A correlation involving ^{1}H NMR spectra and exchange coupling constants of a family of phenoxo-bridged macrocyclic dicopper(II) complexes

Sasankasekhar Mohanta,† Bibhutosh Adhikary,‡ Sujoy Baitalik§ and Kamalaksha Nag*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India. E-mail: ickn@mahendra.iacs.res.in

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The ^{1}H NMR spectra of eleven macrocyclic tetraiminodiphenolate dicopper(II) complexes derived from 4-methyl (or *tert*-butyl)-2,6-diformyl/diacetyl/dibutyrylphenols and linker diamines such as 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane or 1,2-diaminobenzene have been studied in $(CD_3)_2SO$ at 25 °C. The hyperfine-shifted ^{1}H NMR signals have been assigned from their measured longitudinal relaxation times (T_1) and peak areas. The two copper(II) centres in these compounds are strongly antiferromagnetically coupled with the exchange coupling constant $-2J$ ($H = -2JS_1 \cdot S_2$) lying between 690 and 860 cm^{-1}. It is shown that a plot of the chemical shift (δ) due to the phenolate ring protons of the macrocycles at 298 K *vs.* the exchange coupling constant ($-2J$) of the corresponding complexes provides a smooth sigmoidal curve that can be simulated by the expression $-2J = 220.6\,[1 + \exp\{(\delta - 4.12)/2.93\}]^{-1} + 667$.

In recent years ^{1}H NMR spectroscopy has been used as a structural probe to study spin-coupled dinuclear copper(II) complexes.[1–10] The quality of ^{1}H NMR spectra of paramagnetic systems is governed by both nuclear and electronic relaxation processes.[11,12] If nuclear relaxation is very fast, ^{1}H NMR signals become much too broadened to be seen. On the other hand, when the electronic relaxation time (τ_s) is sufficiently short (*ca.* 10^{-11} s), relatively sharp signals can be obtained. Although mononuclear copper(II) complexes exhibit broad spectra due to long τ_s values, fairly sharp spectra are observed for strongly antiferromagnetically coupled dicopper(II) complexes. Recent studies[2–4] have shown that weakly antiferromagnetic or even ferromagnetic dicopper(II) complexes can also exhibit relatively sharp spectra when electronic relaxation times are short.

Magnetic exchange interactions in a large number of phenoxo-bridged macrocyclic tetraiminodiphenolate dinuclear copper(II) complexes derived from the [2 + 2] metal template condensation of 4-methyl(or *tert*-butyl)-2,6-diformyl(or diacyl)phenols and various α,ω-diamines have been reported.[13] The two copper(II) centres in these compounds are strongly antiferromagnetically coupled. To our knowledge, there is no reported study of the ^{1}H NMR spectra of these macrocyclic complexes. The present study is concerned with the ^{1}H NMR spectral behaviour of eleven dicopper(II) complexes shown in Table 1. We have sought to determine whether a correlation can be obtained between the reported solid state exchange coupling constants ($-2J$) and the proton chemical shifts of these compounds observed at room temperature in solution. Such a correlation should be useful to estimate the $-2J$ value of a homologous compound.

† Permanent address: Department of Chemistry, University College of Science, Calcutta 700 009, India.
‡ Permanent address: Department of Chemistry, B. E. College (Deemed University), Howrah 711 103, India.
§ Permanent address: Department of Chemistry, Scottish Church College, Calcutta 700 011, India.

Experimental

Preparation of complexes

All chemicals were obtained from commercial sources and used as received. The reagents 4-methyl(or *tert*-butyl)-2,6-diformylphenols[14] and 4-methyl(or *tert*-butyl)-2,6-diacylphenols[15] were prepared according to known methods.

The macrocyclic dicopper(II) complexes **1**,[16] **2**,[15] **3**,[17] **4**,[18] **5**,[15] **6**,[15] **7**,[16] **8**,[15] **9**,[15] **10**[19] and **11**[20] were prepared as reported earlier. The purity of these compounds was checked by elemental (C, H and N) analyses, which were performed in-house on a Perkin–Elmer 2400H elemental analyzer.

The dizinc(II) complexes reported here are new compounds and they were obtained by the following general procedure. To a boiling methanol solution (50 cm^3) of 4-methyl(or *tert*-butyl)-2,6-diformyl/diacylphenol (2 mmol) and $Zn(ClO_4)_2 \cdot 4H_2O$ (0.67 g, 2 mmol), a solution of 1,2-diaminoethane or 1,3-diaminopropane (2 mmol) in methanol (10 cm^3) was added over a period of 15 min. The resulting bright yellow solution was refluxed for 12 h, after which it was filtered to remove any solid. The filtrate was concentrated on a rotary evaporator to about 20 cm^3 and then kept at room temperature for slow evaporation. The golden yellow or orange yellow crystals that separated were collected by filtration and washed with methanol and diethyl ether. The yields of the products were 80–85%.

$[Zn_2L1(ClO_4)_2] \cdot H_2O$. Anal (%) found: C, 36.8; H, 3.4; N, 7.65; calc. for $C_{22}H_{24}N_4O_3Zn_2(ClO_4)_2$: C, 36.57; H, 3.32; N, 7.76. IR (KBr, ν/cm^{-1}): 1639s (C=N), 1545s (C=C), 1145m, 1109s, 1090s, 627m (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$, δ]: 2.30 (6H, s, Ar-CH_3), 3.97 (8H, s, =N–CH_2), 7.72 (4H, s, Ar-H), 8.65 (4H, s, –CH=N).

$[Zn_2L2(ClO_4)_2]$. Anal (%) found: C, 39.3; H, 3.9; N, 7.8; calc. for $C_{24}H_{26}N_4O_2Zn_2(ClO_4)_2$: C, 39.35; H, 3.55; N, 7.65. IR (KBr, ν/cm^{-1}): 1635s (C=N), 1550s (C=C), 1145m, 1110s, 1090s, 1040m, 627m (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$, δ]: 2.04

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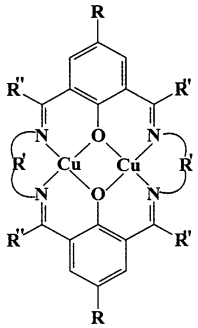
Table 1 The dicopper(II) complexes used in this work



	Complex	R	R′	R″
1	$[Cu_2L1(ClO_4)_2]$	CH_3	$(CH_2)_2$	H
2	$[Cu_2L2(ClO_4)_2]\cdot H_2O$	CH_3	$(CH_2)_3$	H
3	$[Cu_2L3(ClO_4)_2]\cdot H_2O$	CH_3	$(CH_2)_4$	H
4	$[Cu_2L4(ClO_4)_2]\cdot H_2O$	CH_3	$(CH_2)_2$	CH_3
5	$[Cu_2L5(ClO_4)_2]$	CH_3	$(CH_2)_3$	CH_3
6	$[Cu_2L6(ClO_4)_2]$	CH_3	$(CH_2)_3$	$(CH_2)_2CH_3$
7	$[Cu_2L7(ClO_4)_2]$	$C(CH_3)_3$	$(CH_2)_2$	H
8	$[Cu_2L8(ClO_4)_2]\cdot 2H_2O$	$C(CH_3)_3$	$(CH_2)_3$	H
9	$[Cu_2L9(ClO_4)_2]\cdot 2H_2O$	$C(CH_3)_3$	$(CH_2)_3$	CH_3
10	$[Cu_2L10(ClO_4)_2]\cdot H_2O$	CH_3	C_6H_4	H
11	$[Cu_2L11(ClO_4)_2]\cdot H_2O$	CH_3	$(CH_2)_2$, $(CH_2)_3$	H

(4H, m, =N–CH_2–CH_2), 2.28 (6H, s, Ar-CH_3), 3.97 (8H, m, =N–CH_2), 7.52 (4H, s, Ar-H), 8.48 (4H, s, –CH=N).

$[Zn_2L4(ClO_4)_2]$. Anal (%) found: C, 41.1; H, 4.15; N, 7.15; calc. for $C_{26}H_{30}N_4O_2Zn_2(ClO_4)_2$: C, 41.06; H, 3.95; N, 7.37. IR (KBr, ν/cm^{-1}): 1620s (C=N), 1551s (C=C), 1144m, 1130s, 1090s, 625m (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$, δ]: 2.31 (6H, s, Ar-CH_3), 2.43 (12H, s, =C–CH_3), 3.90 (8H, s, =N–CH_2), 7.65 (4H, s, Ar-H).

$[Zn_2L5(ClO_4)_2]\cdot H_2O$. Anal (%) found: C, 42.1; H, 4.6; N, 6.8; calc. for $C_{28}H_{36}N_4O_3Zn_2(ClO_4)_2$: C, 41.7; H, 4.46; N, 6.94. IR (KBr, ν/cm^{-1}): 1615s (C=N), 1550s (C=C), 1150m, 1115s, 1090s, 628s (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$, δ]: 0.82 (4H, m, =N–CH_2–CH_2), 2.32 (6H, s, Ar-CH_3), 3.22 (12H, s, =C–CH_3), 3.81 (8H, m, =N–CH_2), 7.69 (4H, s, Ar-H).

$[Zn_2L6(ClO_4)_2]\cdot H_2O$. Anal (%) found: C, 46.5; H, 5.75; N, 5.9; calc. for $C_{36}H_{52}N_4O_3Zn_2(ClO_4)_2$: C, 47.06; H, 5.66; N, 6.1. IR (KBr, ν/cm^{-1}): 1612s (C=N), 1545s (C=C), 1146m, 1115s, 1095s, 628m (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$, δ]: 1.12 (12H, t, =C–CH_2–CH_3), 1.75 (4H, m, =N–CH_2–CH_2), 2.07 (16H, m, =C–CH_2–CH_2), 2.32 (6H, s, Ar-CH_3), 3.80 (8H, t, =N–CH_2), 7.68 (4H, s, Ar-H).

$[Zn_2L7(ClO_4)_2]\cdot H_2O$. Anal (%) found: C, 42.1; H, 4.7; N, 7.0; calc. for $C_{28}H_{36}N_4O_3Zn(ClO_4)_2$: C, 41.7; H, 4.45; N, 6.95. IR (KBr, ν/cm^{-1}): 1642s (C=N), 1552s (C=C), 1138m, 1115s, 1086s, 626m (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$, δ]: 1.26 [18H, s, Ar–C(CH_3)$_3$], 4.02 (8H, s, =N–CH_2), 7.76 (4H, s, Ar-H), 8.74 (4H, s, –CH=N).

$[Zn_2L8(ClO_4)_2]\cdot 3H_2O$. Anal (%) found: C, 41.55; H, 4.9; N, 6.4; calc. for $C_{30}H_{44}N_4O_5Zn_2(ClO_4)_2$: C, 41.37; H, 5.05; N, 6.44. IR (KBr, ν/cm^{-1}): 1643s (C=N), 1556s (C=C), 1117s, 1084s, 625m (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$, δ]: 1.28 [18H, s, Ar-C(CH_3)$_3$], 2.00 (4H, m, =N–CH_2–CH_2), 3.96 (8H, m, =N–CH_2), 7.72 (4H, s, Ar-H), 8.68 (4H, s, –CH=N).

$[Zn_2L9(ClO_4)_2]\cdot 2H_2O$. Anal (%) found: C, 45.3; H, 5.65; N, 5.9; calc. for $C_{34}H_{50}N_4O_4Zn_2(ClO_4)_2$: C, 44.94; H, 5.45; N, 6.11. IR (KBr, ν/cm^{-1}): 1614s (C=N), 1545s (C=C), 1110s, 1090s, 625m (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$, δ]: 1.24 [18H, s, Ar-C(CH_3)$_3$], 1.70 (4H, m, =N–CH_2–CH_2), 2.74 (12H, s, =C–CH_3), 3.40 (8H, m, =N–CH_2), 7.72 (4H, s, Ar-H).

$[H_2L3(H)_2](ClO_4)_2$. The reaction involving 4-methyl-2,6-diformylphenol, $Zn(ClO_4)_2\cdot 4H_2O$ and 1,4-diaminobutane in a 1 : 1 : 1 molar ratio, when carried out in the same manner as described above, led to the deposition of a red crystalline solid. After 2 h, the product was filtered off and recrystallized from acetonitrile (yield 80%). Zinc was found to be absent in the material isolated. Anal (%) found: C, 49.4; H, 5.3; N, 8.95; calc. for $C_{26}H_{34}N_4O_2(ClO_4)_2$: C, 49.27; H, 5.37; N, 8.84. IR (KBr, ν/cm^{-1}): 3445m, 3381m (O–H···N, N–H···O), 1659s (C=N), 1537s (C=C), 1090s, 627m (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$, δ]: 2.08 (8H, m, =N–CH_2–CH_2), 2.28 (6H, s, Ar-CH_3), 3.97 (8H, m, =N–CH_2), 7.54 (4H, s, Ar-H), 8.81 (4H, s, –CH=N), 13.16 (br, O–H···N).

$[ZnL10(H_2)](ClO_4)_2$. To a boiling methanol solution (50 cm^3) of 4-methyl-2,6-diformylphenol (0.33 g, 2 mmol) and $Zn(ClO_4)_2\cdot 4H_2O$ (0.67 g, 2 mmol), a second methanol solution (20 cm^3) containing 1,2-diaminobenzene (0.22 g, 2 mmol) and triethylamine (0.2 g, 2 mmol) was added over a period of 15 min. The yellow solution turned to bright red and eventually red crystals began to deposit. The product was filtered off after 1 h and recrystallized from acetonitrile [yield 0.55 g (75%)]. Anal (%) found: C, 48.75; H, 3.1; N, 7.45; calc. for $C_{30}H_{22}N_4O_2Zn(ClO_4)_2$: C, 49.02; H, 2.99; N, 7.62. IR (KBr, ν/cm^{-1}): 1620s, 1582s (C=N), 1537s (C=C), 1118s, 1086s, 627m (ClO_4^-). ^{1}H NMR [$(CD_3)_2SO$, δ]: 2.29 (6H, s, Ar-CH_3), 7.51 (4H, m, *m*-Ph), 7.60 (4H, d, *p*-Ph), 7.91 (4H, s, Ar-H), 8.95 (2H, s, –CH=N), 9.11 (2H, s, –CH=N), 15.29 (2H, br, N–H···O).

CAUTION! All the perchlorate salts reported in this study are potentially explosive and therefore should be handled with care.

Physical measurements

Infrared spectra were recorded on a FT-IR Nexus Nicolet spectrometer using KBr discs.

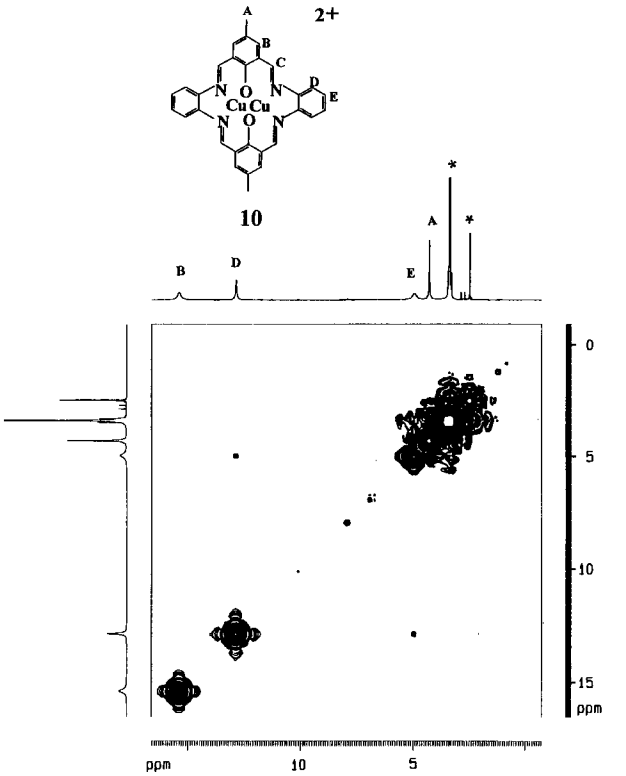


Fig. 1 $\{^1H–^1H\}$COSY spectrum of $[Cu_2L10(ClO_4)_2]\cdot H_2O$ (**10**) in $(CD_3)_2SO$ at 25 °C. The peaks due to the solvent and water are denoted by asterisks.

The 1D and 2D proton NMR spectroscopic measurements were performed on a Bruker Avance DPX-300 spectrometer at 25 °C in $(CD_3)_2SO$ solutions. The chemical shifts were referenced to the residual solvent signal of dimethyl sulfoxide (2.485 ppm). Longitudinal relaxation times (T_1) were measured by the inversion-recovery method. Test T_1 values were chosen covering the range from much less than the fastest relaxing signal to much longer than the slowest one. Magnetization recovery was exponential and least-squares fit of the data gave the T_1 values. The isotropic shifts ($\Delta\delta$) were obtained as the difference between the observed chemical shifts for the signals of the dicopper(II) complexes and the corresponding signals of their dizinc(II) analogues.

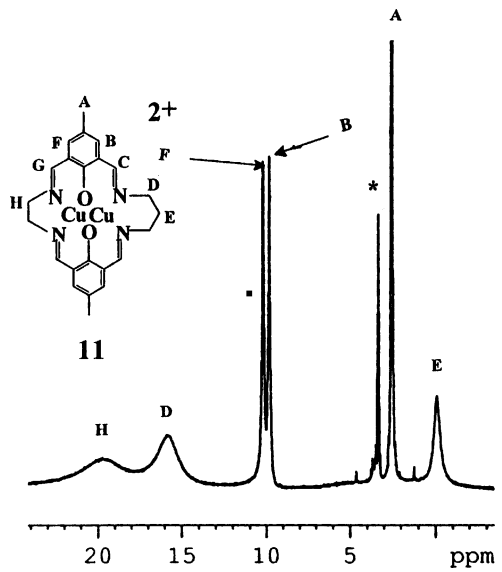


Fig. 2 ^1H NMR spectrum of $[Cu_2L11(ClO_4)_2]\cdot H_2O$ (**11**) in $(CD_3)_2SO$ at 25 °C. The water peak is denoted by an asterisk.

The solid state magnetic susceptibility measurement for **1** was carried out in the temperature range 5–300 K on a Lake Shore Cryotronic vibrating sample magnetometer VSM9309. The susceptibility data were corrected for diamagnetism using Pascal's constants.

Results and discussion

The dizinc(II) complexes reported here were used as ^1H NMR standards for obtaining the isotropic shifts of their corresponding dicopper(II) complexes. The perchlorate salts of the dizinc(II) complexes of L1, L2 and L4–L9 were straightforwardly obtained by reacting a 1 : 1 : 1 mixture of 4-alkyl-2,6-diformyl/diacylphenol, $Zn(ClO_4)_2\cdot 4H_2O$ and 1,2-diaminoethane or 1,3-diaminopropane. Surprisingly, the above reaction carried out with 4-methyl-2,6-diformylphenol, zinc perchlorate and 1,4-diaminobutane affords the perchlorate salt of the metal-free imine-protonated macrocycle $[H_2L3(H_2)](ClO_4)_2$. On the other hand, the reaction with 1,2-diaminobenzene provides the protonated mononuclear zinc(II) complex $[ZnL10(H_2)](ClO_4)_2$. Attempts to obtain the dizinc compound, *inter alia*, using excess metal salt were unsuccessful.

Proton NMR spectra

The ^1H NMR spectra of the dicopper(II) complexes **1**–**11** and the dizinc(II) analogues of **1**, **2** and **4**–**9** were recorded in $(CD_3)_2SO$ at 25 °C. All the paramagnetic complexes exhibit well-resolved hyperfine-shifted signals whose chemical shifts appear within the range −3 to +40 ppm. Typical spectra for complexes **10** and **11** are shown in Fig. 1 and 2, respectively. The relatively narrow range of chemical shifts observed for the complexes indicate that the two copper(II) centres are strongly antiferromagnetically coupled. The majority of the signals are sharp with line widths of less than 100 Hz. For each complex, the signal due to the $=N–CH_2$ protons is the most downfield-shifted and also the broadest because of their close proximity to the metal centre (Cu–H ≈ 3.5–3.6 Å). Significantly, for none of the compounds **1**–**3**, **10** or **11** was the signal due to the N=CH proton (Cu–H ≈ 3.8 Å) observed. The similar absence of the azomethine signal in the spectra of some other phenoxo-bridged dicopper(II) complexes has been reported[1,10] and is attributed to excessive line broadening. Spectral assignments have been made by taking into consideration the areas of the peaks and the measured proton longitudinal relaxation times (T_1). It should be noted that since the protons closer to the copper(II) centres experience stronger paramagnetic effects, consequently their relaxation times (T_1) are expected to be shorter, while their chemical shifts and line widths are larger. For complex **10**, assignment of the aromatic protons has been made from the COSY spectrum (shown in Fig. 1). It may be noted that the signals at 4.29 (A) and 15.40 (**B**) ppm do not have a cross-peak, while the signals at 12.87 (D) and 4.96 (E) ppm are correlated. Accordingly, signals D and E can be attributed to the *o*- and *m*-phenylene protons, respectively, and signal **B** to the phenolate ring protons. Table 2 lists the observed chemical shifts (δ), isotropic shifts ($\Delta\delta$), line widths and longitudinal relaxation times (T_1) for complexes **1**–**11** along with signal assignments. It may noted that a larger shift occurs for the $=N–CH_2$ signal with the decrease in cavity size of the macrocyclic compartment, that is **1** > **2** > **3**. This is reflected also in the spectrum (Fig. 2) of the asymmetric complex **11**, where the two broad signals at 15.76 (D) and 19.61 (F) ppm can be assigned to the $=N–CH_2$ protons of the larger and smaller compartments, respectively. The same

Table 2 ^{1}H NMR data for the dicopper(II) complexes in $(CD_3)_2SO$ at 25 °C

Compound	Assignment	δ	$\Delta\delta^a$	T_1/ms	Line width^b/Hz
1	Ar-CH_3	4.62	2.32	63.1	16
	Ar-H	15.03	7.31	13.5	60
	=N–CH_2	40.31	36.34	2.4	735
2	Ar-CH_3	2.34	0.02	88.1	22
	Ar-H	9.14	1.41	20.6	32
	=N–CH_2	15.15	11.32	3.4	760
	=N–CH_2–CH_2	0.64	−1.14	4.5	105
3	Ar-CH_3	2.93	0.65		20
	Ar-H	9.23	1.69		52
	=N–CH_2	11.65	7.68		560
	=N–CH_2–CH_2	1.13	−0.95		150
4	Ar-CH_3	5.14	2.83	87.1	18
	Ar-H	19.20	11.55	17.4	105
	=N–CH_2	33.90	30.00	2.2	460
	=C–CH_3	−3.05	−5.48	9.6	55
5	Ar-CH_3	2.91	0.59	82.8	33
	Ar-H	11.66	3.97	13.2	69
	=N–CH_2	16.78	12.97	2.4	480
	=N–CH_2–CH_2	0.40	−0.42	5.6	230
	=C–CH_3	−0.22	−3.44	11.0	81
6	Ar-CH_3	2.94	0.62	71.8	16
	Ar-H	11.73	4.05	16.3	63
	=N–CH_2	17.52	13.72	2.9	605
	=N–CH_2–CH_2	0.48	−1.27	6.7	243
	=C–CH_2–CH_2	1.85	−0.22	15.5	50
	=C–$(CH_2)_2$–CH_3	0.93	−0.19	57.2	18
7	Ar-$C(CH_3)_3$	1.18	−0.03	138.2	34
	Ar-H	15.18	7.42	15.9	62
	=N–CH_2	40.20	36.18	2.8	610
8	Ar-$C(CH_3)_3$	1.23	−0.05	125.6	28
	Ar-H	9.41	1.69	18.7	48
	=N–CH_2	15.08	11.12	2.2	750
	=N–CH_2–CH_2	0.66	−1.34	4.4	132
9	Ar-$C(CH_3)_3$	1.33	0.09	118.2	17
	Ar-H	11.80	4.08	15.9	58
	=N–CH_2	17.04	13.64	2.1	510
	=N–CH_2–CH_2	0.38	−1.32	13.3	98
	=C–CH_3	−0.29	−3.03	13.8	52
10	Ar-CH_3	4.29		56.5	18
	Ar-H	15.40		11.7	65
	o-Ph	12.87		32.9	27
	m-Ph	4.96		7.1	71
11	Ar-CH_3	2.44^c			
	Ar-H	10.19		22.8	38
		9.79		21.7	40
	=N–(CH_2)–N=	19.61		6.1	980
	=N–CH_2–CH_2–CH_2–N=	15.76		4.4	540
	=N–CH_2–CH_2–CH_2–N=	−0.13		3.5	135

^{a} $\Delta\delta = \delta Cu_2$ complex $- \delta Zn_2$ complex. ^{b} Full width at half-height. ^{c} Overlapped with solvent signal.

analogy applies also to the pair of signals [9.79 (**B**), 10.19 (F) ppm] due to the phenolate ring protons.

Magnetism

The magnetic susceptibility of **1** was measured in the temperature range 5–300 K. The plots of χ_M *vs.* T and $\chi_M T$ *vs.* T, shown in Fig. 3, are typical of strongly antiferromagnetically coupled dicopper(II) systems. The sharp rise in the susceptibility at low temperatures indicates the presence of a small amount of a mononuclear copper(II) impurity. The variable-temperature susceptibility data were fitted to the modified Bleaney–Bower equation[21]

$$\chi_M = \frac{2N\beta^2 g^2}{3kT}\,[1 + 1/3\,\exp(-2J/kT)]^{-1}\cdot(1-p) + \frac{N\beta^2 g^2}{2kT}\cdot p + \mathrm{TIP} \quad (1)$$

In eqn. (1), $-2J$ ($H = -2JS_1\cdot S_2$) is the singlet–triplet energy gap and the other terms have their usual meaning; p represents the mol fraction of mononuclear impurity, while the temperature-independent paramagnetic susceptibility (TIP) was taken as 120×10^{-6} cm^3 mol^{-1} for the two copper(II) ions. The best fit parameters obtained from nonlinear regression analysis of the data are: $-2J = 760(8)$ cm^{-1}, $g = 2.12(2)$ and $p = 0.012$ with the error residual $R = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi^2_{obs}]^{1/2} = 1.2 \times 10^{-4}$.

Of the eleven compounds listed in Table 1, aside from **1**, the values of the exchange coupling constants for **2**–**6** in the solid state are available from the literature.[13,17,22] The $-2J$ and g values of complexes **1**–**6** are collected in Table 3. We note that the crystal structures of **1**–**4** have been reported.[13,16–18]

Correlation

We have been interested to see whether in this series of compounds the exchange coupling constants obtained in the solid state can be correlated with the chemical shifts of one or more

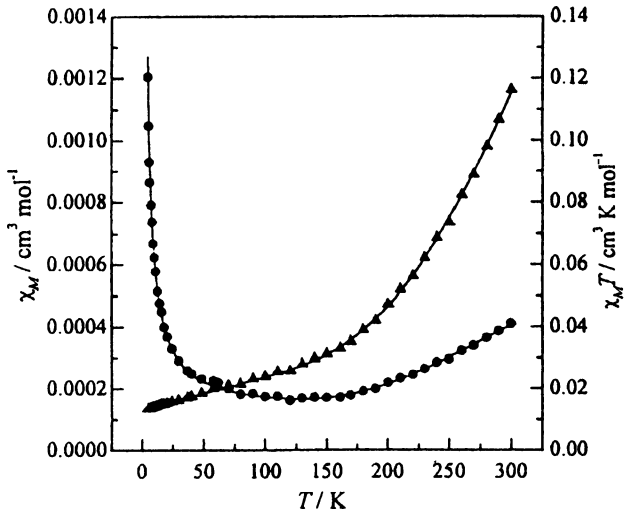


Fig. 3 Variable-temperature magnetic data for $[Cu_2L1(ClO_4)_2]$ (**1**). Filled circles represent χ_M values and filled triangles $\chi_M T$ values. The best fit curves were obtained with $g = 2.12(2)$, $-2J = 760(8)$ cm^{-1}, $p = 0.012$ and TIP $= 120 \times 10^{-6}$ cm^3 mol^{-1}.

signals in solution. From the configurations of the symmetrical macrocyclic complexes **1**–**10**, it is evident that the only proton site that is common to all the compounds is the *meta* position of the phenolate ring (Ar-H). In all the complexes this site is separated from the metal centre by the same number of bonds. Inasmuch as the superexchange interaction between the $d_{x^2-y^2}$ orbitals of the copper(II) centres is mediated through the s and p orbitals of the phenoxide bridge, it is reasonable to expect that the chemical shift or isotropic shift of Ar-H will depend on the magnitude of the exchange coupling constant. The dependence of the isotropic shift on the exchange coupling constant in copper(II) dimers is given by the following expression[23]

$$\Delta\delta = -\frac{g\beta A'}{3(\gamma/2\pi)(kT)}\,[1 + 1/3\,\exp(-2J/kT)]^{-1} \qquad (2)$$

In eqn. (2), A' is the isotropic hyperfine coupling constant between the ligand proton and the triplet spin state of the coupled metal pair, γ is the gyromagnetic ratio and the other symbols have their usual meaning. The analogy between eqn. (1) and (2) indicates that at a given temperature, the χ_M value of a complex should be directly proportional to the isotropic shift of the proton signal. In order to verify this, the χ_M values for complexes **1**–**6** were computed at 298 K using eqn. (1) and the values of $-2J$ and g given in Table 3. A satisfactory linear

Table 3 Magnetic data for the dicopper(II) complexes

Compound	$-2J$/cm^{-1}	g	Ref.
1	760	2.12	This work
2	850	2.14	17
3	857	2.16	17
4	689	2.13	13
5	835	2.12	22
6	806	2.15	17
7	755[a]		
8	851[a]		
9	819[a]		
10	801[a]		
11	844[a,b]		

[a] Estimated by using eqn. (3). [b] The mean δ value of the phenolate ring protons was used to calculate $-2J$.

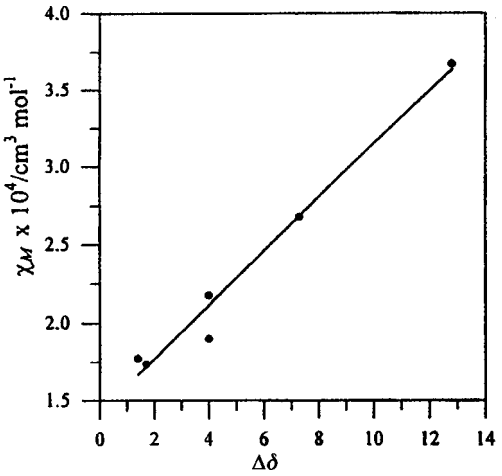


Fig. 4 Plot of calculated χ_M values at 298 K *vs.* isotropic shift ($\Delta\delta$) of the phenolate ring protons for complexes **1**–**6**.

fit has been obtained for the plot of χ_M *vs.* $\Delta\delta$ for the phenolate ring proton (Fig. 4). This correlation indicates that the solid state structural features of the complexes are not affected in solution. Fig. 5 shows the plots of $-2J$ *vs.* $\Delta\delta$ (298 K) and $-2J$ *vs.* δ (298 K) for complexes **1**–**6**. It may be noted that the best fit sigmoidal curve is identical in both cases and can be simulated by the expression

$$-2J = \frac{220.6}{1 + \exp[(\delta - 14.12)/2.93]} + 667 \qquad (3)$$

The $-2J$ values calculated for the remaining complexes using eqn. (3) are given in Table 3.

The reliability of the exchange coupling constants obtained in this way is limited by the accuracy of the input $-2J$s for **1**–**6**, the maximum deviation of which is ± 15 cm^{-1}. A similar deviation of $-2J$ will occur for an error in the chemical shift of 1 ppm. It should be noted that the complexes under consideration have a planar structure and electronic perturbations that may arise due to electron-withdrawing groups bound either to the metal or ligand sites are absent. It has been observed that if the anions remain bound to the metal centres in solution, as in $[Cu_2L_2Cl_2]$,[24] eqn. (3) cannot be

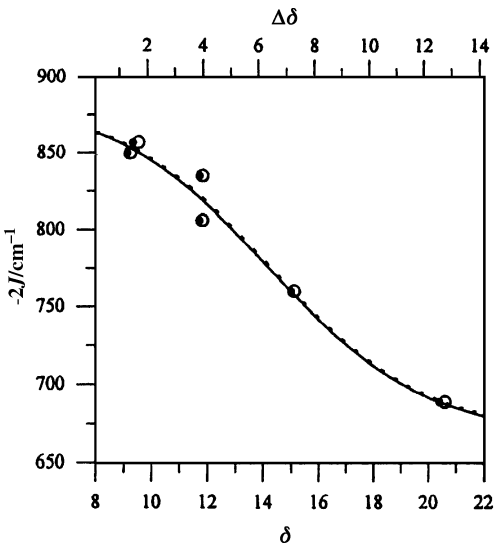


Fig. 5 Plots of exchange coupling constants $-2J$ *vs.* chemical shifts δ (filled circles) and isotropic shifts $\Delta\delta$ (open circles) of the phenolate ring protons for complexes **1**–**6**. The best fit curves are shown by a solid line for δ and a broken line for $\Delta\delta$.

used. Finally, we note that a somewhat similar sigmoidal plot has been reported[25] for the correlation between the room temperature effective magnetic moment μ_{eff} and $-2J$ for a series of hydroxy-bridged dicopper(II) complexes.

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