Mn(IV) and Co(III)-complexes of –OH-rich ligands possessing O$_2$N, O$_3$N and O$_4$N cores: syntheses, characterization and crystal structures

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Abstract

Mn(IV) and Co(III) complexes of tridentate –OH-rich ligands possessing O$_2$N, O$_3$N and O$_4$N donor sets were synthesized, characterized and their structures were established by single crystal X-ray diffraction, where the binding core is O$_4$N$_2$. 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$_2$N 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$_3$)$_2$SO. The FAB mass
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, H2L1 to H2L5 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. H3L3

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 H3L3 suitable for X-ray diffraction study. FTIR (KBr, cm⁻¹): 3320 (br, OH), 1637 (ss, C=N); 1H NMR (DMSO-d6, ppm): 8.53 (s, 1H; HCN), 7.44 (d, 1H, ArH), 7.29 (t, 1H, ArH), 6.81 (m, 2H, ArH), 4.83 (s, 1H, CH2OH), 3.50 (s, 4H, CH2OH); 1.21 (s, 3H, CH3).

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 H2L2 (0.386 g, 2 mmol) and KMnO4 (0.158 g, 1 mmol) in CH3CN (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 CH3CN/diethyl ether. Yield: 0.341 g (78%); m.p. 188–190°C; FTIR (KBr, cm⁻¹): 3433 (br, OH), 1615 (ss, C=N); Anal. Calc. for C22H26N2O4Mn: 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), λmax/nm, (ε/L mol⁻¹ cm⁻¹): 294 (15990), 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 H3L3. Yield: 0.302 g (64%); m.p. 170–172°C; FTIR (KBr, cm⁻¹): 3403 (br, OH), 1610 (ss, C=N); Anal. Calc. for C22H26N2O6Mn: 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), λmax/nm, (ε/L mol⁻¹ cm⁻¹): 298 (9950), 345 (6330), 406 (3500), 474 (1961) and 549 (960).
2.4. \([\text{Mn}(L5)_2]\) \((3)\)

This complex was synthesized by the reaction of H₂L₅ and KMnO₄ adopting the procedure given for 1. The resulting precipitate was collected, dried and re-crystallized from CH₃CN/diethyl ether 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, νOH), 1608 (ss, νC=N); Anal. Calc. for C₃₀H₂₈N₂O₇Mn: C, 67.04; H, 5.53; N, 5.39; Found: C, 67.19; H, 5.71; N, 4.70%; FAB mass: \(m/e = 539\) (M⁺ + 2, 55%); UV–Vis (DMSO), \(λ_{\text{max/nm}}\, (\alpha/L\text{mol}^{-1} \text{cm}^{-1})\): 304 (112400), 317 (128300), 359 (84400), 373 (66700), 412 (14830), 426 (10290), 494 (7260) and 586 (4130).

2.5. \([\text{Co}(HL1)_2]\) \((CH₃CO₂)\) \((H₂O)\) \((4)\)

To H₂L₁ (0.280 mL, 2 mmol) in MeOH (5.0 mL) was added Co(acetate)₂ \(\cdot\) 4H₂O (0.2491 g, 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, νOH), 1648 (ss, νC=N); \(^1\)H NMR (DMSO-d₆, ppm): 8.46 (s, 1H, \(\text{H} = \text{N}\)); 7.38 (d, 1H, ArH), 6.95 (d, 1H, ArH), 6.52 (d, 1H, ArH), 6.43 (t, 1H, ArH), 4.21 (br, 1H, CH₂OH), 4.12 (m, 2H, CH₂OH), 3.15 (m, 2H, CH₂OH); Anal. Calc. for C₁₃H₁₉NO₆Co: C, 51.74; H, 5.43; N, 5.03; Found: C, 51.96; H, 5.52; N, 6.74%; FAB mass: \(m/e = 445\) (M⁺ + 1, 50%); UV–Vis (CH₃OH), \(λ_{\text{max/nm}}\, (\alpha/L\text{mol}^{-1} \text{cm}^{-1})\): 226 (72500), 249 (82600), 350 (69000), 380 (69800), 725 (30) and 752 (40).

2.6. \([\text{Co}(HL2)_2]\) \((\text{CH}_3\text{COO})\) \cdot \text{CH}_3\text{OH}\) \((5)\)

To H₂L₂ (0.386 g, 2 mmol) in MeOH (3.0 mL) was added dropwise Co(acetate)₂ \(\cdot\) 4H₂O (0.2491 g, 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, νOH), 1636 (ss, νC=N); \(^1\)H NMR (DMSO-d₆, ppm): 8.31 (s, 1H, \(\text{H} = \text{N}\)); 7.46 (d, 1H, ArH), 6.96 (s, 1H, ArH), 6.53(d, 1H, ArH); 6.39(d, 1H, ArH), 4.06 (s, 1H, CH₂OH), 2.89 (s, 2H, CH₂OH), 1.58 (s, 3H, CH₃), 1.49 (s, 3H, CH₃); Anal. Calc. for C₂₅H₂₆N₂O₅Co: 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 (CH₃OH), \(λ_{\text{max/nm}}\, (\alpha/L\text{mol}^{-1} \text{cm}^{-1})\): 223 (49500), 250 (58600), 380 (59600), 459 (6400), 476 (540), 512 (484) and 725 (30).

2.7. \([\text{Co}(H₃L3)]\) \((\text{CH}_3\text{COO})\) \cdot \text{CH}_3\text{OH}\) \((6)\)

To H₃L₃ (0.418 g, 2 mmol) in 10 ml MeOH was added dropwise Co(acetate)₂ \(\cdot\) 4H₂O (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 re-crystallized. Yield: 0.4404 g (64%); m.p. >270 °C; FTIR (KBr, cm⁻¹): 3376, (br, νOH), 1633 (ss, νC=N); \(^1\)H NMR (DMSO-d₆, ppm): 51.01 (s, 1H, \(\text{H} = \text{N}\)), 21.42 (s, 1H, ArH), 14.78 (m, 1H, ArH), 11.62 (s, 1H, ArH), 7.28 (m, 1H, ArH), –1.804 (s, 1H, CH₂OH), 4.15 (m, 2H, CH₂OH), 1.09(s, 3H, CH₃); Anal. Calc. for C₁₅H₁₉NO₅Co: 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 (CH₃OH), \(λ_{\text{max/nm}}\, (\alpha/L\text{mol}^{-1} \text{cm}^{-1})\): 272 (14746), 386 (3957), 518 (503), 658 (72) and 679 (153).

2.8. \([\text{Co}(H₄L4)]\) \((\text{CH}_3\text{COO})\) \((7)\)

Compound 7 was synthesized by adopting the procedure given for 6 except using H₄L₄. Yield: 0.3545 g (52%); m.p. >200 °C; FTIR (KBr, cm⁻¹): 3308 (br, νOH), 1632 (ss, νC=N); \(^1\)H NMR (DMSO-d₆, ppm): 51.41 (s, 1H, \(\text{H} = \text{N}\)); 21.76 (s, 1H, ArH), 11.85 (s, 1H, ArH), 7.28 (m, 2H, ArH), 3.36 (s, 1H, CH₂OH), 4.12 (m, 6H, CH₂OH); Anal. Calc. for C₁₈H₂₆N₂O₅Co: 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), \(λ_{\text{max/nm}}\, (\alpha/L\text{mol}^{-1} \text{cm}^{-1})\): 277 (12570), 316 (7270), 357 (5420), 525 (199).

3. X-ray crystallography

Diffraction data were collected for H₂L₃, 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.
4. Results and discussions

The reactions of Mn(VII) and Co(II) with H2L1, H2L2, H3L3, H4L4 and H2L5 possessing O2N, O3N and O4N donor sets yielded complexes having molecular formulae \([\text{Mn}(\text{H}^x\text{L}^y)^2]\) (where \(x = 0, 1; y = 2, 3, 5\)), and \([\text{Co}(\text{H}^z\text{L}^y)^2](\text{CH}_3\text{COO})\) (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 O4N2 ligating core. The complexes were characterized by FTIR, UV–Vis, 1H 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, H3L3, 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 νOH and νC=NH 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 νasym and νsym 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. 1H 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\(_2\)–NH) proton signal by about 0.2 ppm, suggesting the binding of this nitrogen to Co(III). However, the 1H 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 1H NMR spectra. Thus based on 1H 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 μ₀, 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 (μeff) of 4.64, 5.15, 4.39 and 4.55 μ₀, 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 H₃L₃

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.

![Molecular structure of H₃L₃](image)

Fig. 1. Molecular structure of H₃L₃ showing 50% probability thermal ellipsoids using ORTEP for all non-hydrogen atoms. The dashed (- - -) line shows O–H...N intra-molecular hydrogen bond interaction.

### Table 2

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<th>3</th>
<th>5</th>
<th>H₃L₃</th>
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<td>Co(1)–O(1)</td>
<td>C(1)–O(1)</td>
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<td>C(1)–C(2)</td>
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<td>1.841(3)</td>
<td>1.8553(17)</td>
<td>1.392(2)</td>
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<td>Mn(1)–O(4)</td>
<td>Co(1)–N(9)</td>
<td>C(1)–C(6)</td>
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<td>1.8983(19)</td>
<td>1.409(2)</td>
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<td>Co(1)–N(23)</td>
<td>C(2)–C(3)</td>
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<td>C(3)–C(4)</td>
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<td>1.9205(16)</td>
<td>1.388(3)</td>
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4.6. Molecular structure of 3

Both the H₂L₅ ligands present in the coordination sphere act as dianionic and tridentate binding through the Oₚhen, Oₘ₀₉ and Nₐ₈ groups to result in a distorted octahedral Mn(IV) complex of O₅N₂ 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–Oₚₙ, Mn–Oₘ₀₉ and Mn–Nₐ₈ 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].
Both the H₂L₂ 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 O₄N₂ core, with a formula [Co(HL₂)₂](CH₃COO). The molecular structure is shown in Fig. 3. Selected bond lengths and bond angles are given in Table 2. The Co–O_{phen}, 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 –CH₂OH group acts as donor. The stacking of the units of 5 results in the formation of cavities as shown in Fig. 4.

5. Conclusions

The ligands H₂L₁ to H₂L₅ differ only in the number of CH₂OH 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.

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Table 3
Hydrogen bond interaction data for 5 and H₃L₃

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<th>D–H...A</th>
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<th>d(D...A)</th>
<th>( \angle )DHA</th>
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<td>160.0(7)</td>
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Fig. 2. Molecular structure of 3 showing 50% probability thermal ellipsoids using ORTEP for all non-hydrogen atoms.

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.
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 H3L3 (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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