Ferromagnetic vs antiferromagnetic coupling in structurally analogous binuclear complexes based on salen type ligand

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Syntheses of the dinuclear complexes \([\text{Co(C}_2\text{H}_6\text{N}_2\text{O}_2)]_2 (\text{1}), [\text{Cu(C}_2\text{H}_4\text{N}_2\text{O}_2)]_2\text{H}_2\text{O} (\text{2}), [\text{Ni(C}_2\text{H}_4\text{N}_2\text{O}_2)]_2 (\text{3}), [\text{Zn(C}_2\text{H}_4\text{N}_2\text{O}_2)]_2 (\text{4})\) and \([\text{Cd(C}_2\text{H}_4\text{N}_2\text{O}_2)]_2 (\text{5})\) containing the Schiff base ligand \(\text{N,N'-bis(2-hydroxybenzilidene)-2,4,6-trimethylbenzene-1,3-diamine}\) have been described. The complexes under investigation have been characterized by elemental analyses, IR, NMR (¹H, ¹³C), electronic absorption, emission and EPR spectral studies. The structure of (1) has been determined by X-ray single crystal analyses. Variable temperature magnetic susceptibility measurements on (1) and (2) reveal that the former displays antiferromagnetic coupling \((J = -0.21 \pm 0.1 \text{ cm}^{-1})\), while the latter exhibits ferromagnetic coupling \((J = +1.23 \pm 0.1 \text{ cm}^{-1})\).

**Keywords:** Coordination chemistry, Supramolecular assembly, Polymetallic complexes, Dinuclear complexes, Schiff bases, Ferromagnetic coupling, Antiferromagnetic coupling, Electrochemical properties, Cryomagnetic properties, Cobalt, Copper, Nickel, Zinc, Cadmium

The designing and synthesis of supramolecular polynuclear metal complexes have drawn immense current attention because of their intriguing architecture and potential application in various areas. During the past couple of decades, numerous polymetallic complexes have been successfully designed and synthesized by judicious choice of the metal ion and ligands. The conjugated ligands combined with electron rich metal can generate low-energy electronic interactions between the metal centre and ligand, resulting in interesting optical or electronic properties. In this direction, due to their structural lability and sensitivity to molecular environments, complexes containing oxygen and nitrogen donor Schiff bases have drawn special attention. Structural studies have shown that in salens \[\text{salen} = \text{N,N-bis-(salicylidene)-ethylenediamine}\] derived from \(o\)-phenylenediamine the proximity of nitrogen donors allows synchronous coordination to the same metal centre, whereas those based on \(m\) - and \(p\)-phenylenediamines favour the formation of dinuclear complexes.

Transition metal complexes possessing different exchange coupling patterns offer exciting possibilities in the designing of single molecular magnets (SMM) and/or single chain magnets. Achieving ferromagnetic and antiferromagnetic coupling between the metal ions with long metal-metal distances (> 7.0 Å) is a challenging task. In this context, substituted \(m\)-phenylene (\(m\)-N-Φ-N) ligands have been used as the coupler between metal ions and it has been shown that dinuclear complexes based on it exhibit ambiguous magnetic properties. With the objective of developing such systems, dinuclear complexes \([\text{Co(C}_2\text{H}_6\text{N}_2\text{O}_2)]_2 (\text{1}), [\text{Cu(C}_2\text{H}_4\text{N}_2\text{O}_2)]_2\text{H}_2\text{O} (\text{2}), [\text{Ni(C}_2\text{H}_4\text{N}_2\text{O}_2)]_2 (\text{3}), [\text{Zn(C}_2\text{H}_4\text{N}_2\text{O}_2)]_2 (\text{4})\) and \([\text{Cd(C}_2\text{H}_4\text{N}_2\text{O}_2)]_2 (\text{5})\) based on \(\text{N,N'-bis(2-hydroxy-benzilidene)-2,4,6-trimethyl-benzene-1,3-diamine}\) have been prepared. Through this contribution we present the synthesis and characterization of (1)-(5) and X-ray single crystal structure of the representative complex (1). Also, we describe herein our results on cryomagnetic properties of (1) and (2) which display antiferromagnetic and ferromagnetic couplings, respectively. This is the first report dealing with two structurally analogous complexes derived from the same ligand, but having different metal centres exhibiting ferromagnetic and antiferromagnetic coupling.
Materials and Methods

All the reagents were procured from commercial sources and used as received. The solvents were dried and distilled following standard literature procedures.\(^{29}\) The ligand \(N,N^\prime\)-bis(2-hydroxybenzilidene)-2,4,6-trimethylbenzene-1,3-diamine (H\(_2\)L) was prepared and purified following our earlier method.\(^{30}\) Elemental analyses were performed on an Exeter Analytical Inc. (model CE-440) CHN analyser. IR and electronic absorption spectra were acquired on a Perkin-Elmer-577 and Shimadzu UV-1601 spectrophotometers, respectively. \(^1\)H and \(^13\)C NMR spectra in CDCl\(_3\) were obtained on a Jeol AL 300 FT-NMR instrument at an operating frequency of 300 MHz (\(^1\)H) and 75.45 MHz (\(^13\)C). Chemical shifts (\(\delta\)) are given in parts per million (ppm) relative to tetramethylsilane (TMS, \(\delta\) 0.00 ppm). Cyclic voltammetric measurements were performed on a CHI 620c electrochemical analyser at room temperature. The experiments were performed in an air-tight single compartment cell using platinum wire as the counter electrode, a glassy carbon working electrode and Ag/Ag\(^+\) reference electrode.

Magnetic measurements were performed (20 mg) on a Quantum Design SQUID MPMS-XL susceptometer working in the range 2-300 K. The magnetic field was 0.1 T and diamagnetic corrections were made using Pascal’s constants.

**Synthesis of \([\text{Co(C}_2\text{H}_4\text{H}_5\text{N}_2\text{O}_2])_2\] (1)**

To a methanolic solution of L\(^2\) (15 ml, prepared by dissolving H\(_2\)L (0.358 g, 1.0 mmol) and KOH (0.112 g, 2.0 mmol) under stirring over half an hour), Co(NO\(_3\))\(_2\)·6H\(_2\)O (0.465 g, 2.0 mmol) dissolved in methanol (10 ml) was added dropwise and stirred at room temperature for 1 h. Slowly a pink precipitate separated out, which was collected by filtration, washed with methanol and diethyl ether. Pink, block shaped crystals were obtained by slow diffusion of diethyl ether into a dichloromethane solution over a couple of days. Yield: 80 \% (0.660 g) (w.r.t Co(NO\(_3\))\(_2\)·6H\(_2\)O). Anal. (\%) for \(\text{C}_6\text{H}_9\text{Co}_2\text{N}_2\text{O}_2\): Calcd: C, 66.51; H, 4.85; N, 6.74; Found: C, 66.49; H, 4.73; N, 6.63. IR (KBr pellets, cm\(^{-1}\)):

- 3427 (w), 2922 (w), 1603 (vs), 1528 (s), 1439 (s), 1381 (m), 1319 (s), 1185 (m), 1144 (m), 1087 (m), 1022 (w), 981 (w), 920 (w), 831 (vv), 755 (s), 592 (vv), 519 (w). UV-vis (CH\(_2\)Cl\(_2\)), \(\lambda_{max} \text{ nm, } \epsilon M^{-1} \text{ cm}^{-1}\):
- 480 (1.57 \times 10^4), 377 (1.81 \times 10^4), 256 (3.84 \times 10^4).

**Synthesis of \([\text{Cu(C}_2\text{H}_4\text{H}_5\text{N}_2\text{O}_2])_2\]·H\(_2\)O (2)**

Complex (2) was prepared by following the above procedure for (1) using CuNO\(_3\)(PPh\(_3\))\(_2\) (0.651 g, 1.0 mmol) dissolved in a mixture of methanol and dichloromethane (20 ml, 1:1). It was recrystallized from dichloromethane/diethyl ether to afford black crystals. Yield: 35 \% (0.583 g) (w.r.t CuNO\(_3\)(PPh\(_3\))\(_2\)). Anal. (\%) for \(\text{C}_{18}\text{H}_{40}\text{Cu}_2\text{N}_4\text{O}_4\)·H\(_2\)O: Calcd: C, 64.40; H, 4.93; N, 6.53; Found: C, 64.28; H, 4.82; N, 6.29. IR (KBr pellets, cm\(^{-1}\)):

- 3408 (w), 2915 (w), 1606 (vs), 1531 (s), 1441 (s), 1387 (m), 1320 (s), 1193 (m), 1148 (m), 1090 (m), 1031 (w), 916 (w), 831 (vv), 753 (s), 592 (vv), 480 (w). UV-vis (CH\(_2\)Cl\(_2\)), \(\lambda_{max} \text{ nm, } \epsilon M^{-1} \text{ cm}^{-1}\):
- 482 (3.77 \times 10^3), 387 (3.31 \times 10^3), 257 (3.86 \times 10^4).

**Synthesis of \([\text{Ni(C}_2\text{H}_4\text{H}_5\text{N}_2\text{O}_2])_2\] (3)**

It was prepared following the above procedure for (1) except that Ni(NO\(_3\))\(_2\)·6H\(_2\)O was used in place of Co(NO\(_3\))\(_2\)·6H\(_2\)O. Yield: 81 \% (0.669 g) (w.r.t. Ni(NO\(_3\))\(_2\)·6H\(_2\)O). Anal. (\%) for \(\text{C}_{18}\text{H}_{40}\text{Ni}_2\text{N}_4\text{O}_6\): Calcd: C, 66.55; H, 4.86; N, 6.75; Found: C, 66.46; H, 4.73; N, 6.58. IR (KBr pellets, cm\(^{-1}\)):

- 3449 (w), 2918 (w), 1608 (vs), 1531 (s), 1445 (s), 1360 (m), 1326 (s), 1197 (m), 1146 (m), 1082 (m), 1020 (w), 927 (w), 868 (vv), 751 (s), 612 (vv), 498 (w). UV-vis (CH\(_2\)Cl\(_2\)), \(\lambda_{max} \text{ nm, } \epsilon M^{-1} \text{ cm}^{-1}\):
- 440 (5.7 \times 10^3), 328 (1.72 \times 10^4), 254 (3.80 \times 10^3).

**Synthesis of \([\text{Zn(C}_2\text{H}_4\text{H}_5\text{N}_2\text{O}_2])_2\] (4)**

To a suspension containing H\(_2\)L (0.358 g, 1.0 mmol) and KOH (0.112 g, 2.0 mmol) in methanol (15 ml), a solution of (Zn(NO\(_3\))\(_2\))(phen)·2H\(_2\)O (0.472 g, 1.0 mmol) dissolved in the same solvent was added dropwise. The solution was stirred for 4 h and concentrated to dryness under reduced pressure. The solid mass thus obtained was dissolved in dichloromethane, filtered and saturated with diethyl ether to afford white crystalline product, which was separated by filtration, washed with diethyl ether and air dried. Yield 65 \% (0.547 g) (w.r.t. Zn(NO\(_3\))\(_2\))(phen·2H\(_2\)O). Anal. (\%) for \(\text{C}_{18}\text{H}_{40}\text{Zn}_2\text{N}_4\text{O}_6\): Calcd: C, 65.49; H, 4.78; N, 6.64; Found: C 65.42, H 4.82, N 6.64. \(^1\)H NMR: 7.89 (s, 2H, CH=N), 7.36 (t, 2H, J = 7.5 Hz), 7.35 (d, 2H, J = 7.5 Hz), 6.93 (d, 2H, J = 8.4 Hz), 6.85 (s, 1H), 6.60 (t, 2H, J = 7 Hz), 2.30 (3H), 1.5 (s, 6H). IR (KBr pellets, cm\(^{-1}\)):

- 393 (2.9 \times 10^3), 344 (2.3 \times 10^3), 2924 (w), 1609 (vs), 1532 (s), 1342 (m), 1326 (s), 1192 (m), 1143 (m), 1084 (m), 1024 (w), 922 (w), 860 (vv), 753 (s), 648 (vv), 482 (w). UV-vis (CH\(_2\)Cl\(_2\)), \(\lambda_{max} \text{ nm, } \epsilon M^{-1} \text{ cm}^{-1}\):
- 393 (2.9 \times 10^3), 277 (3.12 \times 10^4), 248 (3.22 \times 10^4).
This complex has also been prepared using Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O\textsuperscript{30}. Characterization data matched well with the one prepared from (Zn(NO\textsubscript{3})\textsubscript{2}(phen))2H\textsubscript{2}O with deprotonated H\textsubscript{2}L.

**Synthesis of [Cd(C\textsubscript{6}H\textsubscript{4}NO\textsubscript{2})\textsubscript{2}]\textsubscript{2} (5)**

It was prepared following the above procedure for (1) except that Cd(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O was used in place of Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O. Yield: 79 % (0.737 g). Anal. (%) for C\textsubscript{46}H\textsubscript{40}Cd\textsubscript{3}N\textsubscript{4}O\textsubscript{14}: Calcd: C, 58.92; H, 4.30; N, 5.98; Found: C, 58.89; H, 4.27; N, 5.90. IR (KBr pellets, wavenumbers in cm\textsuperscript{-1}): 3414 (w), 2924 (w), 1603 (vs), 1531 (s), 1449 (s), 1356 (m), 1322 (s), 1194 (m), 1141 (m), 1087 (m), 1027 (w), 921 (w), 863 (w), 754 (s), 1356 (m), 1322 (s), 1194 (m), 1141 (m), 1087 (m), 1027 (w), 921 (w), 863 (w), 754 (s), 642 (vw), 478 (w). \textsuperscript{1}H and \textsuperscript{13}C NMR spectra for (5) could not be recorded due to its poor solubility.

**Crystallographic studies**

Single crystal X-ray data for (1) was obtained on a R-AXIS RAPID II diffractometer at room temperature with Mo-K\textsubscript{α} radiation (\(\lambda = 0.71073\) Å). Structure was solved by direct methods (SHELXS 97) and refined by full-matrix least squares on \(F^2\) (SHELX 97)\textsuperscript{31,32}. Non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and refined using a riding model. Computer program PLATON was used for analyzing the interaction and stacking distances\textsuperscript{33,34}.

Powder X-ray diffraction data (PXRD) for (3) was acquired on a Rigaku D/MAX-2100 diffractometer with Cu-K\textsubscript{α} radiation and a graphite monochromator (wavelength, \(\lambda = 0.154\) nm) over 2\(\theta\) in the range of 20-80° and scan rate of 2° 20/min.

**Results and Discussion**

Hydrated metal nitrates/complexes Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O/CuNO\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}, Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O/[Zn(NO\textsubscript{3})\textsubscript{2}(phen)]2H\textsubscript{2}O, Cd(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O reacted with deprotonated H\textsubscript{2}L to afford dinuclear complexes [Co(C\textsubscript{23}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2})\textsubscript{2}] (1), [Cu(C\textsubscript{23}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2})\textsubscript{2}]2H\textsubscript{2}O (2), [Ni(C\textsubscript{23}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2})\textsubscript{2}] (3), [Zn(C\textsubscript{23}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2})\textsubscript{2}] (4) and [Cd(C\textsubscript{23}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2})\textsubscript{2}] (5)\textsuperscript{26-28}. The synthesis of complexes is depicted in Scheme 1. Notably, the reactions at room temperature afforded exclusively dinuclear complexes with the formulation \([M(C\textsubscript{23}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2})\textsubscript{2}]\) wherein H\textsubscript{2}L chelated the respective metal centres after deprotonation. (Supplementary Data, Fig. S1). To establish the formation of dinuclear complexes \([M(C\textsubscript{23}H\textsubscript{18}N\textsubscript{2}O\textsubscript{2})\textsubscript{2}]\) as the only product, absorption titration studies were performed using 0.1~1.0 equiv of CuNO\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2} and H\textsubscript{2}L. It was observed that in 1:1 molar ratio the absorption spectral features were identical to that for (2), synthesized directly from the reaction of Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O with H\textsubscript{2}L (Supplementary Data, Fig. S2 and 2a) suggesting that the reaction of either CuNO\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2} or Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O with L\textsuperscript{2} afforded (2) as the sole product. Further, the absorption titration studies indicated that complexation is independent of metal-ligand ratio, which has been supported by the reaction of H\textsubscript{2}L and varying the metal to ligand ratio (1: 1 to 1: 0.5).

Due to the steric hindrance of methyl substituents at 2, 4, and 6 positions of the \(m\)-phenylene diamine ring, H\textsubscript{2}L may not be so reactive. In contrast, upon treatment with metal(II) nitrates and/or complexes, it gave \textit{cis}-bis chelated dinuclear complexes at room temperature, which has been confirmed by spectral and structural studies. Despite having three methyl groups, it substituted triphenyl phosphine and 1.10-phenanthroline from CuNO\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2} and [Zn(NO\textsubscript{3})\textsubscript{2}(phen)]2H\textsubscript{2}O, and afforded (2) and (4) confirming high reactivity toward the metal ions. Characterization of (1)-(5) has been achieved by satisfactory elemental analyses and spectral techniques (IR, \textsuperscript{1}H NMR, UV-vis and emission spectra).

**Scheme 1**

Preparation of binuclear complexes (1)-(5)
Crystal structure of (1)

Structure of the representative complex (1) has been determined by X-ray single crystal analyses. It crystallizes in monoclinic system with P2₁/n space group. An ORTEP view along with atom numbering scheme is shown in Fig. 1 and important crystallographic data and selected geometrical parameters summarized in Table 1. Crystal structure determination revealed that the deprotonated ligand crystallizes in monoclinic system with P2₁/n. The distance between two mesitylene spacers are 4.545 Å. Further, the angle between planes containing O1-Co-N1 and O2-Co-N2 is 81.20°, suggesting distorted tetrahedral arrangement of the donor atoms, N1O1 and N2O2, about Co(II). The C–H π interaction between C24 and H17, leads to a 2D spiral network (Supplementary Data, Fig. S3). The interlayer separation in (1) is 4.532 Å.

Simulated PXRD patterns of (1) from single crystal X-ray data and for (3) (Supplementary Data, Fig. S4) show acceptable matches with insignificant differences in 2θ, suggesting that these possesses analogous crystalline phase and that the structure of (3) is similar to that of (1).

Photophysical properties

UV-vis spectra of the ligand and (1)-(4) were acquired in dichloromethane. Electronic absorption spectrum of H₂L displays two bands at 254 and 331 nm (Fig. 2a) assignable to π→π* and n→π* intra-ligand transitions. Significant change in the position of low energy band takes place upon complexation with the metal centre (480, 377, 256, (1); 482, 387, 257, (2); 440, 328, and 254 nm, (3)). The red shift in the position of low energy bands in (1), (2), and (3) with respect to H₂L may arise due to coordination of the ligand through N and O donor atoms. The red shifted weak bands (> 400 nm) may be assigned to metal to ligand charge transfer (MLCT) transition.

Table 1 – Crystal data and refinement parameters and for (1)

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<th>Parameter</th>
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<tr>
<td>Reflections observed [I &gt; 2σ(I)]</td>
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<td>R indices (all data)</td>
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transitions. Complex (4) shows three bands at 393, 277 and 248 nm. The absence of band above 400 nm in this complex may be attributed to the lack of MLCT transitions because of the $d^{10}$ electronic configuration of Zn(II).

In general, ligands possessing salen skeleton exhibit excellent fluorescence in presence of Zn(II) at room temperature (Fig. 2b)\textsuperscript{36-38}. The ligand H₂L itself exhibits a weak fluorescence due to photoinduced electron transfer (PET), which may arise from intramolecular n→π* transitions. Involvement of the lone pair in coordination with the metal centre reduces PET and results in an enhanced fluorescence. As expected, (4) exhibited a 10-fold fluorescence enhancement ($\lambda_{em} = 463$ nm) in comparison to H₂L and other complexes (1)-(3) under investigation. This large enhancement in the fluorescence intensity may be attributed to chelation enhanced fluorescence\textsuperscript{39-44}. Further, (1)-(3) did not show any considerable fluorescence. Complex (5) could not be tested owing to its poor solubility in various solvents. Fluorescence quenching in the case of copper and cobalt complexes may be attributed to its smaller size and paramagnetic behavior\textsuperscript{45}.

EPR spectrum of (2) was obtained at X-band frequency in frozen CH₂Cl₂ solution ($1 \times 10^{-3}$ M) at 120 K (Fig. S5) and at room temperature. The values of $g_\parallel$ and $g_\perp$ in frozen solution at 120 K were 2.19 and 2.071, while 2.23 and 2.09, respectively at room temperature. The $g_\parallel < 2.3$ indicate significant covalent character of the metal ligand bonding\textsuperscript{46}. These parameters, in particular $g_\parallel > g_\perp$, suggested that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ ground state orbital. Indeed, less intense EPR lines in low field side ($g_\parallel$) are indicative of intermediate between $T_d$ and $D_{4h}$ (square planar) and agree well with the geometry of Cu(II) from the crystal structure.

**Magnetic properties**

The magnetic properties of (1) (Co, $T_d$) as $\chi_T$ versus $T$ plot (\(\chi_m\) is the molar magnetic susceptibility for two Co$^{II}$ ion) and the reduced magnetization (M/Nµ$_B$ versus H) is shown in Fig. 3(a). The value of $\chi_mT$ at 300 K is close to 4.2 cm$^3$mol$^{-1}$K, which is as expected for two magnetically quasi isolated spin quartets ($S = 3/2$ with $g > 2.00$). Starting from room temperature, the $\chi_mT$ values decreased smoothly initially and then quickly to 2.5 cm$^3$ mol$^{-1}$ K at 2 K. This feature is characteristic of intramolecular antiferromagnetic interactions. The reduced molar magnetization at 2 K (Fig. 3(a), inset)) indicate that the antiferromagnetic coupling is small, because the shape of curve is practically the Brillouin law with a $M/N\mu_B$ value at 5 $T$ close to 3.1 N\(\mu_B$.

Complex (1) is actually a dinuclear Co(II) entity with distorted $T_d$ geometry (first-order spin-orbit coupling). The fit of susceptibility data has been carried out by means of computer program MAGPACK, which allows calculation of the $D$ parameter of the tetrahedral Co(II) as well as the TIP of the same ion ($S = 3/2$ ions)\textsuperscript{47,48}. The best-fit parameters obtained are $J = -0.21 \pm 0.1$ cm$^{-1}$, $g = 2.03 \pm 0.01$ |D| = 13.2 cm$^{-1}$, TIP$_{Co} = 0.7\times10^{-3}$ cm$^3$ mol$^{-1}$ and $R = 3.1\times10^{-4}$. The noticeable $D$ value for a $T_d$ Co(II) is consistent with the values reported in literature\textsuperscript{49}. Magnetic analyses of Co(II) compounds
are often problematic because of strong magnetic anisotropy at cobalt ions, which cannot be modelled from a simple susceptibility plot. The large metal-metal separations (∼7.3Å) may also be responsible for weak ferromagnetic and antiferromagnetic couplings.

The magnetic properties of (2) as $\chi_M T$ versus $T$ plot ($\chi_M$ is the molar magnetic susceptibility for two Cu$^{II}$ ion) and the reduced magnetization ($M/N\mu_B$ vs $H$) are shown in Fig. 3(b). The value of $\chi_M T$ at 300 K is close to 0.80 cm$^3$ mol$^{-1}$ K, which is as expected for two magnetically quasi isolated spin doublet ($S = 1/2$ ; $g > 2.00$). Starting from room temperature, the $\chi_M T$ values increased quickly to 0.92 cm$^3$ mol$^{-1}$ K at 2 K. This feature is characteristic of intramolecular ferromagnetic interactions. The reduced molar magnetization at 2 K [Fig. 3(b), inset] indicates that the ferromagnetic coupling is small, since the shape of curve is practically the Brillouin law. The $M/N\mu_B$ value at 5 T is close to 1.8 N$\mu_B$, indicating the possibility of the existence of a small zero field splitting ($D$ parameter) of the $S = 1$ ground state.

Complex (2) is actually a dinuclear Cu(II) entity. The fit of susceptibility data has been carried out applying the Bleaney-Bowers formula, using the Hamiltonian $\hat{H} = -JS_1S_2$. The best-fit parameters obtained are $J = + 1.23 \pm 0.1$ cm$^{-1}$, $g = 2.06 \pm 0.01$ and $R = 2.7 \times 10^{-5}$. Small ferromagnetic $J$ value can be interpreted following the literature data on this kind of complexes (or very similar ones). Recently, the synthesis and DFT studies on a very similar copper complex have been reported in which the ferromagnetic coupling could be attributed to a spin polarization mechanism through the aromatic bridges. This feature was studied previously by other workers on analogous systems. On the contrary, very similar complexes show antiferromagnetic behaviour, as has been reported recently by Zhang et al. underlining that these two possibilities (ferro- or antiferromagnetic coupling) apparently depends on very subtle differences and mechanisms.

Conclusions

A novel salicyldiminato Shiff base ligand H$_2$L and five new dinuclear complexes based on it have been synthesized and fully characterized. Structure of (1) has been determined crystallographically. Antiferromagnetic and ferromagnetic behaviour of the structurally similar complexes (1) and (2) have been established by cryomagnetic studies. Further, it has been shown that the zinc complex (4) exhibits strong fluorescent behaviour.

Supplementary Data

CCDC deposition number 743408 for (1) contains the supplementary crystallographic data for complex (1). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the CCDC, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk). Other supplementary data, viz., Figs S1-S4, may be obtained from the authors on request.
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