Polyhedron 28 (2009) 1197-1204

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



First row transition metal complexes of benzyl N'-(2-methoxybenzoyl) hydrazinecarbodithioate (H₂mbhcd): X-ray structures of [Mn(Hmbhcd)₂(*o*-phen)] · DMSO and [Mn₂(Hmbhcd)₂(2,2'-bpy)₂(μ -OAc)₂]

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ARTICLE INFO

Article history: Received 17 October 2008 Accepted 31 December 2008 Available online 9 March 2009

Keywords: N'-acylhydrazinecarbodithioate Mixed ligand complexes Single crystal X-ray Face to edge (C-H \cdots π) interaction Face to face ($\pi \cdots \pi$) interaction

1. Introduction

S-Benzoyldithicarbazate and its derivatives have been under study for many years [1–4], and their properties can be greatly enhanced by the introduction of different substituents [5–9]. These ligands are versatile chelating agents and react with transition metal ions yielding stable metal complexes which are promising bioactive molecules [10-13]. The bioactivity of compounds has been found to be highly dependent on the identity of the metal and the binding sites of the ligands [14–16]. The manganese ion plays an important role in biological systems as the active site of some enzymes [17] and their complexes exhibit interest due to their catalytic antioxidant activity in blocking trace oxidant in vitro [18]. We have reported the synthesis and X-ray studies of N'-(pyridine-3-carbonyl)hydrazine carbodithioic acid ethyl ester (H₂pchc) and N'-(2-methoxybenzoyl)hydrazinecarbodithioic ethyl ester and their Mn(II) and Cd(II) complexes [19,20]. Having been encouraged by these results, we extended our studies on new NOS donor ligands and their metal complexes. In view of the above and with the aim of elucidating the coordination geometry of the complexes of this class of ligands, containing similar -NH-(C=S)SR- skeletal backbones, benzyl N'-(2-methoxybenzoyl)hydrazinecarbodithioate {H₂mbhcd} and its Mn(II), Co(II) and Ni(II) complexes were synthesized and characterized by spectroscopic methods. The single crys-

ABSTRACT

The ligand benzyl *N*-(2-methoxybenzoyl)hydrazinecarbodithioate (H₂mbhcd) (1), having a NOS donor sequence, formed a series of complexes $[M(Hmbhcd)_2]_n \{M = Mn(II), Co(II) \text{ and } Ni(II) (2, 5 \text{ and } 6)\}, [Mn(Hmbhcd)_2(o-phen)] \cdot DMSO (3) and <math>[Mn_2(Hmbhcd)_2(2,2'-bpy)_2(\mu-OAc)_2]$ (4). The complexes 3 and 4 have been obtained as single crystals, containing *o*-phen/2,2'-bpy as coligands. The compounds 2, 5 and 6 have been characterized with the aid of elemental analyses, IR, UV–Vis, magnetic susceptibility and mass spectrometry. Compound 3 crystallized in the triclinic system with the space group $P\overline{1}$ while 4 crystallized in the monoclinic system with the space group $P2_1/c$. The (N,O) donor sites of the uninegative bidentate ligand chelates the Mn(II) center to form a five-membered MnOCN₂ ring in both complexes 3 and 4.

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tals of the Mn(II) complexes were also grown by enhancing their solubility using *o*-phen/2,2'-bpy as coligands and DMSO (dimethyl sulfoxide) solvent.

2. Experimental

2.1. Materials and method

Commercial reagents were used without further purification and all experiments were carried out in the open atmosphere. Methyl 2-methoxy-benzoate was purchased from Sigma Aldrich and was used as such. Carbon disulfide and hydrazine hydrate (SD Fine Chemicals, India) and the solvents (Merck Chemicals, India) were used in the syntheses.

2.2. Preparation of benzyl N'-(2-methoxybenzoyl)hydrazinecarbodithioate (H₂mbhcd)

The preparation and X-ray crystallographic studies of benzyl N'-(2-methoxybenzoyl)hydrazinecarbodithioate (H₂mbhcd) (Fig. 1) has been published elsewhere [21]. M.p. 180 °C.

2.2.1. H₂mbhcd (1)

IR (vcm⁻¹, KBr): v(NH) 3127 m, 3068 m; v(>C=O) 1641s; thioamide I [β (NH) + v(CN)] 1467s; thioamide II [v(CN) + β (NH)] 1250s; v(N–N) 1046 m; v(>C=S) 905; v(CH₂) 2938. ¹H NMR (d_6 -DMSO; δ ppm): 10.73, 10.55 (1H, –NH), 4.56 (m, 2H, >CH₂),



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^{0277-5387/\$ -} see front matter \odot 2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2008.12.061



Fig. 1. Benzyl N'-(2-methoxybenzoyl)hydrazinecarbodithioate.

3.65 (m, 3H, $-\text{OCH}_3$), 7.76-7.10 (9H, aromatic protons). ¹³C NMR (d_6 -DMSO, δ ppm): 56.25 ($-\text{OC}^1\text{H}_3$), 157.25 (C²), 112.31 (C³), 136.97 (C⁴), 121.09 (C⁵), 129.08 (C⁶), 119.21 (C⁷), 164.55 (>C⁸=O), 202.22 (>C⁹=S), 38.04 (>C¹⁰H₂), 133.91 (C¹¹), 128.42 (C¹², C¹⁶), 130.63 (C¹³, C¹⁵), 127.26 (C¹⁴). UV–Vis [λ_{max} , DMSO, nm]: 330, 301, 278, 242.

2.3. Preparation of the complexes

2.3.1. Preparation of $[M(Hmbhcd)_2]_n$ {M = Mn(II) 2, Co(II) 5 and Ni(II) 6}

The complexes **2**, **5** and **6** were prepared by stirring a solution of H_2 mbhcd (2 mmol) in MeOH/CHCl₃ (25 ml) with a solution of $M(OAc)_2 \cdot XH_2O$ (1 mmol) in MeOH for 3–4 h at room temperature. The resulting precipitate was filtered off, washed with an ethanol-chloroform mixture and dried at room temperature under vacuum. The yield ranged from 58% to 67%.

2.3.1.1. [*Mn*(*Hmbhcd*)₂]_n (**2**). Mustard yellow, yield 58%; M.p. 190 °C, μ_{eff} = 5.98 BM. *Anal. Calc.* for C₃₂H₃₀MnN₄O₄S₄ (717.39): C, 53.55; H, 4.21; N, 7.81; S, 17.87; Mn, 7.65. Found: C, 53.12; H, 4.37; N, 8.01; S, 17.69; Mn, 7.99%. IR (vcm⁻¹, KBr): v(NH) 3179 m; v(>C=O) 1601s; thioamide I [β (NH) + v(CN)] 1511s; thioamide II [v(CN) + β (NH)] 1299s; v(N–N) 1102 m; v(>C=S) 842; v(CH₂) 2958. UV–Vis [λ_{max} , DMSO, nm]: 550, 335, 311, 288. MS(FAB) *m*/*z* = 718 [M]⁺.

2.3.1.2. $[Co(Hmbhcd)_2]_n$ (**5**). Dark yellow, yield 62%; M.p. 233 °C (d); μ_{eff} = 5.11 BM. *Anal.Calc.* for C₃₂H₃₀CoN₄O₄S₄ (721.79): C, 53.25; H, 4.19; N, 7.76; S, 17.77; Co, 8.16. Found: C, 53.07; H, 4.18; N, 7.56; S, 16.99; Co, 7.78%. IR (v cm⁻¹, KBr): v(NH) 3179 m; v(>C=O) 1598s; thioamide I [β (NH) + v(CN)] 1514s; thioamide II [v(CN) + β (NH)] 1301s; v(N–N) 1102 m; v(>C=S) 842; v(CH₂) 2925. UV–Vis [λ_{max} . DMSO, nm]: 592, 445, 320. MS(FAB) m/z = 722 [M]⁺.

2.3.1.3. $[Ni(Hmbhcd)_2]_n$ (**6**). Green, yield 64%; M.p. 225 °C; μ_{eff} = 2.99 BM. *Anal. Calc.* for C₃₂H₃₀NiN₄O₄S₄ (721.54): C, 53.27; H, 4.19; N, 7.76; S, 17.77; Ni, 8.13. Found: C, 52.37; H, 4.19; N, 7.63; S, 17.49; Ni, 8.02%. IR (ν cm⁻¹, KBr): ν (NH) 3177 m; ν (>C=O) 1601s; thioamide I [β (NH) + ν (CN)] 1513s; thioamide II [ν (CN) + β (NH)] 1295s; ν (N–N) 1105 m; ν (>C=S) 847; ν (CH₂) 2846. UV–Vis [λ_{max} , DMSO, nm]: 668, 457, 331, 298, 259. MS(FAB) m/z = 721 [M]⁺.

2.3.2. Preparation of [Mn(Hmbhcd)₂(o-phen)] · DMSO (**3**)

Complex **2**, as prepared above, was stirred with a solution of *o*-phen (0.198 g, 1 mmol) in methanol (15 ml) for 1 h. The yellowish turbid suspension obtained was made clear after adding a few drops of DMSO. The clear yellow solution of the complex was kept for crystallization which yielded light yellow transparent crystals of **3** after 16 days.

Light yellow, yield 67%; M.p. 200 °C, μ_{eff} = 6.10 BM. Anal. Calc. for C₄₆H₄₄MnN₆O₅S₅ (976.11): C, 56.60; H, 4.54; N, 8.61; S, 16.42;

Mn, 5.63. Found: C, 56.12; H, 4.07; N, 8.11; S, 16.40; Mn, 6.01%. IR ($\nu \text{ cm}^{-1}$, KBr): $\nu(\text{NH})$ 3181 m; $\nu(\text{>C=O})$ 1602s; thioamide I [$\beta(\text{NH}) + \nu(\text{CN})$] 1501s; thioamide II [$\nu(\text{CN}) + \beta(\text{NH})$] 1300s; $\nu(\text{N-N})$ 1101 m; $\nu(\text{>C=S})$ 910; $\nu(\text{CH}_2)$ 2933; (*o*-phen) 1240; $\nu(\text{SO})$ of DMSO 1018. UV–Vis [λ_{max} , DMSO, nm]: 585, 461, 338, 317, 289.

2.3.3. Preparation of $[Mn_2(Hmbhcd)_2(2,2'-bpy)_2(\mu-OAc)_2]$ (4)

Complex **4** was prepared by stirring a solution of H_2 mbhcd (2 mmol) in MeOH/CHCl₃ (25 ml) with a solution of $Mn(OAc)_2 \cdot 4H_2O$ (1 mmol) in MeOH for 2 h at room temperature followed by the addition of 2,2'-bpy (0.156 g, 1 mmol) to yield a clear yellow solution. This solution was filtered and kept for crystallization for 25 days, which gave yellow transparent crystals of **4**.

Light yellow, yield 61%; M.p. 245 °C, μ_{eff} = 5.90 BM. *Anal.Calc.* for C₅₆H₅₂Mn₂N₈O₈S₄ (1203.18): C, 55.90; H, 4.36; N, 9.31; S, 10.66; Mn, 9.13. Found: C, 55.48; H, 4.30; N, 9.89; S, 10.59; Mn, 9.96%. IR (ν cm⁻¹, KBr): ν (NH) 3181 m; ν (>C=O) 1601s; thioamide I [β (NH) + (CN)] 1512s; thioamide II [ν (CN) + β (NH)] 1312s; ν (N–N) 1106 m; ν (>C=S) 905; ν (CH₂) 2922; (bpy) 1181; ν_{as} (CH₃COO)⁻ 1561; ν_{s} (CH₃COO)⁻ 1480. UV–Vis [λ_{max} , DMSO, nm]: 632, 343, 234.

3. Analyses and physical measurements

Carbon, hydrogen, nitrogen and sulfur contents were estimated on a CHN Model CE-440 Analyzer and on an Elementar Vario EL III Carlo Erbo 1108. By following standard procedures, the complexes were analyzed for their metal content, after decomposition with a mixture of conc. HNO₃ and HCl, followed by conc. H₂SO₄ [22]. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using Hg[Co(NCS)₄] as the calibrant and electronic spectra were recorded on an UV-1700 Pharmaspec spectrophotometer. IR spectra were recorded in the 4000–400 cm⁻¹ region as KBr pellets on a Varian Excalibur 3100 FT-IR spectrophotometer. ¹H and ¹³C NMR spectra were recorded in DMSO- d_6 and on a IEOL AL300 FT NMR spectrometer using TMS as an internal reference. The FAB mass spectra were recorded on a Jeol SX 102/Da-600 mass spectrometer/data system with argon/xenon (6 kv, 10 m A0) as the FAB gas and m-nitrobenzyl alcohol (NBA) was used as the matrix.

4. Crystallographic data collection and structure refinement

X-ray single crystal refinement, diffraction data collection and data reduction for complexes **3** and **4** were performed at 200(2) K with a graphite monochromated Mo K α (λ = 0.71073 Å) radiation source using standard methods [23]. The MERCURY package was used for molecular graphics [24]. Crystal structure diagrams were generated by use of the ORTEP-3 for Windows program [25]. The structures were solved by direct methods (SHELX-97) [26] and refined against all data by full-matrix least-squares on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. Crystallographic data and refinement details for the structural analysis of the complexes are summarized in Table 1 and selected bond lengths and bond angles for complexes **3** and **4** are given in Tables 2 and 4, respectively. The hydrogen bonds are listed in Tables 3 and 5 for complexes **3** and **4**, respectively.

5. Results and discussion

The ligand H_2 mbhcd reacts with $M(OAc)_2 \cdot XH_2O$ in a CHCl₃-MeOH mixture to give polymer complexes with a metal:ligand composition of 1:2. The CHNS elemental analyses and mass spectrometry results are in full agreement with the calculated values of mass percent of elements and molecular weights. In the case of the ligand, the presence of the thioamide functional group –

Table 1

Crystal refinement parameters of the complexes $[Mn(Hmbhcd)_2(o-phen)] \cdot DMSO$ (3) and $[Mn_2(Hmbhcd)_2(2,2'-bpy)_2(\mu-CH_3COO)_2]$ (4).

Parameters	3	4
Empirical formula	C46H44MnN6O5S5	C56H52Mn2N8O8S4
Formula weight	976.11	1203.18
Space group	P1	$P2_1/c$
Crystal system	triclinic	monoclinic
T (K)	200(2)	200(2)
λ (Μο Κα)	0.71073	0.71073
a (Å)	11.5011(4)	9.7502(4)
b (Å)	14.2290(5)	28.1656(11)
c (Å)	15.6479(4)	10.0010(4)
α (°)	74.828(3)	90
β (°)	82.874(3)	100.662(4)
γ(°)	66.705(3)	90
$V(Å^3)$	2269.43(13)	2699.06(19)
Ζ	2	2
$\rho_{\rm calc} ({\rm Mg}/{\rm m}^3)$	1.428	1.480
M (mm ⁻¹)	0.574	0.686
F(000)	1014	1244
Crystal size (mm ³)	$0.52 \times 0.46 \times 0.39$	$0.47 \times 0.42 \times 0.31$
θ Range for data collection	4.73-32.40	4.61-34.67
Index ranges	$-17 \le h \le 14$	$-15 \le h \le 12$
	$-20 \le k \le 19$	$-44 \le k \le 40$
	$-22 \le l \le 22$	$-15 \le l \le 15$
Reflections collected	35710	28540
Independent reflections	14822	10840
Data/restraints/parameters	14822/0/572	10840/0/330
Goodness-of-fit on F^2	1.070	0.932
$R_1^{a}, wR_2^{b} [I > 2\sigma(I)]$	0.0354, 0.0897	0.0657, 0.1361
R_1^{a} , wR_2^{b} (all data)	0.0651, 0.1046	0.1551, 0.1562
Largest difference in peak and hole $(e \text{ Å}^{-3})$	0.499, -0.422	0.842, -0.561

NH–C(=S)SR, indicates that the ligand can exhibit thione–thiol tautomerism. The solid state IR spectrum and XRD of H₂mbhcd do not reveal the presence of –(SH), indicating that in the solid state it remains in the thione form. The ¹H NMR spectrum in DMSO-d₆ is devoid of any signal attributed to the SH proton, indicating that in solution also it remains as the thione form. The ligand behaves as uninegative tridentate/bidentate and facilitates the formation of the metal complexes [M(Hmbhcd)₂]_n {where M = Mn(II) **2**, Co(II) **5** and Ni(II) **6**}, [Mn(Hmbhcd)₂(o-phen)] · DM-SO (**3**) and [Mn₂(Hmbhcd)₂(2,2'-bpy)₂(μ -OAc)₂] (**4**). These are stable towards air and moisture for several days. All the compounds are soluble in a methanol–chloroform mixture and other polar solvents such as DMF and DMSO.

5.1. IR spectra

The IR spectrum of H₂mbhcd in KBr shows two bands at 3127 and 3068 cm⁻¹ due to the presence of two –NH groups. The presence of the thioamide functional group -NH-(C=S)SR gives rise to characteristic bands associated with thioamide I [β (NH) + v(CN)] [mainly due to β NH], thioamide II [v(CN) + β (NH)] [high v(CN)] and thioamide IV [mainly due to v(C=S)]. The bands at 1641, 1467, 1250, 1046 and 905 cm⁻¹ are assigned to v(C=O), thioamide I, thioamide II, v(N-N) and v(C=S), respectively. The bands at 2938 cm^{-1} correspond to v(CH₂) of the benzyl ring. An exhaustive comparison of the IR spectra of the ligand and the complexes gave information about the mode of bonding of the ligand in the metal complexes **2–6**. The IR spectra of the complexes $[Mn(Hmbhcd)_2]_n$ (2), $[Co(Hmbhcd)_2]_n$ (5) and $[Ni(Hmbhcd)_2]_n$ (6) show only one peak at $3177-3179 \text{ cm}^{-1}$, suggesting the loss of one hydrazinic proton and participation of the resulting deprotonated nitrogen in bonding with the metal ion. A negative shift of 40-43 cm⁻¹ in amide I indicates the involvement of the carbonyl oxygen in bonding for complexes **2**, **5** and **6**. A negative shift of $58-63 \text{ cm}^{-1}$ in the v(C=S) band indicates the involvement of the thione sulfur in

Table 2

Selected bond lengths and bond angles for complex 3 (Å and $^\circ\text{)}.$

Bond lengths			
Mn-O(2B)	2.1988(10)	Mn-N(1)	2.2842(12)
Mn-O(2A)	2.2697(10)	Mn-N(2)	2.2903(12)
Mn-N(2B)	2.2154(12)	S(1S)-O(1S)	1.484(2)
Mn-N(2A)	2.2319(13)	S(1S)-C(2S)	1.761(3)
		S(1S)-C(1S)	1.770(3)
Bond angles			
O(2B)-Mn-N(2B)	71.75(4)	N(2B)-Mn-N(2A)	137.49(4)
		O(2B)-C(8B)-N(1B)	119.58(12)
O(2B)-Mn-N(2A)	83.69(4)		
O(2B)-Mn-O(2A)	114.90(4)	N(2A)-Mn-O(2A)	71.61(4)
O(1S) - S(1S) - C(2S)	105.33(15)	C(8A)-O(2A)-Mn	115.66(9)
O(1S) - S(1S) - C(1S)	105.25(13)	C(8B)-O(2B)-Mn	117.92(9)
C(2S)-S(1S)-C(1S)	98.28(17)	C(11)–N(2)–Mn	115.77(9)
C(8A) - N(1A) - N(2A)	118.41(12)	N(2A)-C(9A)-S(1A)	127.05(11)
C(9B)-N(2B)-N(1B)	115.11(11)	N(2A)-C(9A)-S(2A)	109.72(11)
N(1B)–N(2B)–Mn	113.56(9)	C(8B)-N(1B)-N(2B)	117.16(12)

bonding for complexes **2**, **5** and **6**. Furthermore, the bands at 1511–1514, 1295–1301 and 1102–1105 cm⁻¹ due to thioamide I, thioamide II and v(N-N) undergo a shift to higher frequencies of 44–47, 45–51 and 56–59 cm⁻¹, respectively, showing the involvement of the thione sulfur and hydrazinic nitrogen in bonding.

In the IR spectra of complexes **3** and **4**, the bands at 3180–3181, 1601-1603, 1501-1512, 1300-1312, 1101-1106, 906-910 and 2922–2933 cm⁻¹ are assigned to v(NH), v(C=O), thioamide I, thioamide II, v(N-N), v(C=S) and $v(CH_2)$, respectively. The v(C=S)band at 906-910 cm⁻¹ remains practically unchanged in the complexes in comparison to the ligand, suggesting non-involvement of the thione sulfur in bonding, while a negative shift of 38–40 cm⁻¹ for v(C=0) indicates the involvement of this group in bonding. A positive shift in v(N-N) indicates the involvement of the hydrazinic nitrogen in bonding. This is also supported by the positive shift in thioamide I and II. The IR spectra of each of complexes 3 and 4 show a band at 1240 and 1181 cm⁻¹, respectively, for coordinated o-phen and 2,2'-bpy [27]. The peak corresponding to the SO stretching of non-bonded DMSO occurs at 1018 as a strong and broad band [28]. Thus, H₂mbhcd behaves as a uninegative bidenate ligand in complexes 3 and 4 and a uninegative tridentate ligand in complexes **2**, **5** and **6**. The symmetric (1480 cm⁻¹) and asymmetric (1561 cm⁻¹) stretching bands of the acetate anion in complex **4** indicate its bridging bidentate nature [29].

5.2. Magnetic moments and electronic spectra

The $\mu_{\rm eff}$ values of 5.98, 6.10 and 5.90 B.M. for complexes **2**, **3** and **4**, respectively show the presence of a high spin Mn^{2+} ion having five unpaired electrons with the ⁶A_{1g} ground state. Their UV-Vis spectra exhibit one d-d band at 632–550 nm due the ${}^{6}A_{1g} \rightarrow$ ${}^{4}T_{1g}(G)$ transition, suggesting an octahedral geometry around Mn(II) [30]. An additional band at 461 nm in [Mn(Hmbhcd)₂(ophen)] · DMSO (3) is assigned to an intraligand/charge transfer transition. The magnetic moment of 5.11 B.M. and the presence of two well resolved bands at 592 and 445 nm corresponding to the ${}^4T_{1g} \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}$ transitions, respectively, is indicative of a cobalt(II) ion in an octahedral environment for complex 5 [30]. An absorption band at 320 nm in the high-energy region is assigned to an intraligand transition. The magnetic moment of 2.99 B.M. for $[Ni(Hmbhcd)_2]_n$ (**6**) is typical of a high spin octahedral Ni(II) complex and the presence of two bands at 668 and 457 nm are considered to arise from the ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}(F)$ and ${}^{3}T_{1g}(P)$ transitions in an octahedral geometry around Ni(II). The high-energy bands at 331, 298 and 259 nm in the spectrum of $[Ni(Hmbhcd)_2]_n$ are probably due to charge transfer/intraligand transitions [30].

Table 3Hydrogen bonds for complex 3 (Å and °).

D−H···A	d(D-H)	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D\!\cdot\cdot\cdot A)$	<(DHA)
$N(1A)-H(1AD)\cdots O(1A)$	0.88	1.94	2.5950(16)	130.0
$N(1B)-H(1BD)\cdots O(1B)$	0.88	2.00	2.6541(15)	130.5
$C(1A)-H(1AB)\cdots O(1S)$	0.98	2.55	3.339(3)	138.0

Symmetry transformations used to generate equivalent atoms.

5.3. ¹H and ¹³C NMR spectra

The ¹H NMR spectrum of H₂mbhcd shows two signals at 10.73 and 10.55 ppm due to the presence of -NH(CO)- and -NH(CS)-protons, respectively. The peaks at 4.45 and 3.91 ppm correspond to $-CH_2$ and $-OCH_3$ protons. The protons due to the two aromatic rings, i.e. the 2-methoxybenzene ring and the benzyl ring, appear as multiplets between 7.76 and 7.10 ppm. The ¹³C NMR spectrum of H₂mbhcd shows 16 signals due to the presence of 16 carbon atoms. The peaks at δ 202.22 and 164.14 ppm are attributed to the >C=S and >C=O carbons, respectively. The ¹H and ¹³C NMR of complexes could not be recorded due to their paramagnetic nature.

5.4. Mass spectrometry

FAB mass spectral analyses of $[Mn(Hmbhcd)_2]_n$ (2), $[Co(Hmbhcd)_2]_n$ (4) and $[Ni(Hmbhcd)_2]_n$ (6) show the presence of the molecular ion peaks at m/z = 718 $[M]^{+}$, 722 $[M]^{+}$ and 721 $[M]^{+}$, respectively which correspond to the molecular weight of one unit of the polymer. Other peaks at higher m/z values indicate their polymeric nature. Complex 2 gave several important peaks at m/z 684 (45% intensity), 610 (35% intensity), 593 (25% intensity), 509 (35% intensity), 470 (98% intensity) and 386 (75% intensity) corresponding to fragments formed from $[Mn(Hmbhcd)_2]_n$ after release of H₂S, $C_6H_4(-OCH_3)$, PhCH₂S–, $[C_6H_4(OCH_3)-C(O)-NHN-$

Table 4

Selected bond lengths and bond angles for complex 4 (Å and $^\circ$).

Bond lengths			
Mn-O(12) 1	2.0931(17)	Mn-N(1A)	2.238(2)
Mn-O(11)	2.1738(18)	Mn-N(2A)	2.277(2)
Mn-O(2)	2.1889(17)	Mn-N(1)	2.382(2)
O(12)-C(11A)	1.260(3)	O(11)-C(11A)	1.253(3)
		O(12)-Mn 1	2.0931(17)
Bond angles			
O(12) 1-Mn-O(11)	101.22(7)	O(12) 1-Mn-O(2)	88.97(7)
O(11)-Mn-O(2)	90.78(7)	O(12) 1-Mn-N(1A)	167.74(8)
O(11)-Mn-N(1A)	89.09(7)	O(2)-Mn-N(1A)	97.60(7)
O(12) 1-Mn-N(2A)	99.37(7)	O(11)-Mn-N(2A)	94.37(7)
O(2)-Mn-N(2A)	169.15(7)	N(1A)-Mn-N(2A)	72.97(7)
O(12) 1-Mn-N(1)	86.93(7)	O(11)-Mn-N(1)	160.86(7)
O(2) - Mn - N(1)	71.93(7)	C(8)-O(2)-Mn	115.49(15)
N(1A)-Mn-N(1)	85.29(7)	C(11A)-O(12)-Mn 1	138.68(16)
C(11A)-O(11)-Mn	120.96(17)	C(9)-N(1)-Mn	141.72(18)
N(2) - N(1) - Mn	105.58(13)		

Symmetry transformations used to generate equivalent atoms. 1 - x + 1 - y - z.

Table 5

HVGrogen bonds for complex 4 (A and *)	Hydrogen	bonds fo	r complex	4 (Å	and °	۱.
--	----------	----------	-----------	------	-------	----

D−H···A	D(D-H)	$D(H{\cdots}A)$	$d(D{\cdot}{\cdot}{\cdot}A)$	<(DHA)
$N(2)-H(2A)\cdots O(1)$	0.88	1.93	2.614(3)	132.9
$C(10)-H(10B)\cdots O(11) 2$	0.99	2.39	3.331(3)	157.9

Symmetry transformations used to generate equivalent atoms.

2 x - 1, y, z.

C(S)–], 2(PhCH₂S–) and [C₆H₄(OCH₃)C(O)NH–N–C(S)–S–], respectively. The fragments at m/z = 689 (12.5% intensity), 598 (25% intensity), 571 (25% intensity) and 390 (35% intensity) correspond to the fragments formed from [Co(Hmbhcd)₂]_n (**4**) after release of HS, PhCH₂S–, [C₆H₄(OCH₃)–C(O)–NH)–] and C₆H₄(OCH₃)–C(O)–NH–N–C(S)S–], respectively from one unit of the complex. Complex **6** gave important peaks at m/z = 597 (50% intensity), 473 (48% intensity) and 389 (75% intensity), corresponding to the fragments formed from one unit of [Ni(Hmbhcd)₂]_n after release of PhCH₂S–, 2PhCH₂S– and [C₆H₄(OCH₃)C(O)NH–N–C(S)–S–], respectively.

On the basis of the analytical data and spectroscopic studies, tentative structures of the complexes $[M(Hmbhcd)_2]_n$ are given in Fig. 2.

6. Crystal structure description

6.1. Crystal structure description of complex 3

Fig. 3 shows a Mercury view of the Mn(II) complex together with the atom numbering scheme. The metal center in complex **3** is coordinated by an N₄O₂ core from two uninegative bidentate ligands using the hydrazinic nitrogens (N2, after loss of a proton) and carbonyl oxygens. Various bond distances found within the chelate rings are intermediate between single and double bond lengths and shorter or longer than the corresponding bond lengths in comparison to the ligand. The average bond lengths in complex **3** are: O(2A)–C(8A) = 1.2503(18); O(2B)–C(8B) = 1.2569(17), N(1A)–C(8A) = 1.3363(19), N(1B)–C(8B) = 1.3303(19), N(1A)– N(2A) = 1.3872(16), N(1B)–N(2B) = 1.3851(15) Å, which suggest considerable delocalization of charge [31] in the chelate ring.

Transition metal complexes in which bonding of the ligand takes place through a carbonyl oxygen and nitrogen and also bonded with N-heterocyclic bases such as *o*-phen or 2,2'-bpy are prone to exhibit metalloaromaticity [32–36]. The above criteria of metalloaromaticity are fulfilled in complex **3**. The most note-worthy structural feature of complex **3** is that two *ortho*-H atoms from the *o*-phen ring point towards the center of the corresponding Mn–OCN1N2 chelate rings [37]. This delocalized charge in the chelate ring forms an unusual intramolecular C–H… π interaction with the *ortho* hydrogen of the adjacent *o*-phen ring [19,37] (Fig. 4).



 $[M(Hmbhcd)_2]_n \{M = Mn(II) (2), Co(II) (5), Ni(II) (6), R' = CH_2Ph$

Fig. 2. Tentative structure of the complexes $[M(Hmbhcd)_2]_n$ {M = Mn(II), Co(II) and Ni(II)}.

The shortest centroid to centroid separation found between parallel benzyl and o-phen rings is 4.038 Å within the molecule, which rules out the possibility of intramolecular face to face $(\pi \cdots \pi)$ interactions in **3**. The chelate rings around Mn(II) formed by (Hmbhcd)⁻ display a dihedral angle of 73.50° (between the mean planes MnN2AN1AC8AO2A and MnO2BC8BN1BN2B) and indicate strain in both chelate rings. This strain between the chelate rings is also supported by the dihedral angle between the 2-



Fig. 3. Mercury view of [Mn(Hmbhcd)₂(*o*-phen)] DMSO showing the atomic numbering scheme with ellipsoids of 20% probability. Hydrogen atoms are omitted for clarity.



Fig. 4. Crystal structure of $[Mn(Hmbhcd)_2(o-phen)]$, showing an unusual intramolecular C-H··· π interaction with the Mn(II) chelate ring. For clarity other hydrogen atoms and the DMSO molecule are omitted.

Table 6Intermolecular interactions (Å) for complexes 3 and 4.

methoxy benzene ring and the chelate rings. The chelate ring O2BMnN2BN1BC8B and the corresponding 2-methoxy benzene ring lie in the same plane while another chelate ring O2AMnN2A-N1AC8A and its corresponding 2-methoxy benzene ring are nearly planar with a dihedral angle of 14.11°. The dihedral angle between a benzyl ring (mean plane C16BC15BC14BC13BC12BC11B) and one chelate ring (mean plane MnO2BC8BN1BN2B) is 24.30° and between another chelate ring (mean plane C14AC13AC12AC11AC16AC15A) is 62.81°.

6.2. Crystal packing of complex 3

The weak intermolecular interactions are listed in Table 6. The presence of intramolecular hydrogen bonding, N(1B)–H(1BD)···O(1B) = 1.99 Å and N(1A)–H(1AD)···O(1A) = 1.94 Å, provide stability to complex **3**. The two-dimensional framework is formed with the help of intermolecular hydrogen bonding, C10–H10A···O1S (2.604 Å), C1A–H1AB···O1S (2.546 Å) and C3A–H3AA···S1B (2.908 Å). The whole arrangement of molecules in the crystal packing creates channels which enclose DMSO molecules (Fig. 5).

6.3. Crystal structure description of complex 4

Each Mn(II) center is six coordinately bonded through two N atoms of one 2,2'-bpy, one deprotonated nitrogen from a hydrazinic moiety and three oxygen atoms, belonging to two different acetates and one carbonyl oxygen of the ligand 1 (Fig. 6). The two neighboring Mn(II) centers are connected by two bridging acetate ions which results in the formation of a distorted rectangular shaped cavity of size $3.151 \times 3.017 \text{ Å}^2$, labeled as [Mn-O12-C12A-O11-Mn-O12-C12A-O11] (Fig. 6). One molecular unit of $[Mn_2(Hmbhcd)_2(2,2'-bpy)_2(\mu-OAc)_2]$ shows the presence of an intramolecular N-H···O hydrogen bond, with a distance and angle of 2.614(3) Å and 111.2°, respectively. The Mn-O_{acetate} bond lengths of 2.0929(17) and 2.1737(18) Å are relatively shorter than the reported bond length values for bridged Mn-OAc = 2.144(2)-2.203(2) Å, indicating relatively stronger bonding between Mn(II) and oxygen in this system [38]. The bond distance of $Mn-O_{carbonyl} =$ 2.1890(17) Å is comparable to the bond lengths found for [Mn(Hpchc)₂(o-phen)] [19]. The Mn-N_{bpv} distances [2.238(2) and 2.277(2)Å] are slightly longer than the reported values for $Mn-N_{bpv}$, 2.038(3)–2.254(3)Å [39], but the bite angle N(1A)– $Mn-N(2A) = 72.96(7)^{\circ}$ is close to 73°, as observed for chelating 2,2'-bpy complexes [39]. The C-O, C-N and N-N bond distances of 1.262(3), 1.326(3) and 1.406(3) Å, respectively, are intermediate between single and double bond character. All these intermediate distances suggest extensive delocalization of charge in the fivemembered chelate ring of complex 4 [31] and is the basis of metalloaromaticity.

6.4. Crystal packing of 4

A view of the crystal packing along the b axis gives a linear arrangement of Mn(II) centers and increases the chain in one dimension with a $Mn \cdots Mn$ separation of 10.001 Å in

Complex 3		Complex 4			
D–H···A	$d(H \cdots A)$	D−H···A	$D(H \cdots A)$	D–H···A	$d(H{\cdot}{\cdot}{\cdot}A)$
C10-H10A···O1S	2.60	C−H···Cg	2.90	C4A-H4AA011	2.64
C3A–H3AA···S1B	2.90	C1-H1C···S1	2.93	$Cg_{(bpy)} \cdot \cdot \cdot Cg_{(bpy)}$	3.26
C1H−H1A· · ·Cg	2.82	C10-H10BO11	2.39	C4A-H4AA···C11A	2.56



Fig. 5. Molecular packing of complex 3 showing intermolecular hydrogen bonding and the enclosed DMSO (hydrogen atoms are omitted except those taking part in hydrogen bonding).



Fig. 6. Distorted rectangular cavity in the structure of $[Mn_2(Hmbhcd)_2(2,2'-bpy)_2(\mu-OAc)_2]$. Mercury view of $[Mn_2(Hmbhcd)_2(2,2'-bpy)_2(\mu-OAc)_2]$ (4) showing the atomic numbering scheme with an ellipsoidal plot at 20% probability.



Fig. 7. One-dimensional chain due to the presence of face to face interactions and C4A-H4AA...O11 hydrogen bonds. For more clarity the (Hmbhcd)⁻ ligand and hydrogen atoms are omitted (except H4AA).



Fig. 8. Molecular packing of complex 4 showing C-H··· π interactions (hydrogen atoms except H2AA are omitted for clarity).

Table 7 Comparative bond lengths, bond angles and torsional angles for $H_2 mbhcd$ and complexes ${\bf 3}$ and ${\bf 4}.$

H ₂ mbhcd	[Mn(Hmbhcd) ₂ (o-phen)] · DMSO	[Mn(Hmbhcd) ₂ (2,2'-bpy)(µ-OAc) ₂]
S(1)-C(9) 1.656(2)	S(1A)-C(9A) 1.6907(16)	S(1)-C(9) 1.689(3)
	S(1B) -C(9B) 1.6849(14)	
S(2)-C(9) 1.740(2)	S(2A)-C(9A) 1.7833(15)	S(2)-C(9) 1.786(3)
	S(2B)-C(9B) 1.7827(14)	
S(2)-C(10) 1.807(3)	S(2A)-C(10A) 1.8160(16)	S(2)-C(10) 1.810(3)
	S(2B)-C(10B) 1.8083(17)	
O(2) - C(8) 1.222(3)	O(2A) - C(8A) 1.2503(18)	O(2)-C(8) 1.262(3)
	O(2B) - C(8B) = 1.2569(17)	
N(1) - C(8) 1.340(3)	N(1A) - C(8A) 1.3363(19)	N(2)-C(8) 1.326(3)
	N(1B) - C(8B) = 1,3303(19)	
N(1) - N(2) = 1 = 372(3)	N(1A) - N(2A) = 13872(16)	N(1) = N(2) + 1406(3)
n(1) n(2) n(3) 2(3)	N(1R) - N(2R) + 3851(15)	n(1) n(2) n(0)(3)
N(2) - C(0) = 1 = 222(3)	$N(2\Delta) - C(2\Delta) = 1.5051(15)$	N(1) - C(0) = 1.316(3)
N(2) = C(3) 1.323(3)	N(2R) = C(0R) + 1.5151(15) N(2R) = C(0R) + 2.190(19)	N(1) - C(3) = 1.510(3)
	N(2D) - C(3D) = 1.5163(16)	
Bond angles		
C(9)-S(2)-C(10) 104.13(12)	C(9A)-S(2A)-C(10A) 101.91(7)	C(9)-S(2)-C(10) 102.98(13)
	C(9B)-S(2B)-C(10B) 102.45(7)	
O(2)-C(8)-N(1) 120.48(19)	O(2A)-C(8A)-N(1A) 120.35(13)	O(2)-C(8)-N(2) 122.O(2)
	O(2B)-C(8B)-N(1B) 119.58(12)	
O(2)-C(8)-C(7) 122.33(19)	O(2A)-C(8A)-C(7A) 121.17(13)	
	O(2B)-C(8B)-C(7B) 119.91(13)	
N(1) - C(8) - C(7) 117.18(17)	N(1A) - C(8A) - C(7A) 118.46(13)	N(2)-C(8)-C(7) 117.9(2)
	N(1B)-C(8B)-C(7B) 120.50(12)	
N(2)-C(9)-S(1) 123.36(17)	N(2A)-C(9A)-S(1A) 127.05(11)	N(1)-C(9)-S(1) 127.6(2)
	N(2B)-C(9B)-S(1B) 127.90(10)	
N(2) = C(9) = S(2) 110 94(15)	N(2A) - C(9A) - S(2A) 109 72(11)	N(1) - C(9) - S(2) 109 89(19)
	N(2R) - C(9R) - S(2R) + 1087 - 2(11)	
S(1) = C(9) = S(2) = 125 69(13)	S(1A) = C(9A) = S(2A) (123) O4(9)	S(1) = C(9) = S(2) = 122 = 36(15)
5(1) C(3) 5(2) 123.03(13)	S(1R) - C(9R) - S(2R) + 123.0 + (3)	5(1) C(3) 5(2) 122.30(13)
C(11) = C(10) = S(2) = 104 = 53(17)	C(11A) = C(10A) = S(2A) = 111 = 47(12)	C(11) = C(10) = S(2) = 115 = S(2)
C(11) C(10) S(2) 104.55(17)	C(11R) - C(10R) - S(2R) - 117.47(12)	C(11) $C(10)$ $S(2)$ $113.0(2)$
	C(11D) - C(10D) - S(2D) 107.88(11)	
Torsional angles		
C(8)-N(1)-N(2)-C(9)-173.7(2)	C(8A)-N(1A)-N(2A)-C(9A) 179.61(12)	C(9)-N(1)-N(2)-C(8) 172.7(2)
	C(8B)-N(1B)-N(2B)-C(9B)-172.22(12)	
N(2)-N(1)-C(8)-O(2)5.8(4)	N(2A)-N(1A)-C(8A)-O(2A)-4.93(19)	N(1)-N(2)-C(8)-O(2)-1.4(4)
	N(2B)-N(1B)-C(8B)-O(2B) 1.16(19)	
N(2)-N(1)-C(8)-C(7)-173.3(2)	N(2A)-N(1A)-C(8A)-C(7A) 173.73(11)	N(1)-N(2)-C(8)-C(7) 176.8(2)
	N(2B)-N(1B)-C(8B)-C(7B) 178.31(12)	
N(1)-N(2)-C(9)-S(1) 4.9(3)	N(1A)-N(2A)-C(9A)-S(1A)-6.76(18)	N(2)-N(1)-C(9)-S(1)-2.5(3)
	N(1B)-N(2B)-C(9B)-S(1B) 5.76(19)	
N(1)-N(2)-C(9)-S(2)-174.10(18)	N(1A) - N(2A) - C(9A) - S(2A) 168.31(9)	N(2)-N(1)-C(9)-S(2) 173.66(16)
	N(1B)-N(2B)-C(9B)-S(2B)-169.88(9)	
C(10)-S(2)-C(9)-N(2) 170.75(19)	C(10B)-S(2B)-C(9B)-N(2B)-142.08(12)	C(10)-S(2)-C(9)-N(1) 155.33(18)
	C(10A)-S(2A)-C(9A)-N(2A) 142.23(11)	-(, -(-, -(-, -(-, 100003(10)
C(10)-S(2)-C(9)-S(1)-8.2(2)	C(10A) = S(2A) = C(9A) = S(1A) = 42.46(11)	C(10)-S(2)-C(9)-S(1)-283(2)
	C(10B)-S(2B)-C(9B)-S(1B) 42.04(13)	
C(9) = S(2) = C(10) = C(11) = 17374(19)	C(9A) = S(2A) = C(10A) = C(11A) = 93(12)	$C(9) = S(2) = C(10) = C(11) \times S(2)$
-(-, -(-, -(.0) e()	C(9B)-S(2B)-C(10B)-11B) 177.94(14)	

 $[Mn_2(Hmbhcd)_2(2,2'-bpy)_2(\mu-OAc)_2]$. The chain grows infinitely in 1 D along the a axis with the help of C4A–H4AA···O11 and π ··· π interactions between two successive 2,2'-bpy rings (Fig. 7). The distance between the centroids (Cg) of two 2,2'-bpy ligands of two adjacent units of $[Mn_2(Hmbhcd)_2(2,2'-bpy)_2(\mu-OAc)_2]$ is 3.262 Å, which is within the range of $\pi \cdots \pi$ stacking interactions (3.3–3.7 Å). The $\pi \cdots \pi$ stacking interactions between the two units of molecules, intermolecular hydrogen bonding, C4A-H4AA... 011 = 2.641 Å, and short contact of C4A–H4AA····C11A = 2.562 Å connect the sheets into a 1D coordination framework (Fig. 7).

The 2,2'-bpy ligand forms C–H··· π interactions with the phenyl ring of the 2-methoxy benzene ring with a distance of C-H··· Cg_(2-methoxy ring) of 2.907 Å (Fig. 8). There is intermolecular hydrogen bonding, C1-H1C_(2-methoxy benzene ring) ···S1 = 2.931 Å and C10-H10B $\cdot \cdot$ O11 (CH₂ of benzyl ring) = 2.394 Å, which extends the crystal packing and gives a three dimensional framework. The weak intermolecular interactions are listed in Table 6.

Looking at the crystal data and structure of the complexes, it is found that the bond lengths and bond angles in the ligand H₂mbhcd are very similar, but the torsional angles of compounds 3 and 4 differ widely (Table 7). The basic change observed in the structure of the ligand due to metal coordination is in the orientation of the benzyl ring. One benzyl ring, C11A-C12A-C13A-C14A-C15A-C16A, in complex 3 and both benzyl rings, C11-C12-C13-C14–C15–C16, in complex 4 show major deviation in torsional angles [C9A-S2A-C10A-C11A = -93.19°, C9B-S2B-C10B-C11B = 177.96° for complex **3**, C9–S2–C10–C11 = -80.34°, C9–S2–C10– C11 = 80.34° for complex **4**] in comparison to the ligand H₂mbhcd $[C9-S2-C10-C11 = -173.79^{\circ}]$. The O(2)-C(8) bond length in the ligand, 1.222(3) Å, is shorter than the corresponding length {O(2A)-C(8A) = 1.2503(18) Å(3), O(2B) - C(8B) = 1.2569(18) Å(3) and O(2) - C(8B) = 1.2569(18) A(3) A(3) A(3) = 1.2569(18) A(3) A(3) A(3) = 1.2569(18) A(3) A(3) = 1.2569(18) A(3) A(3) = 1.2569(18C(8) = 1.262(3) (4) in the complexes, indicating that the single bond character of the C–O bond has increased due to delocalization of charge. There are slight variations in the N(1)-C(8), N(1)-N(2)and N(2)-C(9) bond lengths in complexes **3** and **4** as compared to the respective bond lengths of H₂mbhcd.

The C–N and N–N bond lengths in the ligand and the complexes show intermediate between single and double bond character. which is also indicative of considerable delocalization of charge in the chelate ring formed by the coordination of the deprotonated hydrazinic nitrogen and carbonyl oxygen in complexes 3 and 4. This delocalization generates aromaticity in the chelate ring of both complexes.

7. Conclusion

In this work, the synthesis and spectral studies of Mn(II), Co(II) and Ni(II)} complexes derived from benzyl N'-(2-methoxybencarbodithioate (H₂mbhcd) are presented. zoyl)hydrazine [Mn(Hmbhcd)₂(o-phen)] · DMSO (3) and [Mn₂(Hmbhcd)₂(2,2' $bpy_2(\mu-OAc)_2$ (4) have been studied by single crystal X-ray crystallography, which indicate that the complexes involve delocalization of charges in the chelate ring.

Acknowledgement

One of the authors (M. Singh) is thankful to CSIR, New Delhi, India for the award of SRF, supported by Grant No. 9/13(160)2008/ EMR-I.

Appendix A. Supplementary data

CCDC 656090, 677286 and 701544 contain the supplementary crystallographic data for 1.3 and 4. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2008.12.061.

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