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Mn(IV) and Co(III)-complexes of –OH-rich ligands possessing O_2N, O_3N and O_4N cores: syntheses, characterization and crystal structures

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Abstract

Mn(IV) and Co(III) complexes of tridentate –OH-rich ligands possessing O_2N, O_3N and O_4N donor sets were synthesized, characterized and their structures were established by single crystal X-ray diffraction, where the binding core is O_4N_2. In the structurally characterized complexes, the coordination geometry about the metal ion was found to be distorted octahedral.

Keywords: Manganese(IV) complex; Cobalt(III) complex; Crystal structure; Magnetic moment; Hydrogen bonds

1. Introduction

The chemistry of hydroxy- (–OH) containing molecules possessing N, O-donor groups are of interest in developing the coordination chemistry in general and biomimetic chemistry in particular of a number of transition metal ions [1–3]. Manganese is an essential component of various biological redox processes, as in catalases [4], and in photosynthesis by oxidizing water to dioxygen [5,6]. In both the processes, the intermediate generated has manganese in its +4 oxidation state and hence the studies associated with Mn(IV) are important in the coordination and bio-mimetic chemistry. While the preparation and structural characterization of multinuclear complexes containing N, O-donor ligands have been studied extensively [7,8] as models for the active site of the photosynthetic enzymes, those of mononuclear Mn(IV) [9,10] complexes have received less attention. The cobalt–salicylidene complexes act as catalysts for the electro-reduction of oxygen [11,12], which is an important cathodic reaction in energy conversion systems such as fuel cells and batteries. In continuation with our interest [13–15] to understand the role of these N, O-donor ligands towards manganese and cobalt, we have studied their reactivity by systematically changing the amine part of the ligand and/or the number of –OH groups present. Thus, the present paper deals with the results of synthesis, characterization and crystal structure determination of six-coordinated Mn(IV) and Co(III) complexes of molecules exhibiting O_2N ligating core. The ligands used and the complexes reported in the study are shown in the Scheme 1.

2. Experimental

Elemental analysis was carried out on a Carlo-Erba elemental analyzer. FTIR spectra were recorded on a Nicolet Impact 400 machine in KBr matrix. UV–Vis spectrophotometric experiments were performed on a Shimadzu UV2101PC. ^{1}H NMR spectra were recorded on DRX-500 spectrometer in $(CD_3)_2SO$. The FAB mass

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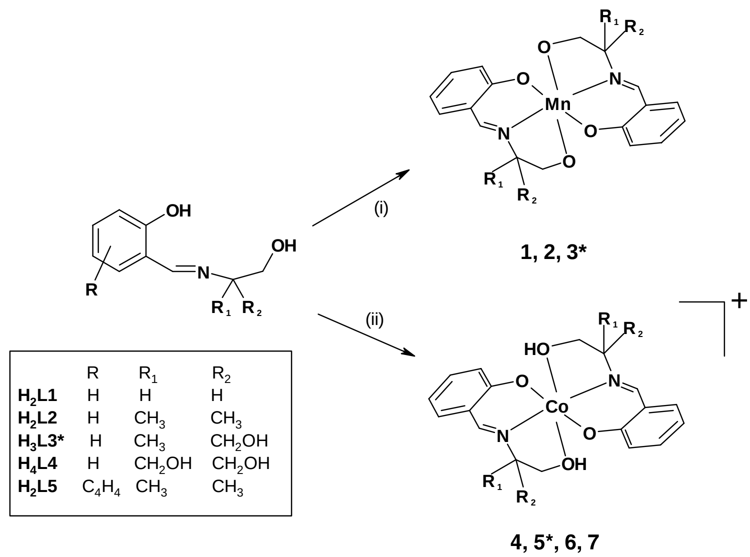

Scheme 1. Manganese and cobalt complexes of –OH-rich molecules. *Structure was established using single crystal XRD study. **1**, **2**, **3**, **4**, **5**, **6**, and **7**, respectively, are $[Mn(L2)_2]$, $[Mn(HL3)_2]$, $[Mn(L5)_2]$, $[Co(HL1)_2]^+$, $[Co(HL2)_2]^+$, $[Co(H_2L3)_2]^+$, $[Co(H_3L4)_2]^+$. Reaction conditions: (i) $KMnO_4$, CH_3CN, RT; (ii) $Co(OAc)_2.4H_2O$, CH_3OH, reflux, 4 h.

spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. *m*-Nitrobenzyl alcohol (NBA) was used as the matrix. Magnetic susceptibility measurements of the complexes at 298 K were carried out on Cahn Instruments Faraday microbalance with curved magnets. All the chemicals used were procured from local sources and purified before use. All the solvents were purified and dried immediately before use. The ligands, H_2L1 to H_2L5 were prepared and confirmed as reported by us earlier [15]. A typical procedure for the syntheses of one of the ligands is presented.

2.1. H_3L3

To salicylaldehyde (1.0 mL, 10 mmol) in MeOH (15 mL) was added 2-amino-2-methyl-1,3-propanediol (1.05 g, 10 mmol) taken in MeOH (15 mL). The reaction mixture was heated to 40 °C for 1 h and then cooled to room temperature followed by concentrating the mixture to result in a thick yellow mass. This was triturated with hexane to form a yellow solid, which was then dried in vacuo. Recrystallization by slow evaporation of the concentrated methanolic solution of the compound kept at room temperature for two days resulted in the formation of needle-shaped single crystals of H_3L3 suitable for X-ray diffraction study. FTIR (KBr, cm^{-1}): 3320 (br, ν_{OH}), 1637 (ss, $\nu_{C=N}$); ^1H NMR (DMSO-d_6, ppm): 8.53 (s, 1H; *H*C=N), 7.44 (d, 1H, Ar*H*), 7.29 (t, 1H, Ar*H*), 6.81 (m, 2H, Ar*H*), 4.83 (s, 1H, CH_2OH), 3.50 (s, 4H, CH_2OH); 1.21 (s, 3H, CH_3).

Irrespective of the ratio of metal to ligand used, all the reactions yielded similar type of products in the corresponding 1:1 and 1:2 reactions. Representative procedures for the syntheses of cobalt and manganese [16] complexes are presented.

2.2. $[Mn(L2)_2]$ (**1**)

The complex, **1** was synthesized by the reaction of H_2L2 (0.386 g, 2 mmol) and $KMnO_4$ (0.158 g, 1 mmol) in CH_3CN (30 ml) with stirring at room temperature. The color of the solution changed from purple to brown and was allowed to stand in dark at room temperature. The resulting precipitate was collected and dried. This was then recrystallized from CH_3CN/diethylether. Yield: 0.341 g (78%); m.p. 188–190 °C; FTIR (KBr, cm^{-1}): 3433 (br, ν_{OH}), 1615 (ss, $\nu_{C=N}$); *Anal.* Calc. for $C_{22}H_{26}N_2O_4Mn$: C, 60.41, H, 5.95, N, 6.41; Found: C, 60.23, H, 6.27, N, 6.73%; FAB mass: $m/e = 438$ ($M^+ + 1$, 100%); UV–Vis (DMSO), λ_{max}/nm, (ε/L mol^{-1} cm^{-1}): 294 (15 990), 343 (9620), 404 (5440), 476 (3040), and 547 (1600).

2.3. $[Mn(HL3)_2]$ (**2**)

This compound was synthesized by adopting the procedure given for **1** except that the ligand used was H_3L3. Yield: 0.302 g (64%); m.p. 170–172 °C; FTIR: (KBr, cm^{-1}) 3403 (br, ν_{OH}), 1610 (ss, $\nu_{C=N}$); *Anal.* Calc. for $C_{22}H_{26}N_2O_6Mn$: C, 56.48, H, 5.54, N, 5.97; Found: C, 56.38, H, 5.70, N, 5.92%; FAB mass: $m/e = 471$ ($M^+ + 2$, 95%); UV–Vis (DMSO), λ_{max}/nm, (ε/L mol^{-1} cm^{-1}): 298 (9950), 345 (6330), 406 (3500), 474 (1961) and 549 (960).

2.4. $[Mn(L5)_2]$ (3)

This complex was synthesized by the reaction of H_2L5 and $KMnO_4$ adopting the procedure given for **1**. The resulting precipitate was collected, dried and recrystallized from CH_3CN/diethylether to result in single crystals of **3** suitable for X-ray diffraction studies. Yield: 0.4075 g (76%); m.p. 200–202 °C; FTIR (KBr, cm^{-1}) 3425 (br, ν_{OH}), 1608 (ss, $\nu_{C=N}$); *Anal.* Calc. for $C_{30}H_{30}N_2O_4Mn$: C, 67.04; H, 5.59; N, 5.21; Found: C, 67.19; H, 5.71; N, 4.70%; FAB mass: $m/e = 539$ ($M^+ + 2$, 55%); UV–Vis (DMSO), λ_{max}/nm, (ε/L mol^{-1} cm^{-1}): 304 (1 12 400), 317 (1 28 300), 359 (84 400), 373 (66 700), 412 (14 830), 426 (10 290), 494 (7260) and 586 (4130).

2.5. $[Co(HL1)_2](CH_3CO_2)(H_2O)$ (4)

To H_2L1 (0.280 mL, 2 mmol) in MeOH (5.0 mL) was added $Co(acetate)_2 \cdot 4H_2O$ (0.2491g, 1.0 mmol) in MeOH (4.0 mL) drop-wise and the resultant reddish-brown reaction mixture was stirred at room temperature for half an hour and then refluxed for 4 h. The reaction mixture was then cooled to room temperature and was filtered. The filtrate along with the washings was concentrated and kept at room temperature to result in crystalline product of **4**. Yield: 0.248 g (55.6%); m.p., 210–212 °C; FTIR (KBr, cm^{-1}): 3431 (br, ν_{OH}), 1648 (ss, $\nu_{C=N}$); ^1H NMR (DMSO-d_6, ppm): 8.46 (s, 1H, *H*C=N), 7.38 (d, 1H, Ar*H*), 6.95 (d, 1H, Ar*H*), 6.52 (d, 1H, Ar*H*), 6.43 (t, 1H, Ar*H*), 4.21 (br, 1H, CH_2OH), 4.12 (m, 2H, CH_2OH), 3.15 (m, 2H, CH_2OH); *Anal.* Calc. for $C_{20}H_{25}N_2O_7Co$: C, 51.74; H, 5.43; N, 6.03; Found: C, 51.96; H, 5.52; N, 6.74%; FAB mass: $m/e = 445$ ($M^+ - 1$, 50%); UV–Vis (CH_3OH), λ_{max}/nm, (ε/L mol^{-1} cm^{-1}): 226 (72 500), 249 (82 600), 350 (6900), 380 (6980), 725 (30) and 752 (40).

2.6. $[Co(HL2)_2](CH_3COO) \cdot CH_3OH$ (5)

To H_2L2 (0.386 g, 2 mmol) in MeOH (3.0 mL) was added dropwise $Co(acetate)_2 \cdot 4H_2O$ (0.2491g, 1.0 mmol) in MeOH (4.0 mL) and the dark reddish-brown solution was refluxed for 4 h. The reaction mixture was then cooled and concentrated when red solid separated out, which was then filtered and washed with hexane by stirring for 3 h. The hexane layer that was pink in color was decanted off and concentrated where upon single crystals of **5** suitable for XRD were formed. Yield: 0.771 g (77%); m.p. 212–214 °C; FTIR (KBr, cm^{-1}): 3460 (br, ν_{OH}), 1636 (ss, $\nu_{C=N}$); ^1H NMR (DMSO-d_6, ppm): 8.31(s, 1H, *H*C=N); 7.46 (d, 1H, Ar*H*), 6.96 (s, 1H, Ar*H*), 6.53(d, 1H, Ar*H*); 6.39(d, 1H, Ar*H*), 4.06 (s, 1H, CH_2OH), 2.89 (s, 2H, CH_2OH), 1.58 (s, 3H, CH_3), 1.49 (s, 3H, CH_3); *Anal.* Calc. for $C_{25}H_{35}N_2O_7Co$: C, 56.18, H, 6.60, N, 5.24; Found: C, 56.50, H, 6.58, N, 5.35%; FAB mass: $m/e = 501$ ($M^+ - 1$, 50%); UV–Vis (CH_3OH), λ_{max}/nm, (ε/L mol^{-1} cm^{-1}): 223 (49 500), 250 (58 600), 380 (5900), 459 (640), 476 (540), 512 (484) and 725 (30).

2.7. $[Co(H_2L3)_2](CH_3COO) \cdot CH_3OH$ (6)

To H_3L3 (0.418 g, 2 mmol) in 10 ml MeOH was added drop-wise $Co(acetate)_2 \cdot 4H_2O$ (0.49819 g, 2.0 mmol) in 20 ml MeOH and the deep-brown solution was stirred at reflux for 4 h. The reaction mixture was then cooled to room temperature and the volume of the solution was reduced when solid product of **6** separated out. This was filtered, washed with methanol and recrystallized. Yield: 0.4404 g (64%); m.p. >270 °C; FTIR (KBr, cm^{-1}): 3376, (br, ν_{OH}), 1633 (ss, $\nu_{C=N}$); ^1H NMR (DMSO-d_6, ppm): 51.01 (s, 1H, *H*C=N), 21.42 (s, 1H, Ar*H*), 14.78 (m, 1H, Ar*H*), 11.62 (s, 1H, Ar*H*), 7.28 (m, 1H, Ar*H*), −1.804 (s, 1H, CH_2OH), 4.15 (m, 2H, CH_2OH), 1.09(s, 3H, CH_3); *Anal.* Calc. for $C_{13}H_{19}NO_6Co$: C, 45.36, H, 5.56, N, 4.07; Found: C, 44.65, H, 5.31, N, 4.27%; FAB mass: $m/e = 533$ ($M^+ - 1$, 90%); UV–Vis (CH_3OH), λ_{max}/nm, (ε/L mol^{-1} cm^{-1}): 272 (14 746), 386 (3957), 518 (503), 658 (72) and 679 (153).

2.8. $[Co(H_3L4)_2](CH_3COO)$ (7)

Compound **7** was synthesized by adopting the procedure given for **6** except using H_4L4. Yield: 0.3545 g (52%); m.p. >200 °C; FTIR (KBr, cm^{-1}): 3308 (br, ν_{OH}), 1632 (ss, $\nu_{C=N}$); ^1H NMR (DMSO-d_6, ppm): 51.41 (s, 1H, *H*C=N); 21.76 (s, 1H, Ar*H*), 11.85 (s, 1H, Ar*H*), 7.28 (m, 2H, Ar*H*), 3.36 (s, 1H, CH_2OH), 4.12 (m, 6H, CH_2OH); *Anal.* Calc. for $C_{24}H_{31}N_2O_{10}Co$: C, 50.89, H, 5.52, N, 4.95; Found: C, 51.71, H, 6.10, N, 5.02%; FAB mass: $m/e = 565$ ($M^+ - 1$, 45%); UV–Vis (DMF), λ_{max}/nm, (ε/L mol^{-1} cm^{-1}): 277 (12 570), 316 (7270), 357 (5420), 525 (199).

3. X-ray crystallography

Diffraction data were collected for $\mathbf{H_3L3}$, **3** and **5** on a Nonius Kappa CCD diffractometer in the ϕ scan + ω scan mode with Mo Kα radiation (0.71069 Å). The structures were determined by direct methods and the refinement of anisotropic thermal parameters based on full-matrix least squares on F^2 were performed using the SHELX 97 [17a] and SIR 92 [17b] programs and the diagrams were generated using ORTEP 3 [18a] and PLUTON 98 programs [18b]. The hydrogen atom positions were all calculated and were treated as riding atoms with fixed thermal parameters. Other details of data collection and structure refinement are provided in Table 1.

Table 1
Summary of crystallographic data for the complexes **3**, **5** and **H_3L3**

	3	**5**	**H_3L3**
Empirical formulae	$C_{30}H_{30}N_2O_4Mn$	$C_{24}H_{31}N_2O_6Co$	$C_{11}H_{15}NO_3$
Molecular weight	537.5	502.44	209.24
T (K)	293(2)	173(2)	293(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/a$	$P2_1$	$P2_12_12_1$
Cell constants			
a (Å)	9.268(5)	10.2447(3)	5.8758(2)
b (Å)	24.356(5)	9.6023(4)	11.2142(3)
c (Å)	11.983(5)	12.2621(4)	16.1711(4)
β (°)	90.510(5)	94.4720(10)	
V (Å^3)	2704.8(19)	1202.58(7)	1065.55(5)
Z	4	2	4
Absorption coefficient, μ (mm^{-1})	0.525	0.755	0.095
D_c (g cm^{-3})	1.320	1.388	1.304
Total reflections	12 666	19 301	1866
Unique reflections	5447	3813	1866
Parameters	352	422	196
R indices (all data)			
R	0.1032	0.0293	0.0430
wR	0.1809	0.0692	0.0836
Final R indices [$I > 2\sigma(I)$]			
R	0.0579	0.0281	0.0356
wR	0.1529	0.0668	0.0800

4. Results and discussions

The reactions of Mn(VII) and Co(II) with H_2L1, H_2L2, H_3L3, H_4L4 and H_2L5 possessing O_2N, O_3N and O_4N donor sets yielded complexes having molecular formulae $[Mn(H_xLy)_2]$ (where $x = 0, 1$; $y = 2, 3, 5$), and $[Co(H_zLy)_2](CH_3COO)$ (where $z = 1, 2, 3$; $y = 1, 2, 3, 4$). In all these complexes the metal ion is bound to two ligand moieties immaterial of whether the reaction is 1:1 or 1:2, thus providing an O_4N_2 ligating core. The complexes were characterized by FTIR, UV–Vis, ^{1}H NMR, FAB mass and room temperature magnetic susceptibility measurements. Structures of one compound each from manganese and cobalt, viz., **3** and **5** were established by single crystal XRD. The crystal structure of one of the ligands, H_3L3, was also determined. The crystallographic data for all these compounds is given in Table 1.

4.1. FTIR and UV–Vis spectra

The FTIR spectra of the compounds **1**–**7** show ν_{OH} and $\nu_{C=N}$ vibrations in the range 3308–3460 and 1608–1648 cm^{-1}, respectively, and the binding of the imine nitrogen was revealed by the lowering of the frequency by about 10–30 cm^{-1}. The presence of acetate group was revealed from the ν_{asym} and ν_{sym} vibrations observed in the regions, 1598 and 1448 cm^{-1}, respectively. An intense absorption band around 360 nm due to phenolate π–π^* transition was observed in all cases. The π–π^* transition associated with the azomethine moiety is shifted to red by 10–15 nm in the manganese complexes and is blue shifted in the cobalt complexes. The shifts are attributed to the binding of the ligand moiety to the respective metal ions.

4.2. ^{1}H NMR studies

The phenolic-OH proton signal disappeared from the spectra of all the complexes **4**–**7** due to the binding of this moiety as Ph–O$^-$ to Co(III). The spectra of **4** and **5** also indicated a down-field shift in the azomethine (–CH=N) proton signal by about 0.2 ppm, suggesting the binding of this nitrogen to Co(III). However, the ^{1}H NMR spectra of **6** and **7** show considerable paramagnetic shift in the positions of all the peaks. Thus in both **6** and **7**, the azomethine proton signal appears as a singlet near 51 ppm and the aromatic proton resonances appear in the region between 7 and 22 ppm. Besides these, peaks due to CH_2 and CH_3 protons are also observed in the ^{1}H NMR spectra. Thus based on ^{1}H NMR spectra, it was possible to derive unambiguously that the complexes are indeed formed.

4.3. Mass spectral studies

The FAB mass spectra of all the complexes showed molecular ion peaks corresponding to their molecular weights consistent with the formulae given (Scheme 1) based on the analytical data as well as with the structures obtained in case of **3** and **5**.

4.4. Magnetic susceptibility measurements

The magnetic susceptibility data at 298 K reveal that **1**, **2** and **3** have a magnetic moment of 3.80, 4.24 and 4.46 μ_B, respectively. These values are marginally higher than the spin only value owing to the incomplete quenching of the orbital magnetic moment by the surrounding ligands. The cobalt complexes, **4**, **5**, **6** and **7** are paramagnetic with magnetic moments (μ_{eff}) of 4.64, 5.15, 4.39 and 4.55 μ_B, respectively. The slight deviation observed with respect to the spin-only value is attributable to the orbital contribution.

4.5. Description of the structure of H_3L3

The ligand assumes an extended configuration where the molecule is involved in an intramolecular H-bond between O(1)–H and N(1). There are three intermolecular H-bond interactions in the lattice; two of which are between O(2) and O(3) mutually connecting the two neighboring molecules. The third intermolecular interaction is between C(9)–H and O(1). The O...O/N (donor–acceptor) distances are in the range 2.63–3.49 Å and O...H–O/N angles are in the range 150°–163°. These can be seen from the data given in Table 3. It is observed that the phenolic proton is transferred to the imine nitrogen in the structure of this molecule as was found earlier in similar molecules reported by us [13,19]. The molecular structure of the ligand is given in Fig. 1. Some important bond lengths and bond angles are given in Table 2.

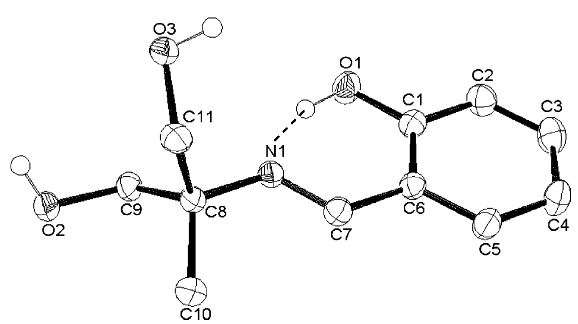

Fig. 1. Molecular structure of H_3L3 showing 50% probability thermal ellipsoids using ORTEP for all non-hydrogen atoms. The dashed (- - -) line shows O–H...N intra-molecular hydrogen bond interaction.

4.6. Molecular structure of 3

Both the H_2L5 ligands present in the coordination sphere act as dianionic and tridentate binding through the O_{phen}, O_{alk} and N_{imi} groups to result in a distorted octahedral Mn(IV) complex of O_4N_2 core with the formula $[Mn(HL5)_2]$. The molecular structure is shown in Fig. 2 and is similar to that reported earlier for Mn(IV) systems containing tridentate ONO ligands [9,10,16]. Selected bond lengths and bond angles are given in Table 2. The bond distances for Mn–O_{phe}, Mn–O_{alk} and Mn–N_{imi} were found to be 1.898(2)–1.914(2), 1.967(3)–1.970(3) and 1.839(2)–1.841(3) Å, respectively. The *trans*-angles observed, 171.0(1)°–173.2(1)° indicate a marginal distortion in the geometry. The bond lengths and bond angles are in agreement with those reported for Mn(IV) complexes [9,16].

Table 2
Selected bond distances (Å) and bond angles (deg) **3**, **5** and H_3L3

3		**5**		H_3L3	
Mn(1)–O(1)	1.839(2)	Co(1)–O(1)	1.8778(16)	C(1)–O(1)	1.356(2)
Mn(1)–O(3)	1.841(3)	Co(1)–O(15)	1.8553(17)	C(1)–C(2)	1.392(2)
Mn(1)–O(4)	1.898(2)	Co(1)–N(9)	1.8983(19)	C(1)–C(6)	1.409(2)
Mn(1)–O(2)	1.914(2)	Co(1)–N(23)	1.9252(19)	C(2)–C(3)	1.383(2)
Mn(1)–N(1)	1.967(3)	Co(1)–O(14)	1.9205(16)	C(3)–C(4)	1.388(3)
Mn(1)–N(2)	1.970(3)	Co(1)–O(28)	1.9464(17)	C(4)–C(5)	1.385(2)
				C(5)–C(6)	1.399(2)
O(1)–Mn(1)–O(3)	93.96(13)	O(1)–Co(1)–N(9)	96.28(8)	C(6)–C(7)	1.456(2)
O(1)–Mn(1)–O(4)	171.58(11)	O(1)–Co(1)–O(14)	178.22(8)	C(7)–N(1)	1.274(2)
O(3)–Mn(1)–O(4)	90.39(12)	O(1)–Co(1)–O(28)	87.89(8)	C(8)–N(1)	1.477(2)
O(1)–Mn(1)–O(2)	90.61(12)	O(1)–Co(1)–N(23)	85.46(8)	C(8)–C(10)	1.523(2)
O(3)–Mn(1)–O(2)	170.95(11)	O(1)–Co(1)–O(15)	91.99(8)	C(8)–C(9)	1.534(2)
O(4)–Mn(1)–O(2)	86.10(11)	N(9)–Co(1)–O(14)	85.27(7)	C(8)–C(11)	1.540(2)
O(1)–Mn(1)–N(1)	91.57(11)	N(9)–Co(1)–O(28)	94.17(7)	C(9)–O(2)	1.425(2)
O(3)–Mn(1)–(1)	83.79(12)	N(9)–Co(1)–N(23)	177.10(8)	C(11)–O(3)	1.422(2)
O(4)–Mn(1)–N(1)	96.07(11)	N(9)–Co(1)–O(15)	86.50(8)		
O(2)–Mn(1)–N(1)	88.28(11)	O(14)–Co(1)–O(28)	91.13(7)	O(1)–C(1)–C(2)	119.19(14)
O(1)–Mn(1)–(2)	83.88(11)	O(14)–Co(1)–N(23)	92.96(7)	O(1)–C(1)–C(6)	121.29(13)
O(3)–Mn(1)–(2)	91.46(12)	O(14)–Co(1)–O(15)	88.97(8)	C(2)–C(1)–C(6)	119.51(14)
O(4)–Mn(1)–(2)	88.81(10)	O(15)–Co(1)–N(23)	95.78(8)	C(5)–C(6)–C(1)	119.07(14)
O(2)–Mn(1)–N(2)	96.80(11)	O(15)–Co(1)–O(28)	179.33(8)	C(5)–C(6)–C(7)	119.09(14)
N(1)–Mn(1)–N(2)	173.19(11)	N(23)–Co(1)–O(28)	83.56(8)	C(1)–C(6)–C(7)	121.73(13)
				C(7)–N(1)–C(8)	120.31(12)

Table 3
Hydrogen bond interaction data for **5** and $\mathbf{H_3L3}$

D–H...A	d(H...A)	d(D...A)	∠DHA	Symmetry
5				
O14–H14A...O52	1.66(2)	2.471(2)	159.0(5)	
O28–H28...O50	1.64(3)	2.453(2)	160.0(7)	
$\mathbf{H_3L3}$				
O1–H1...N1	1.76(3)	2.6307(17)	150.0(2)	
O2–H2...O3	1.90(2)	2.7129(16)	163.0(2)	$[1/2+x, 1/2-y, -z]$
O3–H3...O2	1.88(3)	2.6753(16)	159.0(2)	$[-1+x, y, z]$
C9–H9A...O1	2.53	3.4937	158.0	$[1+x, y, z]$

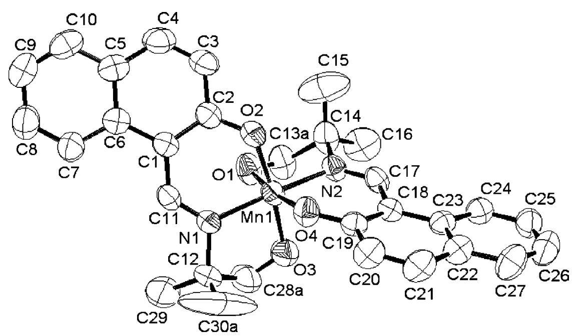

Fig. 2. Molecular structure of **3** showing 50% probability thermal ellipsoids using ORTEP for all non-hydrogen atoms.

4.7. Molecular and crystal lattice structure of 5

Both the H_2L2 ligands present in the coordination sphere act as monoanionic and tridentate bound through O_{phen}, O_{alk} and N_{imi} groups to result in a distorted octahedral Co(III) complex of O_4N_2 core, with a formula $[Co(HL2)_2](CH_3COO)$. The molecular structure is shown in Fig. 3. Selected bond lengths and bond angles are given in Table 2. The Co–O_{phe}, Co–O_{alk}, Co–N_{imi} distances are within the range reported for cobalt complexes [20]. The intermolecular interactions are of both C–H...O and O–H...O type. The O_{alk}–H...O_{oac} interactions are rather strong and exhibit O...O distances of 2.471 and 2.453 Å and O–H...O angles of 159° and 160°. While the two O_{oac} act as acceptors, the –CH_2OH group acts as donor. The stacking of the units of **5** results in the formation of cavities as shown in Fig. 4.

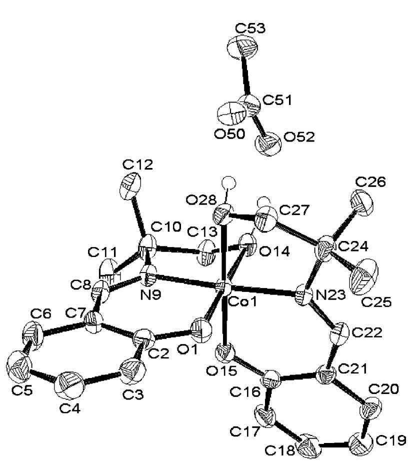

Fig. 3. Molecular structure of **5** showing 50% probability thermal ellipsoids using ORTEP for all non-hydrogen atoms. The counter anion, acetate is also shown.

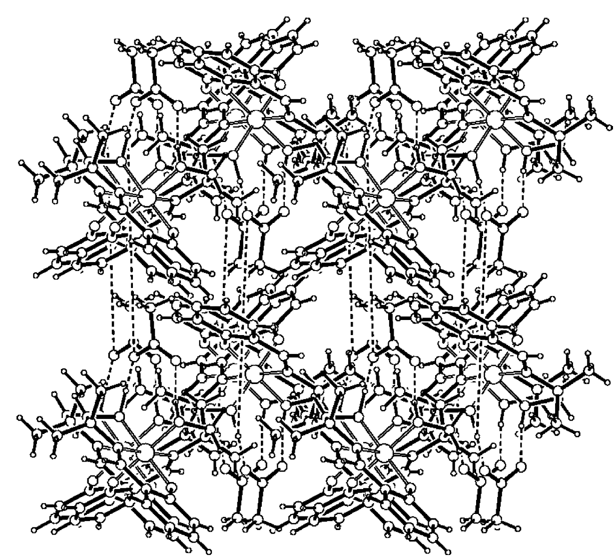

Fig. 4. Packing diagram of **5** showing the cavities formed. The dashed (- - -) lines indicate hydrogen-bond interactions.

5. Conclusions

The ligands H_2L1 to H_2L5 differ only in the number of CH_2OH groups present in it and this reflects on the nature of the substituents. All the reactions resulted in the formation of mononuclear complexes where the metal ion is bound to two ligand moieties. In the manganese complexes, the ligands act as dianionic and are bound to the metal center in a tridentate fashion forming octahedral complexes. Whereas in the cobalt complexes, all these ligands are found to be mono-anionic but bound to the cobalt center in a tri-dentate fashion.

The structurally characterized complexes exhibit distorted octahedral geometry where the distortion is higher in case of **3** as compared to **5**.

6. Supplementary material

Full crystallographic details, excluding structure factors, have been deposited with the Cambridge Crystallographic Data Centre for structure **3** (CCDC 212548), structure **5** (CCDC 212549) and structure $\mathbf{H_3L3}$ (CCDC 212550). These data may be obtained, on request, from the CCDC, 12, Union Road, Cambridge CBZ 1EZ, UK. (Tel.: +44-1223-336408; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/conts/retrieving.html.)

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