (ppm) relative to an internal standard of tetramethylsilane (TMS). Mass spectra were determined on a Finnigan MAT 212, 70 eV instrument. A UV-Visible Double Beam Ratio Recording, Perkin Elmer model LAMBADA 4B, made spectrophotometric measurements in the visible and ultraviolet regions. Magnetic susceptibility measurements were carried out using a Faraday type magnetometer [17]. The intensity of the applied magnetic field was 1.5 Tesla for antiferromagnetic compounds and 1.2 Tesla for magnetic susceptibility measurements at room temperature. The salt $Hg[Co(SCN)_4]$ was used as a calibrating standard. Diamagnetic corrections were applied using Pascal's constant [18]. Thermogravimetric analyses (TGA) were performed on a Schimadzu TGA 50 H instrument under nitrogen in the temperature range 0–1000°C.

2.7 Results and discussion

2.7.1 *Synthesis and thermal stability*

Condensation of 5,5′-methylene bis(salicylaldehyde) with acetylhydrazine or benzoylhydrazine in acidified methanol using a 1 : 2 molar ratio, gave the corresponding 5,5′-methylene bis(*N*-salicylideneacylhydrazine), figure 1. The purity of the prepared acylhydrazones was checked by elemental analysis, ^{1}H NMR spectra as well as electron impact (EI) and/or field desorption (FD) mass spectra. The isolated acylhydrazones were soluble in DMF and DMSO, insoluble in alcohols, tetrahydrofuran or dioxane, and soluble in aq. KOH. Both H_4LMe and H_4LPh are thermally stable; beginning decomposition at *ca* 330 °C.

The reaction of both H_4LMe and H_4LPh with copper(II) acetate, using 1 : 2 molar ratio, afforded the dicopper(II) complexes [Cu_2(LMe) H_2O] and [Cu_2(LPh) 0.5H_2O] 1.5H_2O respectively. Differential thermal analysis (DTA) of [Cu_2(LMe) H_2O] showed an exothermic peak at 187°C corresponding to the dehydration of one water molecule from the inner coordination sphere. This was confirmed by the 3.5% loss in weight observed in thermogravimetric (TG) analysis (calculated 3.53%). After complete dehydration, molecular rearrangement or conformational change may occur. This process was evident from the endothermic peak at 193°C where no weight loss is observed. Decomposition of [Cu_2(LMe)H_2O] started at 310°C and proceeded in three successive steps. DTA of [Cu_2(LPh)0.5H_2O] 1.5H_2O showed a broad endothermic peak at 95°C and a weak exothermic peak at 195°C. The TG curve in this range of temperature revealed a 4.3% weight loss corresponding to the dehydration of *ca.* 1.5 loosely bound water molecules from the outer coordination sphere (calculated 4.1%), followed by *ca* 1.0% weight loss of 1/2 water molecule from the inner coordination sphere (calculated 1.38%).

Reaction of copper(II) chloride with both H_4LMe and H_4LPh, using 2 : 1 molar ratio, gave the expected chloro complexes [Cu_2(H_2LMe)Cl_2] and [Cu_2(H_2LPh)Cl_2]. With copper(II) nitrate, both H_4LMe and H_4LPh gave the corresponding nitrate complexes [Cu_2(H_2LMe)](NO_3)$_2$ and [Cu_2(H_2LPh)](NO_3)$_2$; both choro and nitrate complexes are thermally stable and start decomposition at *ca* 300°C.

2.7.2 *Infrared spectra*

The IR spectra of solid H_4LMe and H_4LPh showed a series of bands at *ca.* 3200–3225, 2900–3050, 1645–1665, 1620–1625, 1570–1580, 1543–1550 cm^{-1}, respectively, due to ν(N-H), ν(C-H), amide I band [ν(C=O)], ν(C=C), ν(C-N), and amide II band [δ(N-H)] of the acylhydrazone (C=N-NH.CO.R) residue. The spectra of both [Cu_2(H_2LMe)Cl_2] and [Cu_2(H_2LPh)Cl_2] showed a series of bands at 3188–3220, 1620, 1560–1580, 1520 cm^{-1}, respectively, due to ν(N-H), ν(C=O), ν(C=N), amide II and amide III bands. Both ν(C=O), amide I and ν(C=N) bands were shifted to lower frequencies relative to the metal free ligands. The presence of both ν(N-H), ν(C=O), amide I and amide II bands and the absence of any bands which can be related to uncoordinated ν(C=O), suggest that both acylhydrazone residues in these complexes are coordinated in the ketoamide form. In these complexes, each acylhydrazone unit is coordinated to the copper(II) via the deprotonated phenoxy oxygen, azomethine nitrogen and ketoamine oxygen. The spectra of $[Cu_2(H_2LMe)](NO_3)_2$ and $[Cu_2(H_2LPh)]$ $(NO_3)_2$ are more or less similar to those recorded for the corresponding chloro complexes, suggesting similar mode of chelation. The nitrate ions in these complexes act as a counter ion with the ν(N-O) at 1380 cm^{-1}.

The IR spectra of the neutral complexes $[Cu_2(LMe)H_2O]$ and $[Cu_2(LPh)0.5H_2O]$ $1.5H_2O$, lack absorptions due to both ν(N-H), amide I [ν(C=O)] and amide II [δ(N-H)] bands, indicating that the two acylhydrazones reacted in the deprotonated enolimine form. The spectra also display a very intense band at *ca.* 1615 cm^{-1} which can be attributed to ν(C=N–N=C). Furthermore, the amide III bands were shifted to higher frequencies as compared to the corresponding metal free ligands probably due to an increase in the double bond character of C–N due to electron delocalization in the enolimine tautomer of the coordinated ligand.

2.7.3 *Electronic absorption spectra*

The ultraviolet solution absorption spectra of both H_4LMe and H_4LPh (2R = Me and Ph) in DMF are similar and showed two absorption bands at *ca* 290 and 335 nm. Similar to the spectra of other *N*-salicylidene Schiff bases [19], the observed two absorptions at *ca* 290 and 335 nm originated from the π-π* transitions of the intramolecular hydrogen bonded *N*-salicylidene residues.

Due to their limited solubility, the solution absorption spectra of the prepared copper(II) complexes were recorded as saturated DMSO or DMF solutions. The spectra show three absorptions at *ca.* 285, 335 and 390–400 nm of the deprotonated *N*-salicylideneacylhydrazine residue. Metal to ligand charge transfer in the 390–400 nm absorption cannot be ruled out. The d–d transitions of copper(II) cannot be detected in such dilute solutions. However, the Nujol mull electronic absorption spectra, show a broad absorption at *ca.* 620–650 nm due to different d–d transitions of copper(II) in square planar environment [20].

2.7.4 *Magnetic susceptibility measurements*

At room temperature, both $[Cu_2(LMe)H_2O]$ and $[Cu_2$ $(LPh)0.5H_2O]1.5H_2O$ show subnormal magnetic moments of *ca.* 1.52 and 1.41 μ_β, respectively, indicating strong Cu(II)–Cu(II) superexchange interaction. The magnetic susceptibilities of both complexes were measured at different temperatures (4.4–300 K) and the variation of both μ_{eff} and χ_M as a function of temperature are depicted, respectively, in figures 2 and 3. The variable temperature magnetic data were fitted to the revised Bleaney–Bowers equation, equation (1), [21], using the isotropic (Heisenberg) exchange Hamiltonian ($H = -2JS_1S_2$) for two interacting $S = 1/2$ centers,

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

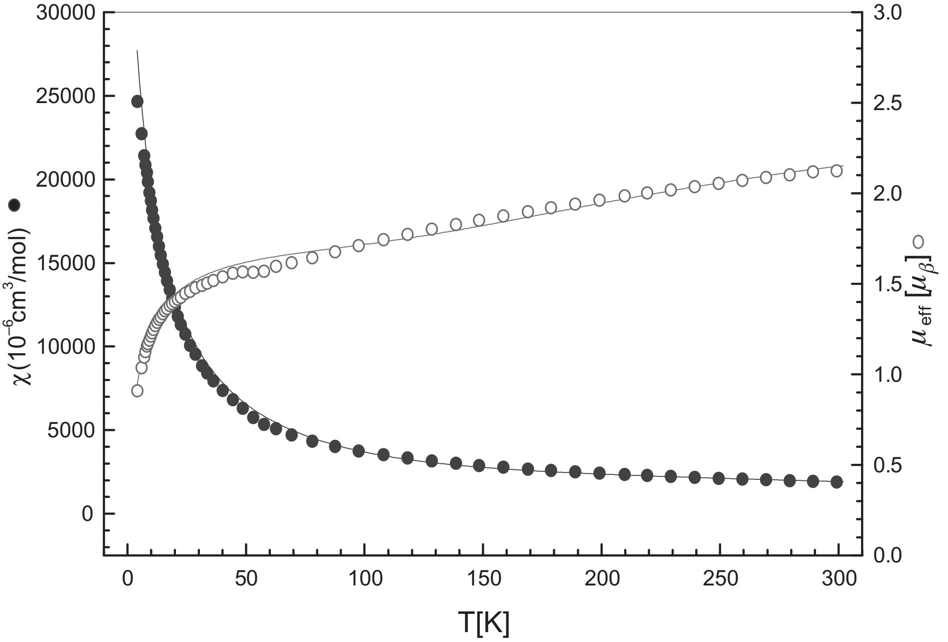

Figure 2. Magnetic susceptibilities $\chi(\bullet)$ and magnetic moments ($^\circ$) vs. temp. for $[Cu_2(LMe)H_2O]$. Solid lines represent the least square fit to equation (1) with $J = -198.0\,cm^{-1}$, $g = 2.05$, $\rho = 0.50$.

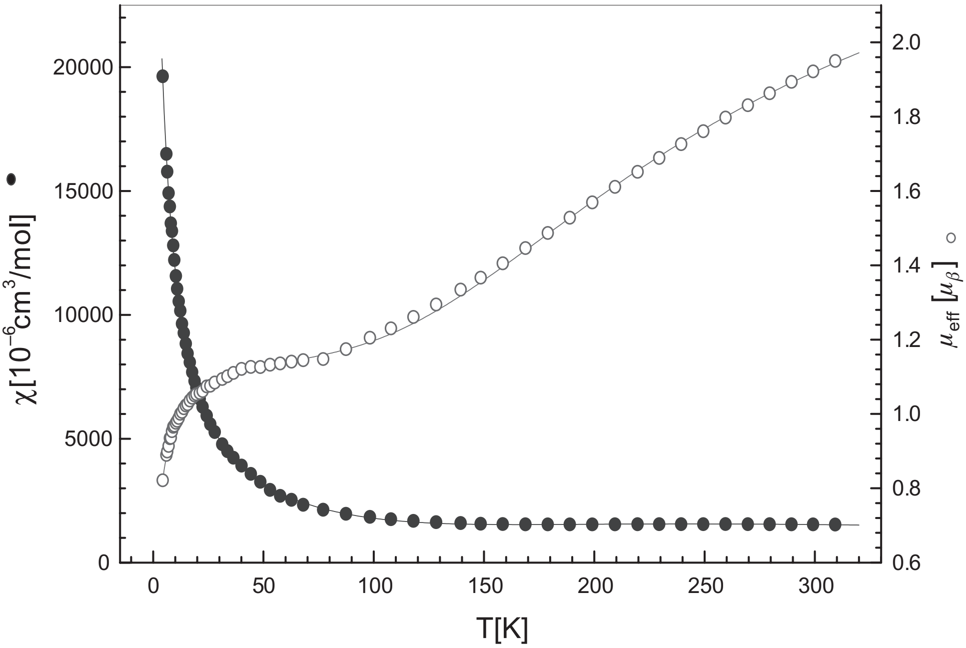

Figure 3. Magnetic susceptibilities $\chi(\bullet)$ and magnetic moments (E) vs. temp. for $[Cu_2(LPh)H_2O]H_2O$. Solid lines represent the least square fit to equation (1) with $J = -175.0\,cm^{-1}$, $g = 2.07$, $\rho = 0.05$.

Table 1. The best fit magnetic parameters for copper(II) complexes derived from 5,5′-methylene bis(*N*-salicylideneacylhydrazines).

Complex	μ_{eff} (296 K)	g	θ	$-2J(cm^{-1})$	ρ
$[Cu_2(LMe)H_2O]$	1.52	2.05	−12.3	396.0	0.50
$[Cu_2(LPh)H_2O]H_2O$	1.41	2.07	−3.3	350.0	0.05
$[Cu_2(H_2LMe)Cl_2]$	1.82	2.05	−0.2	6.1	0.00
$[Cu_2(H_2LPh)Cl_2]$	1.82	2.05	−0.3	8.8	0.00
$[Cu_2(H_2LMe)](NO_3)_2$	1.34	2.07	−3.0	426.0	0.20
$[Cu_2(H_2LPh)](NO_3)_2$	1.36	2.06	−3.3	404.0	0.20

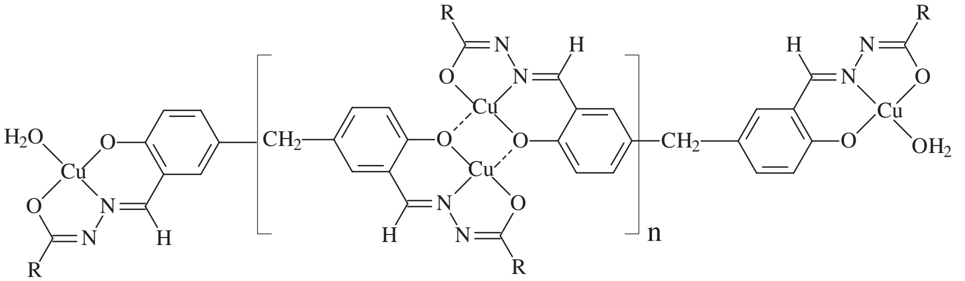

Figure 4. Proposed structure for polymeric neutral complexes $[Cu_2 (LMe) H_2O]$ (R = Me) and $[Cu_2 (LPh) H_2O]H_2O$ (R = Ph).

where Nα is the temperature independent paramagnetism ($60 \times 10^{-6} cm^3 mol^{-1}$ per Cu(II)), ρ is the mole fraction of uncoupled copper(II) centers, and θ is a corrective term for interdimer interactions [22]. The (−2J) values calculated for both $[Cu_2(LMe)H_2O]$ and $[Cu_2(LPh)\ 0.5H_2O]\ 1.5H_2O$, table 1, suggest strong antiferromagnetic exchange coupling, probably due to association via the phenoxy oxygens similar to that reported for other dinuclear copper(II) complexes derived from *N*-salicylideneacylhydrazine [1–12]. Association via μ-phenoxy oxygens gives rise to polymeric (or oligomeric) structures $[\{Cu_2(LMe)H_2O\}_x]$ and $[\{Cu_2(LPh)\ 0.5H_2O\}_x]xH_2O$ as shown in figure 4, where the Cu_2O_2 moiety is coplanar with the planes of coordinated ONO′ tridentate acylhydrazone ligands, permitting efficient overlap between the magnetic orbitals ($d_x^2 - d_y^2$) of copper(II) and the sp^2 hydridized oribits of μ-phenoxy oxygens. Such coplanar association can account for the observed antiferromagnetic spin–spin exchange coupling in these neutral complexes. The extent of association in these copper(II) complexes can be evaluated from the best fit value of the mole fraction of the uncoupled paramagnetic copper(II) centers (ρ) estimated from the Bleaney–Bowers equation (equation (1)). Taking the number of uncoupled copper(II) centers (terminal copper(II) centers) as two, the number of coupled copper(II) centers (N_c) can be estimated from equation (2) [11]:

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

For $[Cu_2(LMe)\ H_2O]$, (ρ) was found to be 0.50 indicating a ratio 2 : 2 between the uncoupled and coupled copper(II) centers. This means that $[\{Cu_2(LMe)H_2O\}_x]$ exists as a tetranuclear complex where two copper(II) are bridged via phenoxy oxygens, while the other two paramagnetic terminal copper(II) remain unassociated as shown

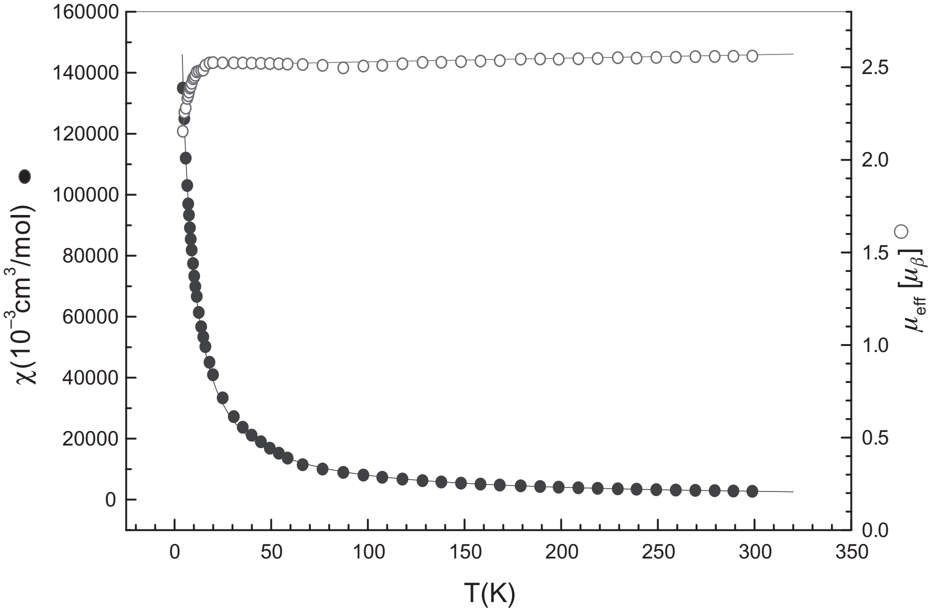

Figure 5. Magnetic susceptibilities χ(•) and magnetic moments (°) vs. temp. for [$Cu_2(H_2LMe)Cl_2$] . Solid lines represent the least square fit to equation (1) with $J = -3.05\,cm^{-1}$, $g = 2.05$, $\rho = 0.00$.

in figure 4 (R = Me, $n = 1$) where $n = (x - 2)$ number of dimeric units. The fourth coordination site around each terminal uncoupled copper(II) is occupied by a water molecule. For [$\{Cu_2(LPh) \cong 0.5H_2O\}_x$] $\cong x1.5H_2O$, the estimated ρ, table 1, was found to be 0.05 indicating higher degree of association compared to the corresponding [$\{Cu_2(LMe)H_2O\}_x$] complex. The value of $\rho = 0.05$ suggests that about 38 copper(II) centers are associated forming an oligomeric chain of 19 dimeric units (figure 4, R = Ph and $n = 19$) in addition to two terminal paramagnetic copper(II) centers. Here again, the fourth coordination site of each terminal copper(II) atom is occupied by a water molecule. It is of interest to note that the number of dimeric units (n) is the statistical average of the number of dimers in different polynuclear chains randomly distributed in the bulk of the complex.

The room temperature magnetic moments of [$Cu_2(H_2LMe)Cl_2$] ($\mu_{eff} = 1.82\,\mu_\beta$) and [$Cu_2(H_2LPh)Cl_2$] ($\mu_{eff} = 1.82\,\mu_\beta$) are within the normal range reported for paramagnetic copper(II) complexes [20]. However, variable temperature (4–300 K) magnetic susceptibility measurements for these chloro complexes suggest weak antiferromagnetic coupling between the copper(II) centers. The variation of both χ_M and μ_{eff} vs. T observed for [$Cu_2(H_2LMe)Cl_2$] is shown in figure 5. Similar behavior was also observed for [$Cu_2(H_2LPh)Cl_2$]. The best fit magnetic parameters (J, g, θ and ρ), obtained by fitting the magnetic data recorded for the chloro complexes to equation (1) are listed in table 1. The weak antiferromagnetic coupling between copper(II) centers observed for these chloro complexes ($-2J = 6.0\text{–}9.0\,cm^{-1}$) suggesting molecular association. Similar to other *N*-salicylideneacylhydrazine copper(II) complexes [2–6, 11,12,23], the coordinated acylhydrazone residues in both [$Cu_2(H_2LMe)Cl_2$] and [$Cu_2(H_2LPh)Cl_2$] can be associated via either coplanar [2–6] or perpendicular Cu_2O_2 bridges [11,12,23] as shown in figure 6 (structure a or b). In coplanar bridging mode,

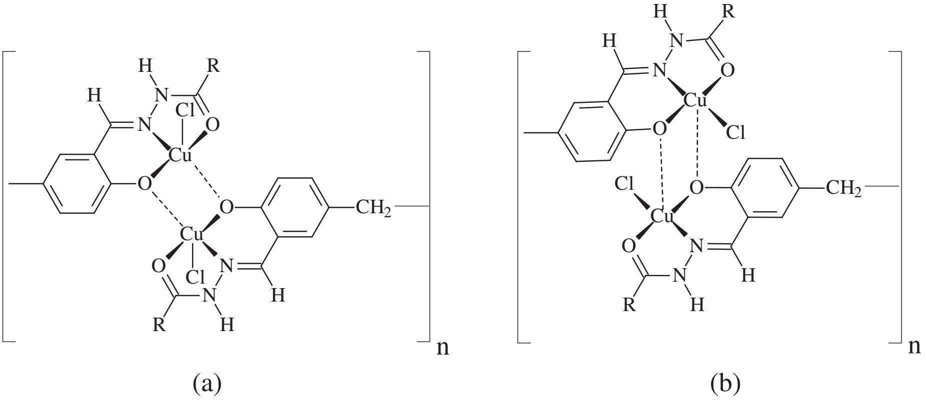

Figure 6. Coplanar (7a) and perpendicular (7b) bridging modes proposed for chloro copper(II) complexes.

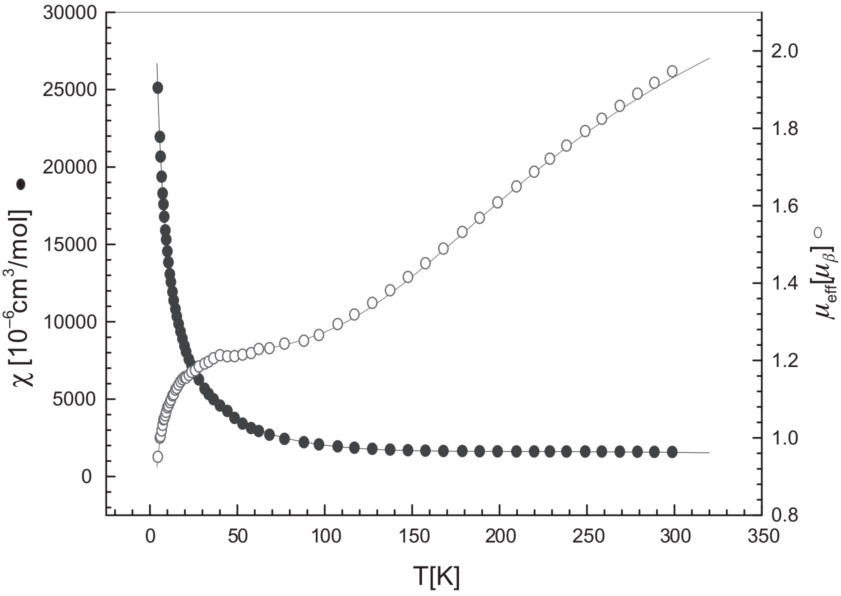

Figure 7. Magnetic susceptibilities χ(●) and magnetic moments (°) vs. temp. for $[Cu_2(H_2LPh)](NO_3)_2$. Solid lines represent the least square fit to equation (1) with $J = -202\,cm^{-1}$, $g = 2.05$, $\rho = 0.20$.

the μ-phenoxy oxygen is situated in the fourth coordination site of the basal plane and strong antiferromagnetic spin–spin coupling is expected. This bridging mode cannot account for the low $-2J$ values recorded for these chloro complexes. Perpendicular bridging mode, on the other hand, where the μ-phenoxy oxygen occupies the fifth apical position will give rise to very weak antiferromagnetic interaction. Accordingly, a polymeric structure with perpendicular bridging mode, as shown in figure 6 (structure a), can be proposed for these chloro complexes.

The subnormal magnetic moments of both $[Cu_2(H_2LMe)](NO_3)_2]$ ($\mu_{eff} = 1.34\,\mu_\beta$) and $[Cu_2(H_2LPh)](NO_3)_2]$ ($\mu_{eff} = 1.36\,\mu_\beta$) as well as the variation of χ_M with temperature, figure 7, suggest strong antiferromagnetic exchange coupling between copper(II) ions similar to that recorded for the corresponding neutral complexes. Fitting the χ_M-T data recorded for $[Cu_2(H_2LMe)](NO_3)_2$ and $[Cu_2\,(H_2LPh)](NO_3)_2]$ to equation (1) gave an energy separation between ground state singlet and excited state triplet (−2J) of about 426 and 404 cm^{-1} ($\rho = 0.20$), respectively. The calculated −2J values, table 1, are within the range reported for copper(II) complexes with coplanar phenoxy oxygen bridges and polymeric structures $[\{Cu_2(H_2LMe)\}_x]x(NO_3)_2$ and $[\{Cu_2(H_2LPh)\}_x]$ $x(NO_3)_2$ can be proposed, respectively, for acetyl- ($\rho = 0.20$, $n = 4$) and benzoylhydrazone ($\rho = 0.20$, $n = 4$) complexes. The fourth coordination sites of the uncoupled Cu(II) may be occupied by monodentate NO_3 groups.

Acknowledgment

Thanks are due to BMBF/Forschungszentrm, Jüelich, ÖA-IB/Wo WTZ for supporting this bilateral project.

References

[1] M.F. Iskander, T.E. Khalil, R. Werner, W. Haase, I. Sovoboda, H. Fuess, *Polyhedron* **19**, 949 (2000).
[2] N.R. Sangeetha, K. Baradi, R. Gupta, C. K. Pal, V. Manivanan, S. Pal, *Polyhedron* **18**, 1425 (1999).
[3] L.L. Koh, O.L. Kon, K.W. Loh, Y.C. Long, J.D. Ranford, A.L.C. Tan, Y.Y. Tjan, *J. Inorg. Biochem.* **72**, 155 (1998).
[4] E.W. Ainscough, A.M. Brodie, A.J. Dobbs, J.D. Ranford, J.M. Waters, *Inorg. Chim. Acta* **267**, 27 (1998).
[5] A.C. Chan, L.L. Koh, P.-H. Leung, J.D. Ranford, K.Y. Sim, *Inorg. Chim. Acta* **236**, 101 (1995).
[6] W. Haase, K. Griesar, M.F. Iskander, Y. Galyamedinov, *Mol. Mat.* **3**, 115 (1993).
[7] A.A. Aruffo, T.B. Murphy, D.K. Johnson, N.J. Rose, V. Schomaker, *Acta Cryst. C: Cryst. Struct. Commun.* **C40**(7), 1164 (1984).
[8] M.S. Palacios, J.M. Dance, *Polyhedron* **7**(7), 543 (1988).
[9] S.I. Levchenkov, V.V. Lukov, H.N. Shcherbakov, V.A. Kogan, *Russ. J. Coord. Chem.* **24**(3), 322 (1998).
[10] V.V. Lukov, S.I. Levchenkov, V.A. Kogan, *Russ J. Coord. Chem.* **24**(12) 887 (1998).
[11] M.F. Iskander, L. El Sayed, N.M.H. Salem, R. Werner, W. Haase, *J. Coord. Chem.* **58**(2), 125 (2005).
[12] J.D. Ranford, J.J. Vittal, Y.M. Wang, *Inorg. Chem.* **37**, 1226 (1998).
[13] M.F. Iskander, L. El Sayed, A.F.M. Hefny, S.E. Zayan, *J. Inorg. Nucl. Chem.* **38**, 2209 (1976).
[14] M.F. Iskander, S.E. Zayan, M.A. Khalifa, L. El Sayed, *J. Inorg. Nucl. Chem.* **36**, 551 (1974).
[15] C.S. Marvel, N. Tarköy, *J. Amer. Chem. Soc.* **79**, 6000 (1957).
[16] G. Schwartzenbach, *Complexometric Titration*, Methuen Co. London, UK.
[17] L. Merz, W. Haase, *J. Chem. Soc. Dalton Trans.* 875 (1980); S. Gehring, P. Fleischhauer, H. Paulus, W. Haase, *Inorg. Chem.* **32**, 54 (1993).
[18] A. Weiss, H. Witte, *Magnetochemie*, Verlag Chemie, Weinheim (1973).
[19] D. Heinert, A.E. Martell, *J. Amer. Chem. Soc.* **85**, 188 (1963); K.K. Chatterjee, B.E. Douglas, *Spectrochimica Acta* **21**, 1625 (1965); M.D. Cohen, S. Flavian, *J. Chem. Soc. (B)*, 321 (1967).
[20] B.J. Hathaway, In *Comprehensive Coordination Chemistry*, Vol. 5, Copper, pp. 594–884, G. Wilkinson, R.D. Gillard, J.A. McLeverty (Eds), Pergamon Press, New York (1987).
[21] O. Kahn, *Molecular Magnetism*, VCH publishers, New York, (1993).
[22] S. Sikorav, I. Bkouche-Waksman, O. Kahn, *Inorg. Chem.* **23**, 490 (1984).
[23] M.F. Iskander, T.E. Khalil, R. Werner, W. Haase, I. Svoboda, H. Fuess, *Polyhedron* **19**, 1181 (2000).