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Synthesis, characterization and physicochemical properties of copper(II) complexes containing salicylaldehyde semicarbazone

Peng Foo Lee, Chang-Tong Yang *, Daming Fan, Jagadese J. Vittal, John D. Ranford *

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

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Abstract

Copper(II) complexes containing a series of salicylaldehyde semicarbazone ligands have been prepared and characterized by a range of physicochemical techniques. The X-ray structure of $[Cu(HBnz_2)Cl]\cdot H_2O$ (**5**) (where $HBnz_2$ is salicylaldehyde-*N*,*N*-dibenzyl semicarbazone) shows the complex is monomeric and the copper atom is four coordinated in a distorted square planar geometry. The ligand chelates the copper in a tridentate fashion through the imine N, carbonyl O and phenolato O with the fourth position being occupied by coordinated Cl. The compound $[Cu(Ph_2)\cdot H_2O]$ (**4**) (where Ph_2 is salicylaldehyde-*N*,*N*-diphenyl semicarbazone) is also formulated as a monomer whereas all other complexes are assumed to have a side-by-side dimeric arrangement of the metal chelating with the phenolate bridging the Cu(II) centres.

Keywords: Copper(II) complexes; Salicylaldehyde semicarbazone; Crystal structures

1. Introduction

Transition metal complexes with potential biological activity are the focus of extensive investigation. Interestingly, complexation with copper enhances the biological activity of a wide variety of organic ligands [1–4]. Such an example is the copper complex of salicylaldehyde benzoylhydrazone (H_2sb), $[Cu(Hsb)Cl]\cdot H_2O$, which exhibits tumour inhibitory activity [5]. $[Cu(Hsb)Cl]\cdot H_2O$ was first found to be a potent inhibitor of DNA synthesis and cell growth [6,7] in a number of human and rodent cell lines [8]. The cytotoxicity of this complex was discovered to exceed many other compounds which were previously known to possess such properties, including those used clinically. The Cu(II) complex of the structurally related ligand salicylaldehyde acetylhydrazone (H_2sa) has also displayed biological activity [9,10].

In this paper we focus on the synthesis of a series of analogues of H_2sb and their Cu(II) complexes. The ligands (Fig. 1) prepared include disubstituted compounds where R1 and R2 are identical, where R1 = R2 = methyl, ethyl, isopropyl, phenyl, benzyl or where R1 = phenyl and R2 = H. Lastly, the complex where R1 and R2 were part of an aliphatic ring was also synthesized, where the substituted group is pipyridine. Compounds prepared have been characterized by a range of physicochemical techniques.

2. Experimental

All reagents were commercially available and were used as received. Solvents were dried by conventional procedures prior to use. Reagents used for the physical measurements were of spectroscopic grade. The yields are reported with respect to the metal salts.

The ^1H NMR spectra were recorded on a Bruker ACF 300FT-NMR spectrometer using TMS as an internal reference at 25 °C in DMSO and the Infrared

* Corresponding authors. Tel.: +65-6874-2683; fax: +65-6779-1691 (C.-T. Yang). Tel.: +65-6779-4241; fax: +65-6779-4241 (J.D. Ranford).
E-mail addresses: chmyct@nus.edu.sg (C.-T. Yang), kubalranford@yahoo.co.uk (J.D. Ranford).

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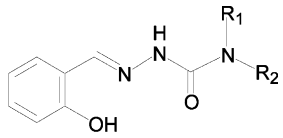

Abbreviation	R_1	R_2
H_2Me_2	Methyl	Methyl
H_2Et_2	Ethyl	Ethyl
H_2iPr_2	i-Propyl	i-Propyl
H_2Ph_2	Phenyl	Phenyl
H_2Bnz_2	Benzyl	Benzyl
H_2Pip	Pipyridyl	
H_2PhH	Phenyl	H

Fig. 1. Salicylaldehyde-*N*,*N*-disubstituted semicarbazone.

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. Conductance measurements were made using a Kyoto Electronics CM-115 conductivity meter using 1 mM solutions. The elemental analyses were performed in the Microanalytical Laboratory, Chemistry 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 N_2 atmosphere using a sample size of 5–10 mg per run. Room-temperature magnetic susceptibility measurements were carried out at a Johnson–Matthey magnetic susceptibility balance with $Hg[Co(SCN)_4]$ as standard. Corrections for diamagnetism were made using Pascal's constants. The reported magnetic moments are per Cu(II) ion.

2.1. Preparation of ligands

Disubstituted amine (15 mmol) was dissolved in dry dichloromethane (25 ml) in a round bottom flask. Triphosgene (5.25 mmol, 1.55 g) was dissolved in dry methylene chloride (25 ml) in a two-necked round bottom flask and pyridine (30 mmol, 2.43 ml) was added to this solution. After placing a magnetic stirrer bar into the triphosgene solution, the two flasks were stoppered tightly. The triphosgene solution was placed in an ice bath on top of a stirrer plate, while the flask was constantly being flushed with N_2 gas. Using a glass syringe, the amine solution was added into the triphosgene solution over a period of 45 min to yield an orange solution. The reaction was then left to stand at room temperature (r.t.) for 3 days with constant N_2 flushing to give a yellow solution.

To the solution of disubstituted carbamic acid chloride was added diethyl ether (63 ml) and this mixture was added dropwise to a solution of hydrazine hydrate (60 mmol, 1.87 ml) in ethanol (30 ml) with vigorous stirring over a period of 1 h. The reaction mixture was left to stir for 30 min. before the solvents were removed on a rotary evaporator at 60 °C. The solution was then extracted with chloroform three times and the solvent again removed by rotary evaporator to give the semicarbazide. A solution of the semicarbazide in ethanol (5 ml) was placed in an ice bath on a stirrer plate. To this was added excess salicylaldehyde (16 mmol, 1.71 ml) in ethanol (5 ml) dropwise with vigorous stirring, over a period of 10 min. A yellow compound was obtained and the reaction mixture was then filtered and washed with cold water to remove excess salicylaldehyde. The yellow product was then dried under vacuum until a constant weight. Recrystallization was not carried out for fear of product decomposition. Yields ranges from 80–90%.

$H_2Me_2 \cdot 1.5H_2O$: m.p. 164–6 °C. *Anal.* Calc. for $C_{10}H_{16}N_3O_{3.5}$: C, 51.0; H, 6.7; N, 18.0. Found: C, 51.3; H, 6.8; N, 17.9%. ^1H NMR (DMSO-d_6): δ 2.91 (s, 6H), 6.85–6.90 (m, 2H), 7.20–7.25 (m, H), 7.35–7.38 (m, H), 8.34 (s, H), 10.48 (s, H), 11.60 (s, H). IR (KBr, cm^{-1}): ν(OH) 3405; ν(NH) 2919, $\nu(COO^-)_{as}$ 1646, $\nu_s(COO^-)$ 1463, ν(phenolic, CO) 1257.

$H_2Et_2 \cdot 0.5H_2O$: m.p. 169–71 °C. *Anal.* Calc. for $C_{12}H_{18}N_3O_{2.5}$: C, 59.0; H, 7.3; N, 18.0. Found: C, 59.0; H, 7.4; N, 17.3%. ^1H NMR (DMSO-d_6): δ 1.09 (t, 6H), 3.31 (q, 4H), 6.85–6.90 (m, 2H), 7.19–7.25 (m, H), 7.34–7.37 (m, H), 8.36 (s, H), 10.40 (s, H), 11.65 (s, H). IR (KBr, cm^{-1}): ν(OH) 3520; ν(NH) 2982, $\nu(COO^-)_{as}$ 1643, $\nu_s(COO^-)$ 1475, ν(phenolic, CO) 1281.

H_2iPr_2: m.p. 191–2 °C. *Anal.* Calc. for $C_{14}H_{21}N_3O_2$: C, 63.8; H, 8.1; N, 15.8. Found: C, 63.8; H, 8.0; N, 16.0%. ^1H NMR (DMSO-d_6): δ 1.24 (d, 12H), 3.75 (m, 2H), 6.84–6.89 (m, 2H), 7.18–7.24 (m, H), 7.31–7.34 (m, H), 8.32 (s, H), 10.32 (s, H), 11.75 (s, H). IR (KBr, cm^{-1}): ν(OH) 3446; ν(NH) 2969, $\nu(COO^-)_{as}$ 1638, $\nu_s(COO^-)$ 1469, ν(phenolic, CO) 1267.

H_2Ph_2: m.p. 198–9 °C. *Anal.* Calc. for $C_{20}H_{17}N_3O_2$: C, 72.2; H, 5.1; N, 12.9. Found: C, 72.5; H, 5.2; N, 12.7%. ^1H NMR (DMSO-d_6): δ 6.82–7.42 (m, 14H), 8.30 (s, H), 10.40 (s, H), 11.28 (s, H). IR (KBr, cm^{-1}): ν(OH) 3436; ν(NH) 2957, $\nu(COO^-)_{as}$ 1641, $\nu_s(COO^-)$ 1462, ν(phenolic, CO) 1258.

H_2Bnz_2: m.p. 195–6 °C. *Anal.* Calc. for $C_{22}H_{21}N_3O_2$: C, 73.6; H, 5.9; N, 11.6. Found: C, 73.5; H, 5.9; N, 11.7%. ^1H NMR (DMSO-d_6): δ 4.51 (s, 4H), 6.84–7.43 (m, 14H), 8.35 (s, H), 10.85 (s, H), 11.52 (s, H). IR (KBr, cm^{-1}): ν(OH) 3416; ν(NH) 2854, $\nu(COO^-)_{as}$ 1634, $\nu_s(COO^-)$ 1453, ν(phenolic, CO) 1260.

H_2Bip_2: m.p. 153–5 °C. *Anal.* Calc. for $C_{13}H_{17}N_3O_2$: C, 59.7; H, 6.9; N, 16.3. Found: C, 59.9; H, 7.1; N, 16.1%. ^1H NMR (DMSO-d_6): δ 1.49 (d, 4H) 1.58 (d, 2H), 3.39 (t, 4), 6.84–7.00 (m, 2H), 7.19–7.25 (m, H), 7.34–7.37 (m, H) 8.31 (s, H), 10.61 (s, H), 11.60 (s, H). IR (KBr, cm^{-1}): ν(OH) 3414; ν(NH) 2856, $\nu(COO^-)_{as}$ 1628, $\nu_s(COO^-)$ 1466, ν(phenolic, CO) 1264.

H_2PhH: m.p. 188–9 °C. *Anal.* Calc. for $C_{14}H_{13}N_3O_2$: C, 66.0; H, 5.0; N, 16.4. Found: C, 65.9; H, 5.1; N, 16.5%. ^{1}H NMR (DMSO-d_6): δ 6.84–7.95 (m, 9H), 8.27 (s, H), 8.86 (s, H), 10.08 (s, H), 11.12 (s, H). IR (KBr, cm^{-1}): ν(OH) 3404; ν(NH) 3050, $\nu(COO^-)_{as}$ 1651, $\nu_s(COO^-)$ 1471, ν(phenolic, CO) 1263.

2.2. Preparation of complexes

The general procedure for complexes preparation is as follows. To a solution of the salicylaldehyde semicarbazone (1.0 mmol) in dichloromethane (50 ml) was added dropwise a solution of $CuCl_2\cdot 2H_2O$ (1.00 mmol, 0.170 g) in methanol (20 ml) with vigorous stirring at r.t. The reaction mixture was filtered cold to give the green or brown complex which was then washed with diethyl ether.

2.2.1. [{Cu(Me$_2$)}$_2$]·H$_2$O (1)

Light brown colour. Yield: 0.216 g (78%). *Anal.* Calc. for $C_{20}H_{24}N_6O_5Cu_2$: C, 43.3; H, 4.3; N, 15.0; H_2O, 3.8. Found: C, 43.2; H, 4.3; N, 15.1; H_2O, 3.7%. IR (KBr, cm^{-1}): ν(OH) 3433, ν(NH) 2862, $\nu_{as}(COO^-)$ 1631, $\nu_s(COO^-)$ 1413, ν(phenolic, CO) 1280.

2.2.2. [{Cu(HEt$_2$)Cl}$_2$] (2)

Light brown colour. Yield: 0.270 g (81%). *Anal.* Calc. for $C_{24}H_{32}N_6O_4Cl_2Cu_2$: C, 43.2; H, 5.0; N, 12.4. Found: C, 43.2; H, 4.8; N, 12.6%. IR (KBr, cm^{-1}): ν(NH) 2847, $\nu_{as}(COO^-)$ 1616, $\nu_s(COO^-)$ 1390, ν(phenolic, CO) 1256.

2.2.3. [{Cu(HiPr$_2$)Cl}$_2$]·4H$_2$O (3)

Green colour. Yield: 0.258 g (65%). *Anal.* Calc. for $C_{28}H_{48}N_6O_8Cl_2Cu_2$: C, 42.6; H, 6.0; N, 10.4; H_2O, 9.0. Found: C, 42.3; H, 6.0; N, 10.5; H_2O, 9.1%. IR (KBr, cm^{-1}): ν(OH) 3440, ν(NH) 2929, $\nu_{as}(COO^-)$ 1618, $\nu_s(COO^-)$ 1406, ν(phenolic, CO) 1263.

2.2.4. [Cu(Ph$_2$)·H$_2$O] (4)

Green colour. Yield: 0.353 g (86%). *Anal.* Calc. for $C_{20}H_{17}N_3O_3Cu$: C, 58.3; H, 4.0; N, 10.2; H_2O, 4.3. Found: C, 58.5; H, 4.1; N, 10.2; H_2O, 4.4%. IR (KBr, cm^{-1}): ν(OH) 3420, ν(NH) 2849, $\nu_{as}(COO^-)$ 1598, $\nu_s(COO^-)$ 1374, ν(phenolic, CO) 1261.

2.2.5. [Cu(HBnz$_2$)Cl]·H$_2$O (5)

Dark green colour. Yield: 0.342 g (72%). *Anal.* Calc. for $C_{22}H_{22}N_3O_3ClCu$: C, 58.1; H, 5.0; N, 9.3; H_2O, 4.1. Found: C, 58.3; H, 4.9; N, 9.3; H_2O, 4.0%. IR (KBr, cm^{-1}): ν(OH) 3461, ν(NH) 2855, $\nu_{as}(COO^-)$ 1603, $\nu_s(COO^-)$ 1378, ν(phenolic, CO) 1270.

2.2.6. [{Cu(HBiP)Cl}$_2$]·0.5H$_2$O (6)

Dark green colour. Yield: 0.260 g (80%). *Anal.* Calc. for $C_{26}H_{33}N_6O_{4.5}Cl_2Cu_2$: C, 44.8; H, 4.6; N, 12.0; H_2O, 1.3. Found: C, 44.6; H, 4.7; N, 12.0; H_2O, 1.3%. IR (KBr, cm^{-1}): ν(OH) 3468, ν(NH) 2854, $\nu_{as}(COO^-)$ 1624, $\nu_s(COO^-)$ 1393, ν(phenolic, CO) 1285.

2.2.7. [{Cu(HPhH)Cl}$_2$] (7)

Light brown colour. Yield: 0.244 g (69%). *Anal.* Calc. for $C_{28}H_{24}N_6O_4Cl_2Cu_2$: C, 47.4; H, 3.4; N, 12.0. Found: C, 47.6; H, 3.4; N, 11.9%. IR (KBr, cm^{-1}): ν(NH) 2842, $\nu_{as}(COO^-)$ 1631, $\nu_s(COO^-)$ 1411, ν(phenolic, CO) 1266.

2.3. X-ray structure determination

The diffraction experiments were carried out on a Bruker AXS SMART CCD diffractometer. The program SMART [11] was used for collecting frames of data, indexing reflection and determination of lattice parameters, SAINT [11] for integration of the intensity of reflections and scaling, SADABS [12] for absorption correction and SHELXTL [13] for space group and structure determination and least-squares refinements on F^2. Selected crystallographic data and refinement details are displayed in Table 1.

3. Results and discussion

3.1. Synthesis

The synthetic route for the disubstituted ligands required moisture-free and oxygen-free conditions as it

Table 1
Crystallographic data and structure refinement details for **5**

Complex	**5**
Formula	$C_{22}H_{22}N_3O_3Cl\ Cu$
f_w	475.42
T (K)	293(2)
Wavelength, λ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	18.9212(1)
b (Å)	7.1327(1)
c (Å)	16.0490(1)
β (°)	100.05(1)
V (Å^3)	2132.70(3)
Z	4
ρ_{calc} (g cm^{-3})	1.481
Absorption coefficient (mm^{-1})	1.178
Reflections collected	13074
Independent reflections	5212
R_{int}	0.0242
Goodness-of-fit	1.023
Final [$I > 2\sigma$], R_1 [a]	0.0385
wR_2 [b]	0.0943

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma\, w(F_o^2-F_c^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$.

involves the use of triphosgene which is sensitive to both of these. Hence, reactions had to be carried out in the dry box, under a nitrogen atmosphere and at ice temperature in order to minimize the possibility of undesired products. Complexation was relatively straightforward, however, the choice of solvent for the ligands was important. Initially ethanol was chosen but it was not satisfactory as gentle heating was required for complete solubilization which was not recommended as decomposition might occur. A series of solvents were tested and dichloromethane was selected as the most suitable.

3.2. Description of crystal structure $[Cu(HBnz_2)Cl]\cdot H_2O$ (5)

An ORTEP diagram of the structure is shown in Fig. 2. Selected bond lengths and angles are given in Table 2. The structure of **5** shows the copper atom is four coordinated and is best described as having a distorted square planar geometry with a NO_2Cl donor set. The ligand chelates the copper in an tridentate fashion emplying the imine N (Cu(1)–N(1) 1.941(2) Å), carbonyl O (Cu(1)–O(2) 1.974(2) Å), and phenolato O (Cu(1)–O(1) 1.902(2) Å). The last position is occupied by coordinated Cl (Cu(1)–Cl(1) 2.222(6) Å). The angles [O(1)–Cu(1)–O(2), 172.3(6)°] and [N(1)–Cu(1)–Cl(1) 170.2(5)°] at Cu(1) support the square planar geometry. The bond angle and length data for **5** agree with the equivalent values of those for $CuCl(H_2saladhp)\cdot H_2O$ ($H_3saladhp$ = 1,3-dihydroxy-2-methyl-(salicylideneamino)-propane) [14] and $[CuCl(Hsbh)]\cdot H_2O$ (H_2sbh = salicylaldehyde benzoylhydrazone) [15].

The O–H protons of lattice water are involved in strong and weak inter-molecular hydrogen-bonding to the O atom [O(1S)–H(1S)···O(1), 2.45 Å; O(1S)–H(2S)···O(1), 2.11 Å] of the carbonyl group and chloride atom [O(1S)–H(1S)···Cl(1), 2.48 Å] in an adjacent molecule. The H atom of the protonated amide participates in strong intermolecular hydrogen-bonding to oxygen O(1S) [N(2)–H(2)···O(1S), 2.04 Å] of lattice water. Hydrogen bond parameters for **5** are given in Table 3.

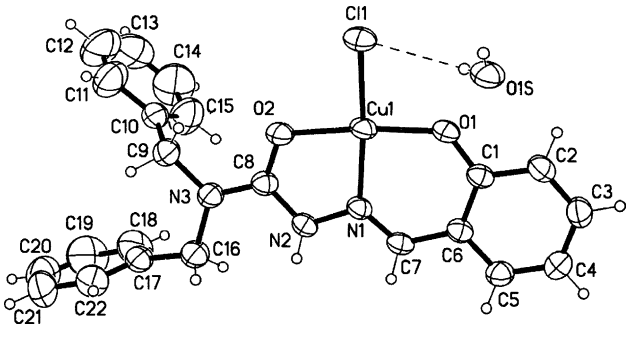

Fig. 2. An ORTEP view showing the coordination environment of **5**.

Table 2
Selected bond lengths (Å) and bond angles (°) for **5**

Bond lengths			
Cu(1)–O(1)	1.902(2)	Cu(1)–N(1)	1.941(2)
Cu(1)–O(2)	1.974(2)	Cu(1)–Cl(1)	2.222(6)
N(1)–C(7)	1.290(3)	N(1)–N(2)	1.378(2)
N(2)–C(8)	1.363(3)	N(3)–C(8)	1.343(3)
O(1)–C(1)	1.327(2)	C(8)–O(2)	1.261(2)
Bond angles			
O(1)–Cu(1)–N(1)	92.3(7)	O(1)–Cu(1)–O(2)	172.3(6)
N(1)–Cu(1)–O(2)	80.8(6)	O(1)–Cu(1)–Cl(1)	91.4(4)
N(1)–Cu(1)–Cl(1)	170.2(5)	O(2)–Cu(1)–Cl(1)	96.0(5)
C(7)–N(1)–N(2)	118.6(2)	C(7)–N(1)–Cu(1)	128.6(1)
N(2)–N(1)–Cu(1)	112.8(1)	C(8)–N(2)–N(1)	113.8(2)
C(8)–N(3)–C(9)	117.8(2)	C(8)–N(3)–C(16)	119.7(2)
C(9)–N(3)–C(16)	121.3(2)	C(1)–O(1)–Cu(1)	127.8(1)
C(8)–O(2)–Cu(1)	113.5(1)	O(1)–C(1)–C(6)	124.4(2)

3.3. Physical characterization

The IR absorption band in the region 3400–3500 cm^{-1} confirms the hydrates in all the complexes except **2** and **7** [16]. This is further supported by the weight loss observed in thermogravimetry, TG. For all the complexes, the sharp band in the region 2842–2929 cm^{-1} has been assigned to N–H stretching modes [17]. The band in the region 1598–1631 cm^{-1} is due to the asymmetric vibration of coordinated carboxylate group [$\nu_{as}(CO_2^-)$] and the band in the region 1374–1413 cm^{-1} may be attributed to the symmetric stretching vibration of carboxylate group [$\nu_s(CO_2^-)$]. For all the complexes, the difference between $\nu_{as}(COO^-)$ and $\nu_{sym}(COO^-)$ stretching frequencies is >200 cm^{-1}, thus suggesting a terminal coordination mode for the carboxylate group [18–20]. This observation was confirmed by the X-ray structure of **5**.

Electronic spectral data in Nujol mull are given Table 4 along with molar conductivity and room temperature magnetic data. The mull transmittance spectra exhibit a charge transfer transition (CT) at approximately 400 nm, often being poorly resolved shoulders. The band is similar to that found for the related $Cu(Hsb)^+$ [4] and $Cu(Hsa)^+$ [5] complexes which was assigned to a ligand to copper(II) transition. This band may also contain a Cl → Cu ligand-to-metal CT component for **2**, **3**, **5**, **6** and **7**, respectively. The d–d absorption bands at 630, 620 and 630 nm for **1**, **4** and **5**, respectively, were assigned to the square planar geometry [21] as seen in the crystal structure of **5**. The rather broad d–d absorption band (ca. 670 nm) for **2**, **3**, **6** and **7** was assigned to a square pyramidal geometry, as present in related copper(II) complexes [4,5].

For all the complexes, molar conductivity values in DMSO fall below the range expected for 1:1 electrolytes suggesting that the counter–ions remained bound to the

Table 3
Hydrogen bond distances (Å) and bond angles (°) in **5**

D–H	d(D–H)	d(H···A)	∠ DHA	d(D···A)	A	Symmetry
N2–H2	0.86	2.04	145	2.784(2)	O1S	$[-x+1, -y+1, -z+1]$
O1S–H1S	0.70	2.45	126	3.115(2)	O1	
O1S–H1S	0.70	2.48	166	3.464(2)	Cl1	
O1S–H2S	0.75	2.11	171	2.815(2)	O1	$[-x+1, y-1/2, -z+1/2]$

Table 4
Magnetic, electronic absorption and conductivity data for complexes

Complex	Absorption bands [a]		Molar conductivity [b] (S cm^2 mol^{-1})	Magnetic moment μ_B (BM)
	CT	d–d		
1	390 (sh)	630 (br)	19	1.39
2	395 (sh)	680 (br)	18	1.50
3	405 (sh)	670 (br)	28	1.44
4	400 (sh)	620 (br)	17	1.83
5	400 (sh)	630 (br)	20	2.03
6	385 (sh)	670 (br)	21	1.35
7	400 (sh)	675 (br)	21	1.47

[a] As Nujol mull transmittance.
[b] In DMSO.

complexes even in such a strongly coordinating solvent [22]. There is continued interest in the magnetic properties of di- and oligomeric Cu(II) complexes from theoretical and biological viewpoints [23,24]. Complexes **4** and **5** have normal moments (1.83μ_B for **4** and 2.04μ_B for **5**) and are consistent with uncoupled Cu(II) ions formulated as monomers. All other complexes have lower magnetic moments (1.35–1.50μ_B) indicating an antiferromagnetic coupling and have been assumed a side-by-side arrangement of the metal chelates with phenolato bridges between the Cu(II) centres, as found in $[\{Cu(Hsa)(H_2O)\}_2]\cdot(NO_3)_2$ [5]. Cytotoxicity testing is presently being conducted.

4. Summary

We have prepared Cu(II) complexes of substituted salicylaldehyde semicarbazones. Complexes $[Cu(Ph_2)\cdot H_2O]$ and $[Cu(HBnz_2)Cl]\cdot H_2O$ were formulated as monomers based on normal magnetic moments as well as the X-ray crystal structure of $[Cu(HBnz_2)Cl]\cdot H_2O$. The formulation of other complexes as dimers with a side-by-side arrangement of the metal chelates possessing a phenolato bridge between the Cu(II) centres is based on the magnetic exchange coupling observed and other physicochemical properties.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 200158. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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