

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

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Syntheses of the dinuclear complexes [Co(C₂₃H₁₈N₂O₂)₂] (1), [Cu(C₂₃H₁₈N₂O₂)₂·H₂O] (2), [Ni(C₂₃H₁₈N₂O₂)₂] (3), [Zn(C₂₃H₁₈N₂O₂)₂] (4) and [Cd(C₂₃H₁₈N₂O₂)₂] (5) containing the Schiff base ligand 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 areas¹⁻⁶. During the past couple of decades, numerous polymetallic complexes have been successfully designed and synthesized by judicious choice of the metal ion and ligands⁷⁻¹¹. 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 properties¹²⁻¹⁵. In this direction, due to their structural lability and sensitivity to molecular environments, complexes containing oxygen and nitrogen donor Schiff bases have drawn special attention¹⁶⁻²⁰. Structural studies have shown that in salens [salen = 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 complexes²¹⁻²⁴.

Transition metal complexes possessing different exchange coupling patterns offer exciting possibilities in the designing of single molecular magnets

(SMM) and/or single chain magnets²⁵. Achieving ferromagnetic and antiferromagnetic coupling between the metal ions with long metal-metal distances ($> 7.0 \text{ \AA}$) is a challenging task^{22,26-28}. 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^{26-28,21-24}. With the objective of developing such systems, dinuclear complexes [Co(C₂₃H₁₈N₂O₂)₂] (1), [Cu(C₂₃H₁₈N₂O₂)₂·H₂O] (2), [Ni(C₂₃H₁₈N₂O₂)₂] (3), [Zn(C₂₃H₁₈N₂O₂)₂] (4) and [Cd(C₂₃H₁₈N₂O₂)₂] (5), based on 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'*-bis(2-hydroxybenzylidene)-2,4,6-trimethylbenzene-1,3-diamine (H_2L) was prepared and purified following our earlier method³⁰. 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. 1H 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 (1H) and 75.45 MHz (^{13}C). Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS, δ 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 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 $[Co(C_{23}H_{18}N_2O_2)_2]_2$ (1)

To a methanolic solution of L^{2-} (15 ml, prepared by dissolving H_2L (0.358 g, 1.0 mmol) and KOH (0.112 g, 2.0 mmol) under stirring over half an hour), $Co(NO_3)_2 \cdot 6H_2O$ (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 $Co(NO_3)_2 \cdot 6H_2O$). Anal. (%) for $C_{46}H_{40}Co_2N_4O_4$: 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 (vw), 755 (s), 592 (vw), 519 (w). UV-vis (CH_2Cl_2 , λ_{max} nm, $\epsilon M^{-1} cm^{-1}$): 480 (1.57×10^3), 377 (1.81×10^4), 256 (3.84×10^4).

Synthesis of $[Cu(C_{23}H_{18}N_2O_2)_2]_2 \cdot H_2O$ (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. $CuNO_3 \cdot (PPh_3)_2$). Anal. (%) for $C_{46}H_{40}Cu_2N_4O_4 \cdot H_2O$: 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 (vw), 753 (s), 592 (vw), 480 (w). UV-vis (CH_2Cl_2 , λ_{max} nm, $\epsilon M^{-1} cm^{-1}$): 482 (3.77×10^3), 387 (3.31×10^4), 257 (3.86×10^4).

Complex (2) was also prepared by the reaction of $Cu(NO_3)_2 \cdot 3H_2O$ (0.465 g, 2.0 mmol) with H_2L (0.358 g, 1.0 mmol) in presence of KOH (0.112 g, 2.0 mmol). Yield 82 % (wrt $Cu(NO_3)_2 \cdot 3H_2O$)³⁰.

Synthesis of $[Ni(C_{23}H_{18}N_2O_2)_2]_2$ (3)

It was prepared following the above procedure for (1) except that $Ni(NO_3)_2 \cdot 6H_2O$ was used in place of $Co(NO_3)_2 \cdot 6H_2O$. Yield: 81 % (0.669 g) (w.r.t. $Ni(NO_3)_2 \cdot 6H_2O$). Anal. (%) for $C_{46}H_{40}Ni_2N_4O_4$: 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 (vw), 751 (s), 612 (vw), 498(w). UV-vis. (CH_2Cl_2 , λ_{max} nm, $\epsilon M^{-1} cm^{-1}$): 440 (5.7×10^3), 328 (1.72×10^4), 254 (3.80×10^4).

Synthesis of $[Zn(C_{23}H_{18}N_2O_2)_2]_2$ (4)

To a suspension containing H_2L (0.358 g, 1.0 mmol) and KOH (0.112 g, 2.0 mmol) in methanol (15 ml), a solution of $(Zn(NO_3)_2(phen) \cdot 2H_2O)$ (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. $Zn(NO_3)_2(phen) \cdot 2H_2O$). Anal. (%) for $C_{46}H_{40}Zn_2N_4O_4$: Calcd: C, 65.49; H, 4.78; N, 6.64; Found: C 65.42, H 4.82, N 6.46. 1H 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, $J = 7.2$ Hz), 2.30 (s, 3H), 1.5 (s, 6H). IR (KBr pellets, cm^{-1}): 3423 (w), 2924 (w), 1609 (vs), 1532 (s), 1442 (s), 1352 (m), 1326 (s), 1192 (m), 1143 (m), 1084 (m), 1024 (w), 922 (w), 860 (vw), 753 (s), 648 (vw), 482 (w). UV-vis (CH_2Cl_2 , λ_{max} nm, $\epsilon M^{-1} cm^{-1}$): 393 (2.9×10^4), 277 (3.12×10^4), 248 (3.22×10^4).

This complex has also been prepared using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ³⁰. Characterization data matched well with the one prepared from $(\text{Zn}(\text{NO}_3)_2(\text{phen}) \cdot 2\text{H}_2\text{O})$ with deprotonated H_2L .

Synthesis of $[\text{Cd}(\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2)]_2$ (**5**)

It was prepared following the above procedure for (**1**) except that $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was used in place of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Yield: 79 % (0.737 g). Anal. (%) for $\text{C}_{46}\text{H}_{40}\text{Cd}_2\text{N}_4\text{O}_4$: Calcd: C, 58.92; H, 4.30; N, 5.98; Found: C, 58.89; H, 4.27; N, 5.90. IR (KBr pellets, cm^{-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 (vw), 754 (s), 642 (vw), 478 (w). ^1H and ^{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_α radiation ($\lambda = 0.71073 \text{ \AA}$). Structure was solved by direct methods (SHELXS 97) and refined by full-matrix least squares on F^2 (SHELX 97)^{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 analysing the interaction and stacking distances^{33,34}.

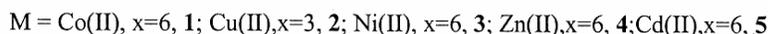
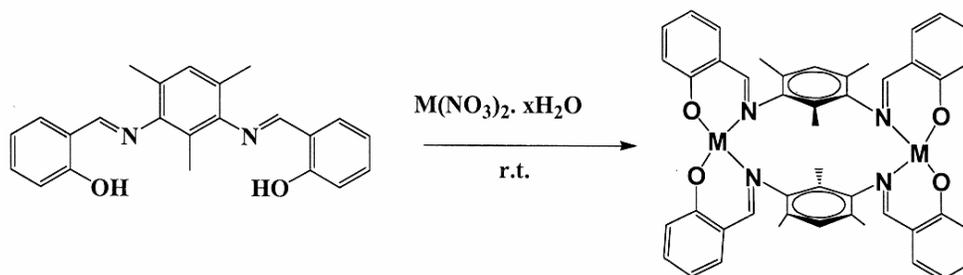
Powder X-ray diffraction data (PXRD) for (**3**) was acquired on a Rigaku D/Max-2100 diffractometer with Cu-K_α radiation and a graphite monochromator (wavelength, $\lambda = 0.154 \text{ nm}$) over 2θ in the range of $20\text{--}80^\circ$ and scan rate of $2^\circ 2\theta/\text{min}$.

Results and Discussion

Hydrated metal nitrates/complexes $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}/\text{CuNO}_3(\text{PPh}_3)_2$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/[\text{Zn}(\text{NO}_3)_2(\text{phen}) \cdot 2\text{H}_2\text{O}]$ $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

reacted with deprotonated H_2L to afford dinuclear complexes $[\text{Co}(\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2)]_2$ (**1**), $[\text{Cu}(\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2)]_2 \cdot \text{H}_2\text{O}$ (**2**), $[\text{Ni}(\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2)]_2$ (**3**), $[\text{Zn}(\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2)]_2$ (**4**) and $[\text{Cd}(\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2)]_2$ (**5**)²⁶⁻²⁸. The synthesis of complexes is depicted in Scheme 1. Notably, the reactions at room temperature afforded exclusively dinuclear complexes with the formulation $[\{\text{M}(\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2)\}_2]$, wherein H_2L chelated the respective metal centres after deprotonation. (Supplementary Data, Fig. S1). To establish the formation of dinuclear complexes $[\{\text{M}(\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2)\}_2]$ as the only product, absorption titration studies were performed using 0.1~1.0 equiv of $\text{CuNO}_3(\text{PPh}_3)_2$ and H_2L . 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 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with H_2L (Supplementary Data, Fig. S2 and 2a) suggesting that the reaction of either $\text{CuNO}_3(\text{PPh}_3)_2$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with L^{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_2L 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_2L may not be so reactive. In contrast, upon treatment with metal(II) nitrates and/or complexes, it gave *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 $\text{CuNO}_3(\text{PPh}_3)_2$ and $[\text{Zn}(\text{NO}_3)_2(\text{phen}) \cdot 2\text{H}_2\text{O}]$, 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, ^1H NMR, UV-vis and emission spectra).



Preparation of binuclear complexes (**1**)-(**5**)

Scheme 1

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 $P2_1/n$ space group. An ORTEP view alongwith 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 L^{2-} bridges and chelates two Co(II) centres through phenolic oxygen and imino nitrogen from two adjacent ligands to form a centrosymmetric complex adopting distorted tetrahedral geometry (Fig. 1).

The Co-N and Co-O bond distances in (**1**) are normal (Supplementary data, Table S1), with an average of 2.000(5) and 1.906(5) Å, respectively. The N(O)-Co-O(N) bite angles range from 92.4(3) to 132.7(3)° (N2-Co1-N1(112.60°), O2-Co1-N2 (95.45°) O2-Co1-O1 (110.8°), O1-Co1-N2 (122.8°), O1-Co1-N1 (95.2°) and O2-Co1-N1 (122.1°)). This observation is consistent with the distorted tetrahedral geometry about Co(II) centre in other related complexes^{26,27}. The distortion in geometry may arise from geometric ligand strain being slightly enhanced by the Jahn-Teller effect of Co(II) ion. Fundamentally, d^7 (Co²⁺) electronic configuration gives a distorted tetrahedral coordination geometry about the metal centre. Two Co(II) centres in **1** are separated through *m*-mesitylene spacer by 7.130 Å, which is slightly longer in comparison with other related complexes^{23,26,27}. The mesitylene rings from two coordinated ligands are *anti* disposed. The interlayer centroid-centroid distance between two mesitylene spacers are 4.545 Å. Complex (**2**) is structurally similar to (**1**) with a

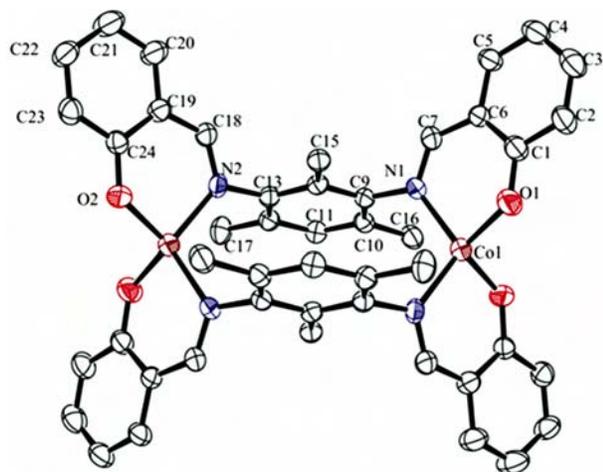


Fig. 1 – ORTEP view of (**1**) (hydrogen atoms omitted for clarity).

slightly longer Cu-Cu distances³⁰. 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 \cdots 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 possess 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 H_2L displays two bands at 254 and 331 nm (Fig. 2a) assignable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ 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 H_2L 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)

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

Empirical formula	C ₄₆ H ₄₀ N ₄ O ₄ Co ₂
FW	830.68
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> (Å)	10.558(2)
<i>b</i> (Å)	15.078(3)
<i>c</i> (Å)	13.178(3)
β (°)	111.39(3)
Volume (Å ³)	1953.4(7)
Color and habit	Red, block
Z	4
Density _{calcd.} (g cm ⁻³)	1.412
Absorption coefficient (mm ⁻¹)	0.899
<i>F</i> (000)	860
Crystal size (mm ³)	0.09 × 0.08 × 0.07
θ range (deg.)	3.09 to 27.45
Reflections collected	17946
Independent reflections	4397 [$R_{int} = 0.0717$]
Reflections/restraint/parameters	4397/0/257
Reflections observed [$I > 2\sigma(I)$]	2244
Goodness-of-fit on F^2	1.088
Final <i>R</i> ind [$I > 2\sigma(I)$]	$R1 = 0.0734$; $wR2 = 0.2007$
<i>R</i> indices (all data)	$R1 = 0.1576$; $wR2 = 0.3018$

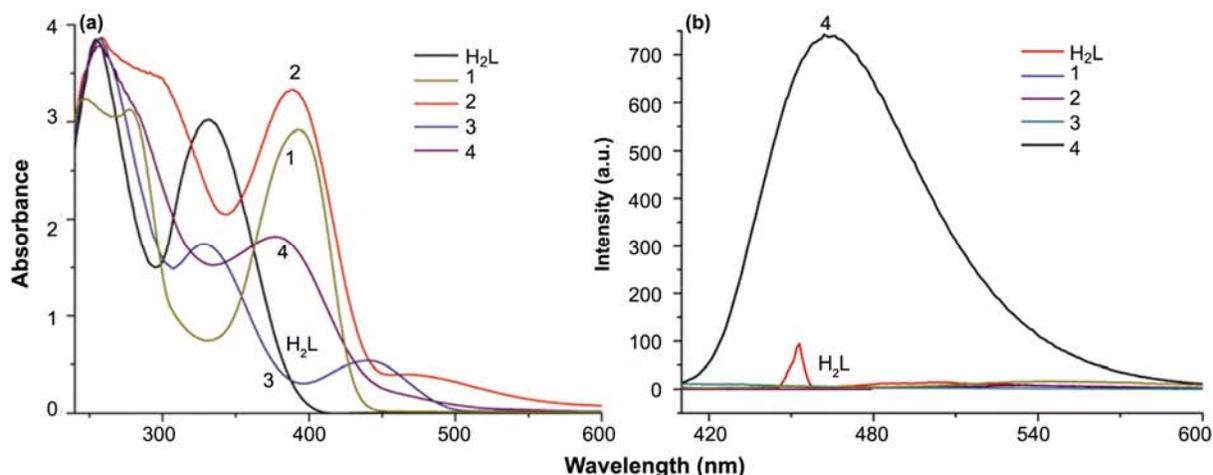


Fig. 2 – (a) UV-vis spectra of (1)-(4) (1×10^{-3} M; dichloromethane) and (b) Fluorescence spectra of H₂L and (1) - (4). [λ_{ex} = 350 nm, λ_{em} = 453 nm for H₂L and 462 nm for (1) - (4) (1×10^{-6} M, dichloromethane).

transitions³⁵. 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)³⁶⁻³⁸. The ligand H₂L itself exhibits a weak fluorescence due to photoinduced electron transfer (PET), which may arise from intramolecular $n \rightarrow \pi^*$ 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 (λ_{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 fluorescence³⁹⁻⁴⁴. 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 behavior⁴⁵.

EPR spectrum of (2) was obtained at X-band frequency in frozen CH₂Cl₂ solution (1×10^{-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 bonding⁴⁶. 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 $\chi_M T$ versus T plot (χ_M is the molar magnetic susceptibility for two Co^{II} ion) and the reduced magnetization ($M/N\mu_B$ versus H) is shown in Fig. 3(a). The value of $\chi_M T$ at 300 K is close to $4.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which is as expected for two magnetically quasi isolated spin quartets ($S = 3/2$ with $g > 2.00$). Starting from room temperature, the $\chi_M T$ values decreased smoothly initially and then quickly to $2.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ 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)^{47,48}. The best-fit parameters obtained are $J = -0.21 \pm 0.1 \text{ cm}^{-1}$, $g = 2.03 \pm 0.01$, $|D| = 13.2 \text{ cm}^{-1}$, $\text{TIP}_{\text{Co}} = 0.7 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ and $R = 3.1 \times 10^{-4}$. The noticeable D value for a T_d Co(II) is consistent with the values reported in literature⁴⁹. Magnetic analyses of Co(II) compounds

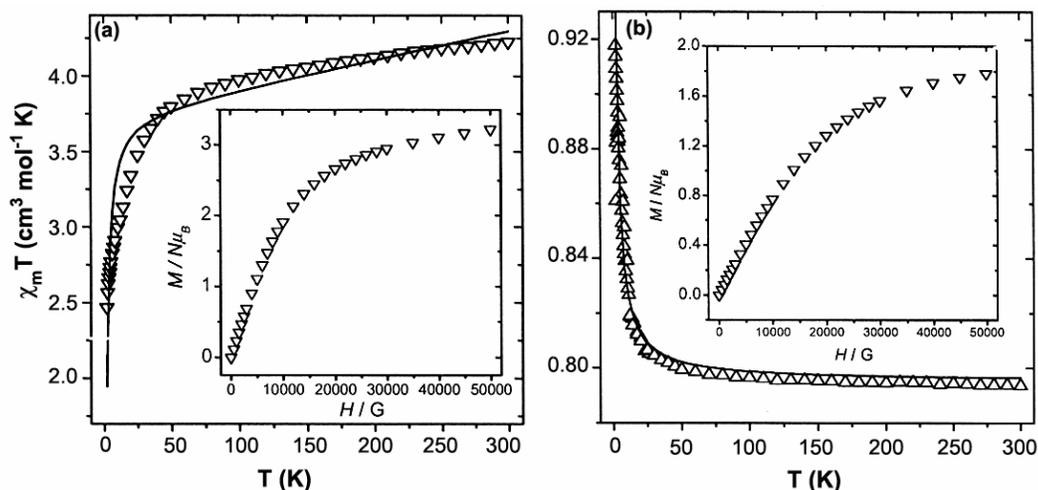


Fig. 3 – Thermal dependence of $\chi_M T$ in (a) complex (1) and (b) complex (2). [The triangles and lines represent, respectively, the experimental data and simulation using the parameters obtained in the fit process; the inset shows M versus H plot per cobalt and copper ion for (1) and (2), respectively at 2 K].

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 ($\sim 7.3 \text{ \AA}$) may also be responsible for weak ferromagnetic and antiferromagnetic couplings.

The magnetic properties of (2) as $\chi_M T$ versus T plot (χ_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 $0.80 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, 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 $0.92 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ 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 $\text{Cu}(\text{II})$ entity. The fit of susceptibility data has been carried out applying the Bleaney-Bowers formula, using the Hamiltonian $\hat{H} = -JS_1S_2$ ⁵⁰. The best-fit parameters obtained are $J = +1.23 \pm 0.1 \text{ cm}^{-1}$, $g = 2.06 \pm 0.01$ 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 bridges²⁶⁻²⁸. This feature was studied previously by other workers on analogous systems²⁶⁻²⁸. On the contrary, very similar complexes show antiferromagnetic behaviour, as has been reported recently by Zhang *et al.*⁵⁰ underlining that these two possibilities (ferro- or antiferromagnetic coupling) apparently depends on very subtle differences and mechanisms⁵¹.

Conclusions

A novel salicyldiminato Schiff base ligand H_2L 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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