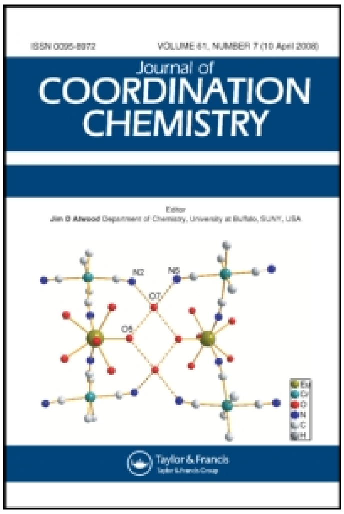

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Synthesis, Spectral and Thermal Studies of BIS-2,6-Dimethanolpyridine Complexes of Co(II), Ni(II), Cu(II) and Zn(II) Saccharinates: Crystal Structures of [Ni(dmpy)$_2$](sac)$_2$·2H$_2$O and [Zn(dmpy)$_2$](sac)$_2$·2H$_2$O

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SYNTHESIS, SPECTRAL AND THERMAL STUDIES OF BIS-2,6-DIMETHANOLPYRIDINE COMPLEXES OF Co(II), Ni(II), Cu(II) AND Zn(II) SACCHARINATES: CRYSTAL STRUCTURES OF $[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$ AND $[Zn(dmpy)_2](sac)_2 \cdot 2H_2O$

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The new transition metal saccharinate complexes of 2,6-dimethanolpyridine (dmpy) have been synthesized and characterized by elemental analyses, magnetic measurements, UV–Vis and IR spectra. Co(II), Ni(II), Cu(II) and Zn(II) form mononuclear octahedral complexes formulated as $[M(dmpy)_2](sac)_2 \cdot H_2O$, where sac is the saccharinate anion. The dmpy ligand coordinates to the metal ions as a tridentate *N*,*O*,*O*′-donor ligand through the amine nitrogen and two hydroxyl oxygen atoms, while the sac ion is present as the counter-ion. The crystal structures of the $[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$ and $[Zn(dmpy)_2](sac)_2 \cdot 2H_2O$ complexes were determined by single X-ray diffraction. The crystals are isostructural with the triclinic crystal system ($P\bar{1}$) and both the Ni(II) and Zn(II) ions have distorted octahedral coordination by two dmpy ligands in a meridional configuration. Both crystal structures are stabilized by hydrogen bonds and aromatic π–π stacking interactions forming a three-dimensional network.

Keywords: Metal saccharinates; 2,6-dimethanolpyridine complexes; Crystal structures; π–π Interactions

INTRODUCTION

Saccharin ($C_7H_5NO_3S$, also named *o*-sulphobenzimide) and its water soluble alkali and earth-alkali salts are widely used as a non-caloric artificial sweetener [1]. Saccharin (sacH) has a dissociable amine proton and is readily deprotonated to form the corresponding saccharinate [sac = $(C_7H_4NO_3S)^-$] anion. The sac anion coordinates to different metal ions [2–9] and its coordination behavior is mainly due to the presence of other co-ligands. The sac anion is directly bonded to the metal ions in some mixed-ligand metal complexes with pyridine [10–13], bipyridine [14–18], dipyridylamine [19], imidazole [20–22], monoethanolamine [23–25] and diethanolamine [25], while bulky ligands such as phenanthroline (phen) [26–28] and triethanolamine (tea) [29–31] usually

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prevent the coordination of sac, which consequently remains outside the coordination sphere as a counter-ion. There are also some complexes in which one sac anion coordinates to the metal ions, while the other sac anion is present as the counter-ion [18,32–34].

As part of our research project on the synthesis, spectral, thermal and structural characterization of mixed-ligand metal complexes of sac with *N* and *O*-donor ligands [23,25,28–31,35–38], the present article reports the synthesis, characterization and spectral properties of the new Co(II), Ni(II), Cu(II) and Zn(II) complexes of 2,6-dimethanolpyridine (dmpy) with sac together with the molecular and crystal structures of $[Ni(dmpy)_2[(sac)_2 \cdot 2H_2O$ and $[Zn(dmpy)_2](sac)_2 \cdot 2H_2O$. Although the crystal structures of the isostructural Co(II) and Cu(II) complexes were reported elsewhere [39], their spectral and thermal data are presented in this article.

EXPERIMENTAL

Materials and Instrumentation

2,6-Dimethanolpyridine (dmpy), sodium saccharinate dihydrate, and all metal salts were purchased from Merck. All other analytical grade chemicals and solvents were purchased commercially and used as received.

Electronic spectra were measured on a Unicam UV2 spectrophotometer in 10^{-3} M methanolic solutions in the 200–800 nm range. IR spectra were recorded on a Mattson FTIR spectrophotometer as KBr pellets. Room temperature magnetic susceptibility measurements were carried out using a Sherwood Scientific MXI model Gouy magnetic balance. The elemental analyses (C, H and N) were carried out at the TUBITAK Marmara Research Centre, using a Carlo Erba 1106 microanalyzer. Thermal analysis curves (TG, DTA and DTG) were obtained using a Rigaku TG8110 thermal analyzer in a static air atmosphere. A sample size of 5–10 mg and a heating rate of 10°C min^{-1} were used.

Preparation of Metal Complexes

The starting metal complexes of sac, $[M(sac)_2(H_2O)_2] \cdot 2H_2O$ (M = Co, Ni, Cu and Zn) were prepared according to the conventional methods described in the literature [3–6]. The bis(saccharinato)tetraaqua Co(II), Ni(II), Cu(II) and Zn(II) complexes (1.0 mmol) were dissolved in the methanol–isopropanol mixture (1 : 1) (30 mL) with stirring and mixed with the dmpy ligand (2.0 mmol) dissolved in methanol (15 mL) at room temperature. The resulting solutions were left to stand at room temperature and allowed to evaporate slowly over a few days for crystallization. The crystals of the metal complexes were collected by suction filtration, washed with acetone and dried in air. Table I lists analytical data together with the decomposition points and colors of the complexes.

X-ray Crystallography

Suitable crystals of the Ni(II) and Zn(II) complexes were mounted on a glass fiber and X-ray diffraction data for both complexes were recorded on a BRUKER SMART 1000 CCD area detector at 298 ± 2 K. The determination of unit cell and

TABLE I Analytical data for the metal complexes

Complexes	*Color*	*Decomp. point*	*Molecular weight*	*Anal. found (calc.)* (%)			*Yield* (%)
				C	*H*	*N*	
$[Co(dmpy)_2](sac)_2 \cdot 2H_2O$ $C_{28}H_{30}N_4O_{12}S_2Co$	Pale pink	176	737.61	45.29 (45.59)	4.24 (4.10)	7.39 (7.60)	81
$[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$ $C_{28}H_{30}N_4O_{12}S_2Ni$	Greenish blue	170	737.39	45.77 (45.61)	4.28 (4.10)	7.33 (7.60)	88
$[Cu(dmpy)_2](sac)_2 \cdot 2H_2O$ $C_{28}H_{30}N_4O_{12}S_2Cu$	Pale blue	147	742.22	45.02 (45.31)	4.29 (4.07)	7.46 (7.55)	86
$[Zn(dmpy)_2](sac)_2 \cdot 2H_2O$ $C_{28}H_{30}N_4O_{12}S_2Zn$	White	130	744.05	45.24 (45.20)	4.09 (4.06)	7.32 (7.53)	87

the data collection were performed with Mo K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods [40] and refined by a full-matrix least-squares procedure [41]. Molecular drawings were obtained using ORTEPIII [42]. Hydroxyl and water hydrogen atoms were found in difference maps and were refined with geometric restraints (O–H = 0.82 Å for both H atoms and H···H = 1.30 Å for water H atom) and with $U_{iso}(H) = 1.5 \times U_{eq}(O)$ [41]. Other H atoms were placed in calculated positions 0.93 Å from their parent carbon atoms with $U_{iso}(H) = 1.2 \times U_{eq}(C)$. The details of data collection, refinement and crystallographic data are summarized in Table II.

RESULTS AND DISCUSSION

Synthesis

Metal complexes of dmpy are very rare and only three metal complexes were reported in the literature [43–45]. The new Co(II), Ni(II), Cu(II) and Ni(II) complexes were synthesized from the reaction of the respective metal saccharinates, $[M(sac)_2(H_2O)_2] \cdot 2H_2O$, with the dmpy ligand in the mixture of methanol and isopropanol. The aqua ligands in the metal saccharinates are labile and readily displaced by neutral ligands. However, the addition of the bulky dmpy ligand to solutions of the aqua complexes resulted in substitution of both the aqua and sac ligands, and the formation of air-stable complexes of $[M(dmpy)_2](sac)_2 \cdot 2H_2O$, where M is Co(II), Ni(II), Cu(II) and Zn(II). The complexes are monomeric with a M : dmpy molar ratio of 1 : 2 and show an octahedral coordination geometry around the metal ions. All complexes contain two lattice water molecules and do not exhibit melting points, but decompose after dehydration at the temperatures given in Table I. All the complexes were obtained in good yields (over 80%) and the analytical data are consistent with the proposed formulation of the complexes, and also confirmed by X-ray crystallography as reported in this article and also elsewhere for the Co(II) and Cu(II) complexes [45]. All the complexes are soluble in methanol, warm water and DMSO, and sparingly soluble in ethanol, and insoluble in acetone.

Description of Crystal Structures

The molecular structure of $[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$ is shown in Fig. 1 and the structure of the Zn(II) complex is not presented, since both structures are identical. The selected

TABLE II Crystal data, data collection and structure refinement parameters for $[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$ and $[Zn(dmpy)_2](sac)_2 \cdot 2H_2O$

Complex	$[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$	$[Zn(dmpy)_2](sac)_2 \cdot 2H_2O$
Empirical formula	$C_{28}H_{30}N_4O_{12}S_2Ni$	$C_{28}H_{30}N_4O_{12}S_2Zn$
Formula weight	737.39	744.05
Temperature (K)	298(2)	298(2)
Radiation (Å)	Mo K_α, 0.71073	Mo K_α, 0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.1544(4)	8.1410(3)
b (Å)	12.4805(5)	12.5163(5)
c (Å)	15.7510(7)	15.7368(7)
α (°)	93.195(1)	92.989(1)
β (°)	97.501(1)	97.608(1)
γ (°)	97.877(1)	98.001(1)
V (Å^3)	1569.85(12)	1569.84(11)
Z	2	2
D_{calcd} (Mg m^{-3})	1.560	1.574
μ (mm^{-1})	0.821	0.985
F(000)	764	768
Crystal size (mm^3)	$0.73 \times 0.30 \times 0.23$	$0.41 \times 0.39 \times 0.20$
θ range (°)	2.18–30.05	2.18–29.99
Index ranges	$-11 \leq h \leq 9$; $-17 \leq k \leq 15$; $-21 \leq l \leq 22$	$-11 \leq h \leq 11$; $-17 \leq k \leq 15$; $-22 \leq l \leq 20$
Reflections collected	13570	12405
Independent reflections	8840 [R(int) = 0.0148]	8911 [R(int) = 0.0179]
Independent reflections (> 2σ)	6904	6577
Absorption correction	Multiscan	Multiscan
Max/min transmissions	0.828/0.744	0.821/0.674
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restrains/parameter	8840/10/448	8911/10/448
Goodness-of-fit on F^2	1.002	0.949
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0334$, $wR2 = 0.0854$	$R1 = 0.0362$, $wR2 = 0.0877$
R indices (all data)	$R1 = 0.0475$, $wR2 = 0.0909$	$R1 = 0.0541$, $wR2 = 0.0940$
Max/min $\Delta\rho$ (e Å^3)	0.344/– 0.359	0.379/– 0.492

bond geometries are summarized in Tables III and IV. These isostructural complexes crystallize in space group ($P\bar{1}$). They consist of a complex cation, two sac ions and two water molecules of crystallization. In the complex cation, the Ni(II) or Zn(II) ions are octahedrally coordinated by a pair of neutral dmpy ligands constituting a MN_2O_4 chromophore with a meridional arrangement. Each dmpy ligand behaves as a tridentate ligand using all donor atoms, the amino N and two hydroxyl O atoms, and forms two five-membered metallocyclic chelate rings, while the sac ions are not involved in coordination and remain outside of the primary coordination sphere.

The M–N bond distances range from 1.9760(13) to 1.9833(13) Å and from 2.0184(14) to 2.0324(14) Å for the Ni(II) and Zn(II) complexes, respectively, while the M–O bond distances are in the range 2.0809(12)–2.1177(12) Å and 2.1373(14)–2.1799(14) Å for the Ni(II) and Zn(II) complexes, respectively. All the bond distances are comparable with those in the corresponding Co(II) and Cu(II) complexes [45]. The M–N bonds are significantly shorter than the M–O bonds in both complexes and this results in formation of a compressed distorted octahedral geometry along the N atoms, since the N atoms occupy axial positions, while the O atoms constitute the plane of the MN_2O_4 core. Significant distortions are also evident from the angles in the coordination polyhedra. The *trans* and *cis* angles are in the range of 156.75(6)–177.16(6)° and

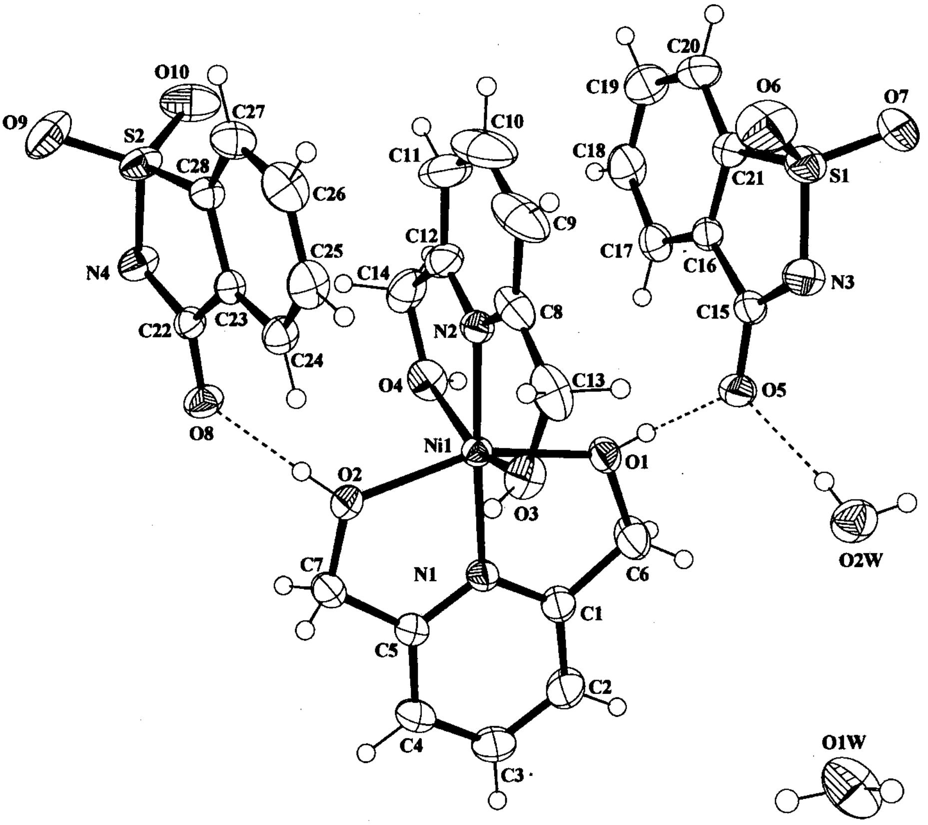

FIGURE 1 Asymmetric unit of $[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$ with the atom numbering scheme. The displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small circles of arbitrary radii.

78.13(5)–103.25(6)°, respectively, for Ni(II), and 153.25(5)–173.74(6)° and 76.46(5)–107.67(6)°, respectively, for Zn(II) complexes. The largest deviations from the ideal values were observed in the N1–M–O4 and O1–M–O2 angles. These distortions are presumably a consequence of the steric constraints imposed by the tripodal dmpy ligand [39].

Both dmpy ligands are essentially planar with an average rms deviation of 0.06(2) Å in the Ni(II) complex and 0.05(2) Å in the Zn(II) complex. The planes of the two dmpy ligands are nearly perpendicular to each other and the dihedral angles between the corresponding planes are 84.10(2)° for both Ni(II) and Zn(II) complexes. Both hydroxyl O atoms deviate slightly from the dmpy planes by *ca.* 0.14(2) Å. The sac anions are also planar with average rms deviations of 0.033 and 0.034 Å for the Ni(II) and Zn(II) complexes, respectively. In both complexes, the sac ions adopt a parallel alignment with each other and dihedral angles between the corresponding planes are 14.75(5) and 15.25(6)° for the Ni(II) and Zn(II) complexes, respectively. One of the pyridine rings (Cg1 = N2–C8–C9–C10–C11–C12) is located between the phenyl rings (Cg2 = C16–C17–C18–C19–C20–C21 and Cg3 = C23–C24–C25–C26–C27–C28) of the two sac ions. The planes of Cg1, Cg2 and Cg3 also adopt a parallel alignment and the dihedral angles between Cg1 and Cg2, and Cg1 and Cg3 are 7.04(13) and 9.82(12)° for the Ni(II) complex, and are

TABLE III Selected bond distances (Å) and angles (°) for $[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$ and $[Zn(dmpy)_2](sac)_2 \cdot 2H_2O$

	$[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$	$[Zn(dmpy)]_2(sac)_2 \cdot 2H_2O$
M–N1	1.9833(13)	2.0324(14)
M–N2	1.9760(13)	2.0184(14)
M–O1	2.0809(12)	2.1373(14)
M–O2	2.1080(12)	2.1528(14)
M–O3	2.1177(12)	2.1799(14)
M–O4	2.1104(12)	2.1503(14)
N1–M–N2	177.16(6)	173.74(6)
N1–M–O1	78.61(5)	76.81(6)
N1–M–O2	78.13(5)	76.46(5)
N1–M–O3	99.22(5)	98.02(6)
N1–M–O4	103.25(6)	107.67(6)
N2–M–O1	99.59(5)	99.71(5)
N2–M–O2	103.64(5)	107.01(5)
N2–M–O3	78.62(5)	76.89(6)
N2–M–O4	78.98(6)	77.63(6)
O1–M–O2	156.75(5)	153.25(5)
O1–M–O3	92.80(5)	93.86(6)
O1–M–O4	93.17(5)	94.56(6)
O2–M–O3	90.88(5)	90.95(6)
O2–M–O4	92.15(5)	92.42(6)
O3–M–O4	157.47(6)	154.17(6)

TABLE IV Hydrogen bonding geometry for $[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$ and $[Zn(dmpy)_2](sac)_2 \cdot 2H_2O$[a]

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	<DHA(°)
$[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$				
O1 H1···O5	0.836(15)	1.733(16)	2.5683(16)	177(2)
O2 H2···O8	0.817(15)	1.810(16)	2.6269(16)	178(2)
O3 H3···O1W#1	0.797(15)	1.852(16)	2.6345(19)	167(3)
O4 H4···O2W#1	0.822(15)	1.809(16)	2.6136(19)	166(3)
O1W H2···O8#2	0.797(16)	2.048(17)	2.8391(18)	171(3)
O1W H1···N4#3	0.800(16)	2.294(18)	3.074(2)	165(3)
O2W H2···O5	0.806(16)	1.996(16)	2.7956(19)	172(3)
O2W H1···O7#4	0.796(16)	2.090(18)	2.846(2)	159(3)
C17 H17···O1	0.93	2.57	3.328(2)	139
C20 H20···O10#5	0.93	2.51	3.275(3)	139
C27 H27···O7#6	0.93	2.57	3.305(2)	136
$[Zn(dmpy)_2](sac)_2 \cdot 2H_2O$				
O1 H1···O5	0.838(16)	1.737(17)	2.5750(18)	178(3)
O2 H2···O8	0.818(16)	1.804(17)	2.6200(18)	175(3)
O3 H3···O1W#1	0.820(17)	1.817(18)	2.624(2)	168(3)
O4 H4···O2W#1	0.812(17)	1.812(18)	2.612(2)	168(3)
O1W H1···O8#2	0.813(17)	2.017(17)	2.815(2)	167(3)
O1W H2···N4#3	0.820(17)	2.243(18)	3.045(2)	166(3)
O2W H1···O5	0.799(17)	1.991(17)	2.782(2)	170(3)
O2W H2···O7#4	0.812(17)	2.078(18)	2.870(2)	165(3)
C17 H17···O1	0.93	2.57	3.344(2)	140
C20 H20···O10#5	0.93	2.55	3.293(3)	137
C27 H27···O7#6	0.93	2.57	3.321(2)	138

[a] Symmetry transformations used to generate equivalent atoms: #1 $x-1, y, z$; #2 $x+2, y, z$; #3 $-x, -y, -z+1$; #4 $-x+1, -y+1, -z+2$; #5 $-x-1, -y, -z+2$; #6 $-x, -y, -z+2$.

6.81(13) and 10.68(12)° for the Cu(II) complex. As a consequence of this packing, the phenyl rings or the sac ions and pyridine rings are connected by weak π–π interactions: Cg1–Cg2 = 3.6302(12) Å and Cg1–Cg3 = 3.5850(11) Å for the Ni(II) complex, and Cg1–Cg2 = 3.6317(12) Å and Cg1–Cg3 = 3.5982(12) Å for the Zn(II) complex.

Due to isomorphism, both crystals also possess similar packing of molecules. Therefore, only the packing diagram of the Ni(II) phase is presented in Fig. 2. The crystals exhibit a number of hydrogen bonds (Table IV). The hydrogen atoms of the hydroxyl H atoms of the dmpy ligands are involved in intermolecular hydrogen bonding with the water molecules and the carbonyl O atoms of the neighboring sac ions, while the H atoms of the two water molecules form bifurcated hydrogen bonds with the negatively charged amine N, carbonyl and sulfonyl O atoms of the sac ions. Additionally, the phenyl H atoms also form weak C–H···O interactions with the hydroxyl and sulfonyl O atoms. The crystal packing is determined by the hydrogen bonding as well as weak aromatic py-sac π–π stacking interactions forming a 3-dimensional network.

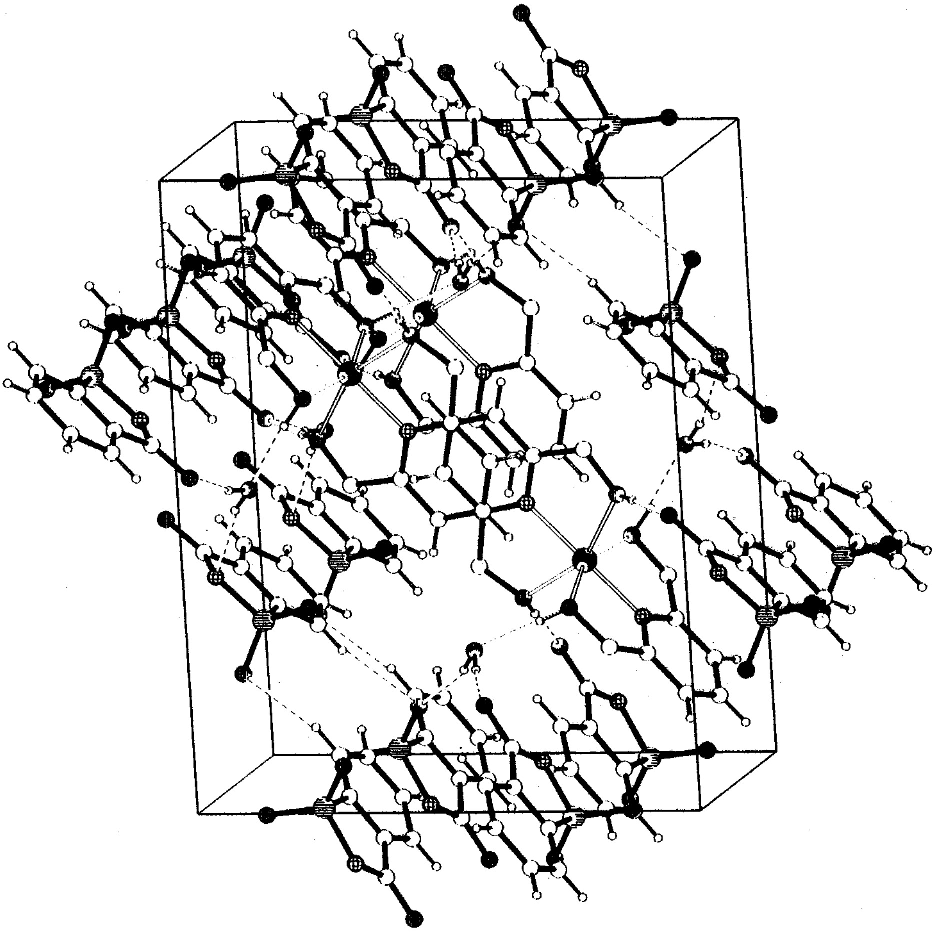

FIGURE 2 Packing diagram of $[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$ showing hydrogen bonding scheme and aromatic π–π interactions.

Spectral and Magnetic Characteristics

The IR spectra of all the complexes resemble each other indicating a similar structural relationship. The most important peaks in the IR spectra of the complexes are given in Table V. The peaks in the frequency range of 3200–3580 cm^{-1} are attributed to the ν(OH) vibrations of both the hydroxyl groups and the lattice water molecules. Splitting and broadening of the peaks indicates the involvement of the hydroxyl groups and water molecules in coordination and hydrogen bonding, respectively. The comparatively weak peaks between 2800 and 3100 cm^{-1} are due to the vibrations of the CH_2 groups of the dmpy ligand. The stretching vibration of C=N of the pyridine ring at *ca.* 1600 cm^{-1} was not clearly observed because of the overlap of the ν(C=O) vibration of the sac ions. However, the N-coordination of the dmpy ligand is confirmed by the adsorption bands at around 610 cm^{-1} due to δ(py) [46]. The ν(C=O) vibrations of sac appear *ca.* 1610 cm^{-1} as very strong bands for all complexes, while the stretching vibrations of ν_{asym} (SO_2) and ν_{sym}(SO_2) occur at *ca.* 1290 and 1160 cm^{-1}, respectively. The medium peaks at about 1555, 1450 and 1362 cm^{-1} correspond to the ring ν(C–C) vibrations. The weak bands below 500 cm^{-1} may be attributed to metal to ligand vibrations [46].

The electronic transitions in the complexes are listed in Table V. The sharp and intense peaks centered at 247 and 274 nm are assigned to the π–π^* and n–π^* transitions in the dmpy ligand. The band at 274 nm overlaps with the transitions of the sac ion in the range 270–300 nm in the metal complexes. The *d–d* transitions are observed between 400 and 950 nm as relatively weak and broad bands and are usually consistent with octahedral geometry [47]. The Zn(II) complex did not display any peak in the visible region, but only exhibits the ligand transitions.

The room temperature magnetic moments indicate that the metal complexes exhibit high-spin configuration. The effective magnetic moments of the Co(II), Ni(II) and Cu(II) complexes are 4.14, 2.93 and 1.53 B.M., respectively, and agree well with the calculated values of the spin-only magnetic moments of the octahedral coordination geometry around the metal ions (Table V).

Thermal Analysis

All the complexes show similar thermal behavior; thermoanalytical data are given in Table VI. The first stage of decomposition corresponds to endothermic dehydration of the complexes and the two lattice water molecules are lost in a single stage in the temperature range 70–150°C to give anhydrous complexes of $[M(dmpy)_2](sac)_2$. The elimination of the two dmpy molecules occurs in the second decomposition stage with two or three endothermic peaks and ends at around 450°C. The IR spectral data of the intermediated formed at 450–460°C suggest the formation of the respective metal saccharinates, which exothermically decompose to give the corresponding metal oxides as the final decomposition products at higher temperatures. The decomposition behavior of the complexes in air is typical for the other complexes containing sac [38]. All the experimental mass loss values are found to be in very good agreement with the corresponding calculated values. The first DTA peak temperatures for the removal of the dmpy ligands follows the order Co (213°C) > Ni (205°C) > Cu (182°C) > Zn (160°C) and may be an indication of the metal–ligand bond strength.

TABLE V IR and electronic spectra and magnetic moments of the metal complexes

Complex	*$\nu(OH)$*	*$\nu(CH)$*	*$\nu(C{=}O)$*	*$\nu_{asym}(SO_2)$*	*$\nu_{sym}(SO_2)$*	λ_{max} (nm)		μ_{eff} (B.M.)	
						Ligand	*d–d*	*Found*	*(Calcd.)*
$[Co(dmpy)_2](sac)_2 \cdot 2H_2O$	3550–3200 sbr	3086w, 2842w	1611vs	1295vs	1159vs	243, 289	515	4.14	(3.87)
$[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$	35560–205 sbr	3085w, 2840w	1613vs	1298vs	1157vs	243, 285	394, 650, > 950	2.93	(2.83)
$[Cu(dmpy)_2](sac)_2 \cdot 2H_2O$	3540–3250 sbr	3079w, 2850w	1607vs	1293s	1161vs	244, 287	770	1.53	(1.73)
$[Zn(dmpy)_2](sac)_2 \cdot 2H_2O$	3550–3200 sbr	3085w, 2838w	1611vs	1295vs	1162vs	234, 258, 290	–	Dia.	

TABLE VI Thermoanalytical data for the metal complexes

Complex	*Stage*	*Temp. range* (°C)	$DTG_{\max}$ (°C)[a]	*Mass loss* (%)		*Total mass loss* (%)		*Solid residue*
				Found	*Calcd.*	*Found*	*Calcd.*	
$[Co(dmpy)_2](sac)_2 \cdot 2H_2O$	1	98–137	122(+)	5.0	4.9			$[Co(dmpy)_2](sac)_2$
	2	176–459	213(+), 385(+)	37.8	37.7			$Co(sac)_2$
	3	465–695	512(−), 566(−)	49.0	49.4	91.8	92.0	Co_2O_3
$[Ni(dmpy)_2](sac)_2 \cdot 2H_2O$	1	111–148	130(+)	5.3	4.9			$[Ni(dmpy)_2](sac)_2$
	2	170–418	205(+), 278(+), 385(+)	37.1	37.7			$Ni(sac)_2$
	3	425–550	510(−), 525(−)	49.3	49.4	91.7	92.0	NiO
$[Cu(dmpy)_2](sac)_2 \cdot 2H_2O$	1	98–140	113(+)	5.0	4.9			$[Cu(dmpy)_2](sac)_2$
	2	159–347	182(+), 252(+), 298(+)	37.3	37.5			$Cu(sac)_2$
	3	355–735	476(−)	49.1	49.0	91.4	91.4	CuO
$[Zn(dmpy)_2](sac)_2 \cdot 2H_2O$	1	72–121	87(+)	5.1	4.8			$[Zn(dmpy)_2](sac)_2$
	2	121–418	160(+), 213(4)	37.3	37.4			$Zn(sac)_2$
	3	420–750	450(−), 574(−)	48.5	49.0	90.9	91.2	ZnO

[a] (+): Endothermic; (−): exothermic.

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Supplementary Data

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication nos. CCDC 172034 for the Ni(II) complex and CCDC 172035 for the Zn(II) complex. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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