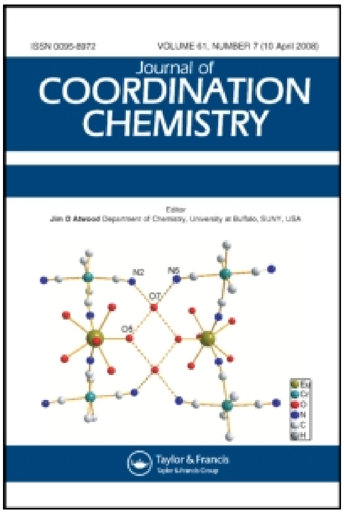

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Synthesis, Spectral and Structural Characterization of the First Bis-2-Pyridylethanol Complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) Saccharinates: Crystal Structures of Diaquabis(2-Pyridylethanol)Iron(II) and Copper(II) Saccharinates

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SYNTHESIS, SPECTRAL AND STRUCTURAL CHARACTERIZATION OF THE FIRST BIS-2-PYRIDYLETHANOL COMPLEXES OF Mn(II), Fe(II), Co(II), Ni(II), Cu(II) AND Zn(II) SACCHARINATES: CRYSTAL STRUCTURES OF DIAQUABIS(2-PYRIDYLETHANOL)IRON(II) AND COPPER(II) SACCHARINATES

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The first 2-pyridylethanol (pyet) complexes of manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) saccharinates, were synthesized and characterized by elemental analyses, magnetic measurements, UV–Vis, and IR spectroscopic techniques. Crystal and molecular structures of the iron(II) and copper(II) complexes were determined by single crystal X-ray diffractometry. The experimental data showed that all the complexes are mononuclear with a general formula $[M(H_2O)_2(pyet)_2](sac)_2$, where sac is the saccharinate anion. All the metal ions are octahedrally coordinated by two aqua and two pyet ligands. The pyet ligand acts as a bidentate ligand through its amine nitrogen and hydroxyl oxygen atoms forming a six-membered chelate ring, while the sac ions remain outside the coordination sphere. All the complexes are isomorphous with a monoclinic space group $P2_1/n$ and $Z = 2$.

Keywords: 2-Pyridylethanol complexes; Metal saccharinates; Crystal structures

INTRODUCTION

Saccharin is widely used as a noncaloric artificial sweetening agent [1]. Its deprotonated form, saccharinate (sac), coordinates to different metal ions rather easily, since it has different donor atoms such as the negatively charged imino nitrogen, one carbonyl and two sulfonyl oxygen atoms. The sac ligand acts as a mono- or bidentate-ligand and in some cases, also as a bridging ligand between two metal centers. Naumov and Jovanovski [2] critically reviewed structural data of metal complexes of this ligand.

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Our own interest in sac lies in the preparation and characterization of metal complexes of the polyfunctional ligand in the presence of other co-ligands especially with hydroxymethyl or hydroxyethyl groups such as ethanolamines and substituted py derivatives. We observed that the coordination behavior of the sac anion 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 monoethanolamine [3–6], diethanolamine [6, 7], monoethanolethylenediamine [8] and 2-pyridylmethanol [9, 10] while bulky ligands such as triethanolamine [11–15] and 2,6-dimethanolpyridine [16, 17] usually prevent the coordination of sac, which consequently remains outside the coordination sphere as a counter-ion. In this article, we report the synthesis and, spectral characterization of new transition metal–sac complexes with 2-pyridylethanol (pyet) together with the single crystal X-ray structures of the iron (II) and copper (II) complexes.

EXPERIMENTAL

Materials and Instrumentation

2-Pyridylethanol, 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 8×10^{-3} M butanol or aqueous solutions in the 200–900 nm range. IR spectra were recorded on a Shimadzu FTIR-8900 spectrophotometer as KBr pellets. Room temperature magnetic susceptibility measurements were carried out using a Sherwood Scientific MXI model Gouy magnetic balance. The C, H, N and S analyses were performed on a Vario EL Elemental Analyzer.

Preparation of the Metal Complexes

The starting bis(saccharinato)tetraaquametal(II) complexes, $[M(sac)_2(H_2O)_4] \cdot 2H_2O$ (M = Mn, Fe, Co, Ni, Cu and Zn) were prepared according to conventional methods described in the literature [18–21]. The manganese(II), iron(II), copper(II) and zinc(II) complexes (1.0 mmol) were dissolved in 30 mL of ethanol, a methanol–butanol mixture (1 : 1), butanol, and methanol, respectively, with stirring whereas the cobalt(II) and nickel(II) complexes were dissolved in distilled water (30 mL). These solutions were mixed with the liquid pyet ligand (2.0 mmol, 0.25 g) at room temperature and 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 iron(II) and copper(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 133 ± 2 K. The determination of unit cell and the intensity data collection were performed with Mo-K_α radiation ($\lambda = 0.71073$ Å). The details of

TABLE I Analytical data for the metal complexes

Complexes	*Color*	*Decomp. Point* (°C)	*Molecular Weight*	*Anal. found (calc.)* (%)				*Yield* (%)
				C	*H*	*N*	*S*	
$[Mn(H_2O)_2(pyet)_2](sac)_2$	White	173	737.61	47.79	4.23	7.75	9.11	42
$C_{28}H_{30}N_4O_{10}S_2Mn$				(47.93)	(4.31)	(7.98)	(9.14)	
$[Fe(H_2O)_2(pyet)_2](sac)_2$	Brown	193	702.55	47.62	4.28	7.84	9.21	43
$C_{28}H_{30}N_4O_{10}S_2Fe$				(47.87)	(4.10)	(7.97)	(9.13)	
$[Co(H_2O)_2(pyet)_2](sac)_2$	Orange	177	705.63	47.35	4.31	7.80	9.25	47
$C_{28}H_{30}N_4O_{10}S_2Co$				(47.66)	(4.28)	(7.94)	(9.09)	
$[Ni(H_2O)_2(pyet)_2](sac)_2$	Blue	172	705.41	47.55	4.34	7.54	9.38	50
$C_{28}H_{30}N_4O_{10}S_2Ni$				(47.67)	(4.28)	(7.94)	(9.09)	
$[Cu(H_2O)_2(pyet)_2](sac)_2$	Pale blue	169	710.24	47.66	3.87	7.98	9.11	42
$C_{28}H_{30}N_4O_{10}S_2Cu$				(47.35)	(4.26)	(7.88)	(9.03)	
$[Zn(H_2O)_2(pyet)_2](sac)_2$	White	102	712.07	46.98	4.27	7.87	9.22	59
$C_{28}H_{30}N_4O_{10}S_2Zn$				(47.23)	(4.25)	(7.87)	(9.00)	

TABLE II Crystal data, data collection and structure refinement parameters for $[Fe(H_2O)_2(pyet)_2](sac)_2$ and $[Cu(H_2O)_2(pyet)_2](sac)_2$

Complex	$[Fe(H_2O)_2(pyet)_2](sac)_2$	$[Cu(H_2O)_2(pyet)_2](sac)_2$
Empirical formula	$C_{28}H_{30}N_4O_{10}S_2Fe$	$C_{28}H_{30}N_4O_{10}S_2Cu$
Formula weight	702.53	710.22
Temperature (K)	133(2)	133(2)
Radiation (Å)	Mo-K_α (0.71073)	Mo-K_α (0.71073)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	8.8359(6)	8.8385(4)
b (Å)	8.7846(6)	8.7972(4)
c (Å)	19.2304(10)	19.0159(10)
α (°)	90	90
β (°)	101.251(3)	100.658(3)
γ (°)	90	90
V (Å^3)	1463.97(16)	1453.06(12)
Z	2	2
D_{calcd} (mg m^{-3})	1.594	1.623
μ (mm^{-1})	0.724	0.962
F (000)	728	734
Crystal size (mm^3)	$0.51 \times 0.38 \times 0.35$	$0.35 \times 0.26 \times 0.26$
θ range (°)	2.16–30.03	2.18–30.03
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-27 \le l \le 27$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-26 \le l \le 26$
Reflections collected	29819	29681
Independent reflections	4270 [R(int) = 0.0184]	4249 [R(int) = 0.0200]
Completeness to $\theta = 30.00°$	99.6%	99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max./min. transmissions	0.7461/0.6521	0.8945/0.7724
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restrains/parameter	4270/0/217	4249/0/217
Goodness-of-fit on F^2	1.077	1.046
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0270$, $wR2 = 0.0795$	$R1 = 0.0235$, $wR2 = 0.0665$
R indices (all data)	$R1 = 0.0292$, $wR2 = 0.0809$	$R1 = 0.0247$, $wR2 = 0.0672$
Max./min. $\Delta\rho$ (e Å^3)	0.463/−0.251	0.363/−0.349

crystal data, data collection and structure refinement are listed in Table II. Absorption corrections (program SADABS) were applied to data sets. The structures were solved by direct methods (SHELXS97) [22] and refined by a full-matrix least-squares procedure on F^2 using SHELXL97 [23]. All nonhydrogen atoms were refined with anisotropic parameters. Hydrogen atoms bonded to carbon were included using a riding model, starting from calculated positions and other hydrogen atoms were refined freely.

RESULTS AND DISCUSSION

Synthesis

To our knowledge, no metal complex of pyet has been reported in the literature and the complexes presented in this article will be the first pyet complexes. The new manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes were synthesized from the direct reaction of the respective metal saccharinates, $[M(sac)_2(H_2O)_4]\cdot 2H_2O$, with the pyet ligand in solution. The substitution mechanism of pyet into the initial aqua metal saccharinato complexes may be suggested as follows. The weakest bound ligands in the initial complexes are the aqua ligands which should be easily displaced by other ligands. However, the addition of the bidentate pyet ligand to the solutions of the initial complexes resulted in the substitution of two aqua ligands in addition to two sac ligands at *trans* positions and the other two aqua ligands remained coordinated to the metal ions. The air-stable complexes formulated as $[M(H_2O)_2(pyet)_2](sac)_2$ are monomeric with a M : pyet molar ratio of 1 : 2 and show an octahedral coordination geometry around the metal ions.

All the complexes were obtained in reasonable yields (over 40%) 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. The complexes do not exhibit melting points and decompose at the temperatures given in Table I. The manganese(II), cobalt(II), nickel(II) and zinc(II) complexes are soluble in water and the iron(II) and copper(II) are soluble in propanol.

Crystal Structures

The crystallographic study reveals that the iron(II) and copper(II) complexes are isomorphous and crystallize in the monoclinic space group $P2_1/n$. The molecular structure of $[Fe(H_2O)_2(pyet)_2](sac)_2$ with the atom numbering scheme is shown in Fig. 1 and the structure of the copper(II) complex is not presented, since both structures are similar. The selected bond lengths and angles are summarized in Table III. The iron(II) and copper(II) complexes consist of a complex cation and two sac ions. In the complex cations, the iron(II) or copper(II) ions sit on a crystallographic center of symmetry and are six coordinated by four oxygen atoms (two from two neutral pyet ligands and two from water ligands) and two nitrogen atoms from two pyet ligands, constituting a centrosymmetric MN_2O_4 chromophore. Contrary to the complexes of 2-pyridylmethanol complexes [10], the sac ions are not involved in coordination and remain outside of the primary coordination sphere. Each pyet ligand acts as a bidentate ligand using all donor atoms, the amino nitrogen and hydroxyl oxygen atoms, and forms a six-membered metallocyclic chelate ring. The amine nitrogen and hydroxyl oxygen atoms of two pyet ligands form the equatorial plane and two water oxygen atoms occupy the axial positions.

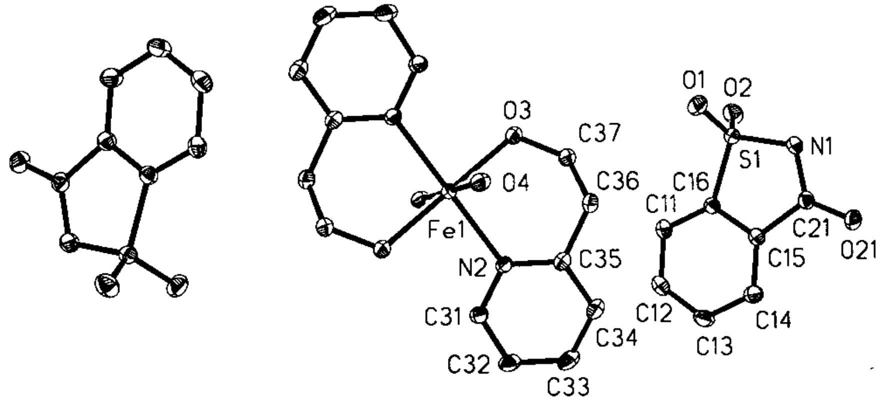

FIGURE 1 A view of $[Fe(H_2O)_2(pyet)_2](sac)_2$ with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are removed for clarity.

TABLE III Selected bond and hydrogen bonding geometry for $[Fe(H_2O)_2(pyet)_2](sac)_2$ and $[Cu(H_2O)_2(pyet)_2](sac)_2$

Bond distances (Å) and angles (°)	$[Fe(H_2O)_2(pyet)_2](sac)_2$	$[Cu(H_2O)_2(pyet)_2](sac)_2$
M–N2	2.1647(8)	2.0088(8)
M–O3	2.1328(8)	2.0412(8)
M–O4	2.1335(8)	2.3117(9)
O3–M–N2	89.23(3)	91.09(3)
O4–M–N2	93.76(3)	95.03(3)
O3–M–O4	92.62(3)	92.48(3)

Hydrogen bonding[a]				
$[Fe(H_2O)_2(pyet)_2](sac)_2$				
D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	< DHA(°)
O4–H41...O2#1	0.82(2)	2.01(2)	2.819(1)	171(2)
O4–H42...N1#2	0.87(2)	1.86(2)	2.721(1)	171(2)
O3–H3...O21#3	0.84(2)	1.83(2)	2.647(1)	166(2)
$[Cu(H_2O)_2(pyet)_2](sac)_2$				
O3–H3...O21#4	0.86(2)	1.78(2)	2.620(1)	167(2)
O4–H41...O2#5	0.85(2)	2.03(2)	2.872(1)	169(2)
O4–H42...N1	0.83(2)	1.93(2)	2.754(1)	170(2)
C33–H33...O1#6	0.95	2.44	3.340(1)	159
C14–H14...O4#7	0.95	2.59	3.274(1)	129

[a] Symmetry transformations used to generate equivalent atoms: #1 $x+1/2, -y-1/2, z-1/2$; #2 $-x+3/2, y+1/2, -z+1/2$; #3 $x-1/2, -y-1/2, z-1/2$; #4 $-x+1, -y, -z+1$; #5 $-x, -y, -z+1$; #6 $-x+1/2, y+1/2, -z+1/2$; #7 $x, y+1, z$.

The M–N bond distances are 2.1647(8) and 2.0088(8) Å for the iron(II) and copper(II) complexes, respectively, while the M–O_{pyet} and M–O_{water} bond distances are 2.1328(8) and 2.1335(8) Å for the iron(II) complex and 2.0412(8) and 2.3117(9) Å for the copper(II) complex. Although the Cu–O_{pyet} bond distance of the copper(II) complex is significantly short, the Cu–N bond distances are comparable with those of the copper(II) complex of the 1,1-di-2-pyridylethanol ligand [24]. All Fe–ligand bonds in the iron(II) complex are similar and form a regular octahedron, while in the copper(II) complex the two Cu–O_{water} bonds directed to the axial positions are significantly longer than both Cu–N_{pyet} and Cu–O_{pyet} bonds at equatorial positions of the coordination polyhedron and this results in the formation of an elongated distorted octahedral geometry along the water oxygen atoms. The distortion in the copper(II) complex is a consequence of the Jahn–Teller effect. The significant distortion in the copper phase is also evident from the angles in the coordination polyhedron. The *cis* angles are in the range of 89.23(2)–93.76(3)° and 91.09(3)–95.03(3)° for the iron(II) and copper(II) complexes, respectively. The largest deviations from the ideal values were observed in the N2–M–O4(water) angle.

The sac anions are essentially planar with average RMS deviations of 0.012 and 0.011 Å for the iron(II) and copper(II) complexes, respectively. The pyet ligands are also planar with an average r.m.s. deviation of 0.008 Å in the iron(II) complex and 0.009 Å in the copper(II) complex. However, the OH groups significantly deviate from the best planes of the pyet ligands by 1.02 and 1.10 Å in the iron(II) and copper(II) complexes, respectively. As a consequence of isomorphism, both iron(II) and copper(II) crystals also possess similar packing of molecules. Therefore, only the packing diagram of the iron(II) phase is presented in Fig. 2. The crystals exhibit a number of hydrogen bonds (Table III). The hydrogen atoms of the water molecules form relatively strong hydrogen bonds with the negatively charged amine N and sulfonyl oxygen atoms of the sac neighboring ions, while the hydrogen atom of the hydroxyl group of the pyet ligands are involved in intermolecular hydrogen bonding with the carbonyl oxygen atoms of the adjacent sac ions. Additionally, some hydrogen atoms of the aromatic rings of pyet and sac in the copper(II) complex also form weak C – H · · · O interactions

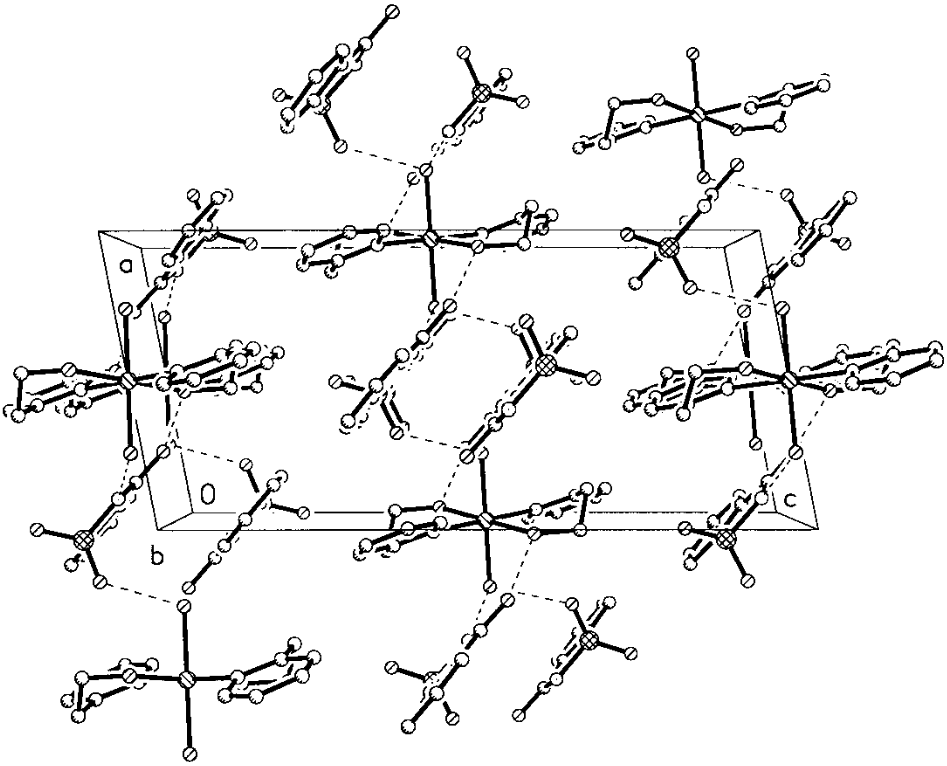

FIGURE 2 Packing diagram of $[Fe(H_2O)_2(pyet)_2](sac)_2$ showing hydrogen bonding scheme.

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

Complexes	*$\nu(OH)$*	*$\nu(CH)$*	*$\nu(C{=}O)$*	*$\nu_{asym}(SO_2)$*	*$\nu_{sym}(SO_2)$*	λ_{max} (nm); ε ($M^{-1}cm^{-1}$)[a]		μ_{eff} (B.M.) *found (calcd.)*
						Ligand	*d–d*	
$[Mn(H_2O)_2(pyet)_2](sac)_2$	3420 s	3950 w, 2840 w	1630 vs	1270 vs	1150 vs	231, 241, 290 (925), (900), (250)	–	5.85 (5.92)
$[Fe(H_2O)_2(pyet)_2](sac)_2$	3398 s	2900 w, 2839 w	1630 vs	1267 vs	1151 vs	227, 254, 278 (1125), (1200), (1300)	368 (107)	5.30 (4.90)
$[Co(H_2O)_2(pyet)_2](sac)_2$	3411 s	2903 w, 2841 w	1628 vs	1267 s	1151 vs	230, 279 (351), (359)	509 (20)	4.17 (3.87)
$[Ni(H_2O)_2(pyet)_2](sac)_2$	3418 s	2903 w, 2841 w	1628 vs	1267 vs	1151 vs	226, 240, 285 (475), (462), (450)	390, 657, 713 (5), (3), (4)	2.75 (2.83)
$[Cu(H_2O)_2(pyet)_2](sac)_2$	3476 s	3068 w, 2899 w	1628 vs	1265 vs	1151 vs	247, 296 (1450), (1475)	578 (400)	1.55 (1.73)
$[Zn(H_2O)_2(pyet)_2](sac)_2$	3420 s	2980 w, 2840 w	1610 vs	1265 vs	1150 vs	225, 272 (1050), (1000)	–	Dia.

[a] ε values given in parentheses.

with the water and sulfonyl oxygen atoms (Table III). The network of the hydrogen bonds stabilizes the crystal packing forming a three-dimensional network.

Spectroscopic Characterization

The IR data support the conclusion that all the complexes studied are isomorphous, since the IR spectra of all the complexes resemble each other indicating a similar structural relationship. Selected IR bands are summarized in Table IV. The absorption bands centered at around $3400\,\mathrm{cm}^{-1}$ are attributed to the ν(OH) vibrations of both the hydroxyl groups and the lattice water molecules. Splitting and broadening of the bands indicates the involvement of the hydroxyl groups and water molecules in coordination and hydrogen bonding, respectively. The comparatively weak bands in the range 2800 and $3100\,\mathrm{cm}^{-1}$ are due to the vibrations of the CH_2 groups of the pyet ligand. The stretching vibration of C=N of the pyridine ring at *ca.* $1600\,\mathrm{cm}^{-1}$ was not clearly observed because of the overlap of the ν(C=O) vibration of the sac ions. The ν(C=O) vibrations of sac appear between 1610 and $1630\,\mathrm{cm}^{-1}$ as very strong bands, while the stretching vibrations of $\nu_{\mathrm{asym}}(SO_2)$ and $\nu_{\mathrm{sym}}(SO_2)$ occur at *ca.* 1265 and $1150\,\mathrm{cm}^{-1}$, respectively. The bands for the SO_2 moiety of the complexes studied seem to be markedly lower than those of the corresponding sac complexes with 2-pyridylmethanol [17]. The IR bands at about 1330 and $970\,\mathrm{cm}^{-1}$ are assigned to the asymmetric and symmetric stretching modes of the CNS unit as proposed by Quinzani [25]. The comparatively weak bands below $500\,\mathrm{cm}^{-1}$ may be attributed to the metal to ligand vibrations [26].

The electronic transitions in the complexes are listed in Table IV. The sharp and intense peaks between 224 and 240 nm are assigned to the π–π^* and n–π^* orbital transitions of the pyet ligand. The transition bands of the sac ion are in the range 270–300 nm. The visible spectra of the cobalt(II), nickel(II) and copper(II) complexes show relatively weak and broad bands, which are due to *d*–*d* transitions and are consistent with octahedral geometry. The zinc(II) complex did not display any peak in the visible region, but only exhibits the intraligand transitions.

Magnetic Susceptibilities

The room temperature magnetic moments of the metal complexes are in the range normally found for a high-spin octahedral configuration (Table IV). The effective magnetic moments of the manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) complexes are 5.85, 5.30, 4.17, 2.75 and 1.55 B.M., respectively, and agree well with the calculated values of the spin-only magnetic moments of the octahedral coordination geometry.

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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 186116 for $[Fe(H_2O)_2(pyet)_2](sac)_2$ and CCDC 186117 for $[Cu(H_2O)_2(pyet)_2](sac)_2$. 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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