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Some Mixed Ligand Complexes of Mn(III): Synthesis, Characterization and Application

SEEMA and SUDHA YADAVA*
Department of Chemistry, Deen Dayal Upadhaya Gorakhpur University, Gorakhpur-273 009, India
E-mail: dr_sudhayadava@yahoo.co.in

Few novel mixed ligand complexes of Mn(III) have been synthesised. These complexes are characterized by magnetic susceptibility, electronic conductivity and spectral (UV and IR) methods. The thermogravimetric studies have also been done. These complexes are with general formula $[Mn(\beta\text{-diketone})_2X]_2(en)$; β-diketone are acetylacetone, benzoylacetone, dibenzoylmethane; X = NCS^-, N_3^-, Cl^-, Br^- and en = ethylenediamine. These Mn(III) mixed ligand complexes are dimeric and bridged by ethylenediamine ligand. Azido complexes are bridges by the azido ligand also. Mn(III) is in six coordinated state. The magnetic moments for all these complexes indicate the presence of four unpaired electrons per manganese. The electronic conductivity data show the non-electrolytic nature for all the complexes. The TG study shows the absence of coordinated H_2O molecule. Studies on six fungal strains and five bacterial strains have been done with these complexes and their antifungal and antibacterial properties are observed. Their role in conversion of high molecular weight coal fraction into low molecular weight coal fraction is also studied by viscosity measurement method and the results obtained show the delignification property for all these Mn(III) mixed ligand complexes.

Key Words: Manganese(III) mixed ligand complexes, Fungitoxicity, Bacteriotoxicity, Delignification.

INTRODUCTION

Manganese in its +3 oxidation state forms complexes with charged and neutral ligands[1]. There are several reports about[2-5] synthesis and characterization of Mn(III) octahedral complexes of high-spin[6]. Mn(III) octahedral complexes are susceptible to Jahn-Teller distortions, causing them to deviate from idealized O_h symmetry either by a trigonal elongation or compression[7]. HFEPR studies clearly show an axial (tetragonal) elongation which is the natural form of Jahn-Teller distortion for the octahedral high-spin $3d^4$ ions[8]. In most of the Mn(III) complexes with porphyrinic configuration of square pyramidal geometry and also in octahedral complexes with O/N donor atom ligands axial elongation is observed[9]. The kinetic and equilibrium studies on substitution reaction of the chloro*bis*(β-diketonato) Mn(III) complexes with other β-diketonato ligand have been done earlier[10]. A number of publications describing various Mn(III) complexes underscore the importance of high-spin ($3d^4$, S = 2)[11-15]; Mn(III) in its role as building block in molecular magnets[16-20] as a catalyst[21,22] and in biochemical reaction cycles[23-27]. Lignin is the main parent material in the formation of low rank coal (lignite)[28]. Some authors have designated lignite as demethylated and dehydrated lignin[29]. Mn(III) is highly unspecific and oxidizes a large number of aromatic and aliphatic compound present in lignin[30]. Mn in (III) oxidation state is stabilized *via* chelation with organic acids such as oxalate, malonate, malate, tartrate or lactate[31-32]. Chelated Mn(III) in turn acts as diffusible redox mediator that oxidizes phenols[33], certain methoxylated nitro and chloro aromatics and organic acids[34]. Mn(III) high-spin chelate complexes are gaining the interest due to their application as chemical analogue of Mn-peroxidase enzyme. This is the reason for the synthesis and characterization of these Mn(III) mixed ligand complexes. Their catalytic properties have also been explored by a novel viscosity measurement method.

EXPERIMENTAL

Thiocyanato*bis*(acetylacetonato)manganese(III)ethylenediamine (1): 2 g powder thiocyanato*bis*(acetylacetonato)manganese(III)[35] was refluxed with 1 mL of ethylenediamine for 15 h. After refluxion the obtained product was cooled for 1 h at room temperature (27 ºC) resulting dark brown shining crystal of thiocyanato-*bis*(acetylacetonato)manganese(III)ethylenediamine. Which were obtained in pure form by drying under vaccum and recrystallized with diethyl ether, 1.5 g (34.19 %), m.p. 158 ºC, anal. calcd. (%) for $C_{15}H_{24}N_4O_4S_2Mn_2$: C, 42.21; H, 5.32; N, 8.21; S, 9.37; Mn, 16.01.

Azido*bis*(acetylacetonato)manganese(III)ethylenediamine (2): 2 g Azido*bis*-(acetylacetonato)manganese(III)[35] was refluxed with 1 mL ethylenediamine for 16 h. Brown crystals of azido*bis*(acetylacetonato)manganese(III)ethylenediamine were obtained under vaccum drying which were recrystallized with diethyl ether. 1.5 g (42.44 %), m.p. 160 ºC, anal. calcd. (%) for $C_{13}H_{24}N_5O_4Mn_2$: C, 43.41; H, 5.97; N, 11.52; Mn, 18.05.

Chloro*bis*(acetylacetonato)manganese(III)ethylenediamine (3): It was prepared by the refluxion of 2 g of chloro*bis*(acetylacetonato)manganese(III)[35] and 1 mL ethylenediamine as above mention method and recrystallized with diethyl ether. 1.5 g (33.25 %), m.p. 162 ºC, anal. calcd. (%) for $C_{13}H_{24}N_2O_4Cl_2Mn_2$: C, 41.44; H, 5.7; N, 4.40; Cl, 11.12; Mn, 17.25.

Bromo*bis*(acetylacetonato)manganese(III)ethylenediamine (4): Bromo*bis*-(acetylacetonato)manganese(III)ethylenediamine was prepared from bromo*bis*-(acetylacetonato)manganese(III)[35] and ethylenediamine in the same manner as mentioned earlier for the complex **1**, **2** and **3**. 1.5 g (33.75 %), m.p. 163 ºC, anal. calcd. (%) for $C_{13}H_{24}N_2O_4Br_2Mn_2$: C, 36.37; H, 5.00; N, 3.86; Br, 22.01; Mn, 15.13.

Thiocyanato*bis*(benzoylacetonato)manganese(III)ethylenediamine (5): 2 g of powder thiocyanatobis(benzoylacetonato)manganese(III)[35] was refluxed with 1 mL of ethylenediamine for 15 h. After refluxion the obtained product was cooled for 1 h at room temperature (27 ºC). The dark brown shining crystallized of thiocyanato*bis*(benzoylacetonato)manganese(III)ethylenediamine were obtained drying under vaccum. Which were recrystallized with diethyl ether. 1.5 g (31.42 %), m.p. 180 ºC, anal. calcd. (%) for $C_{18}H_{30}N_4O_4S_2Mn_2$: C, 56.76; H, 4.77; N, 6.02; S, 6.89; Mn, 11.81.

Azido*bis*(benzoylacetonato)manganese(III)ethylenediamine (6): 2 g of azido*bis*(benzoylacetonato)manganese(III)[35] was refluxed with 1 mL ethylenediamine for 16 h. The brown crystals obtained under vaccum were recrystallized with diethyl ether. 1.5 g (39.76 %), m.p. 185 ºC, anal. calcd. (%) for $C_{16}H_{30}N_5O_4Mn_2$: C, 58.86; H, 5.18; N, 8.18; Mn, 12.83.

Chloro*bis*(benzoylacetonato)manganese(III)ethylenediamine (7): It was prepared by 2 g of chloro*bis*(benzoylacetonato)manganese(III)[35] and 1 mL ethylenediamine as above mention method for complex **5** and **6** and recrystallized with diethylether. 1.5 g (31.22 %), m.p. 192 ºC, anal. calcd. (%) for $C_{16}H_{30}N_2O_4Cl_2Mn_2$: C, 56.93; H, 5.0; N, 3.16; Cl, 8.03; Mn, 12.41.

Bromo*bis*(benzoylacetonato)manganese(III)ethylenediamine (8): Bromo*bis*(benzoylacetonato)manganese(III)ethylenediamine was prepared from bromo*bis*(benzoylacetonato)manganese(III)[35] and ethylenediamine in the same way as mentioned earlier for the complexes **5**, **6** and **7**. 1.5 g (31.94 %), m.p. 209 ºC, anal. calcd. (%) for $C_{16}H_{30}N_2O_4Br_2Mn_2$: C, 51.75; H, 4.55; N, 2.88; Br, 16.41; Mn, 11.28.

Thiocyanato*bis*(dibenzoylmethanato)manganese(III)ethylenediamine (9): 2 g powder thiocyanato*bis*(dibenzoylmethanato)manganese(III)[35] was refluxed with 1 mL ethylenediamine for 15 h. After refluxion the obtained product was cooled for 1 h at room temperature (27 ºC) resulting dark brown shining crystals of thiocyanatobis(dibenzoylmethanato)manganese(III)ethylenediamine. Which were obtained in pure form by drying under vaccum and recrystallized with diethyl ether, 1.5 g (34.19 %), m.p. 158 ºC, anal. calcd. (%) for $C_{15}H_{24}N_4O_4S_2Mn_2$: C, 68.05; H, 4.64; N, 5.68; S,5.68; Mn, 9.74.

Azido*bis*(dibenzoylmethanato)manganese(III)ethylenediamine (10): 2 g azido*bis*(dibenzoylmethanato)manganese(III)[35] was refluxed with 1 mL ethylenediamine for 16 h. Brown crystals of azido*bis*(dibenzoylmethanato) manganese(III)-ethylenediamine were obtained under vaccum drying which were recrystallized with diethyl ether. 1.5 g (42.44 %), m.p. 160 ºC, anal. calcd. (%) for $C_{13}H_{24}N_5O_4Mn_2$: C, 67.37; H, 4.75; N, 6.34; Mn, 9.95.

Chloro*bis*(dibenzoylmethanato)manganese(III)ethylenediamine (11): It was prepared by the refluxion of 2 g of chloro*bis*(dibenzoylmethanato)manganese(III)[35] and 1 mL of ethylenediamine as above mention method and recrystallized with diethyl ether. 1.5 g (33.25 %), m.p. 162 ºC, anal. calcd. (%) for $C_{13}H_{24}N_2O_4Cl_2Mn_2$: C, 65.65; H, 4.62; N, 2.47; Cl, 6.27; Mn, 9.69.

Bromo*bis*(dibenzoylmethanato)manganese(III)ethylenediamine (12): Bromo-*bis*(dibenzoylmethanato)manganese(III)ethylenediamine was prepared from bromo*bis*(dibenzoylmethanato)manganese(III)[35] and ethylenediamine in the same manner as mentioned earlier for the complex **1**, **2** and **3**. 1.5 g (33.75 %), m.p. 163 ºC, anal. calcd. (%) for $C_{13}H_{24}N_2O_4Br_2Mn_2$: C, 60.88; H, 4.29; N, 2.29; Br, 13.08; Mn, 9.0.

RESULTS AND DISCUSSION

The elemental analysis of these complexes suggests 1:2 (metal:ligand) stiochiometry while the molecular weights suggest the dimeric nature. All these mixed ligand complexes are quite stable at room temperature when stored over P_2O_5. They are soluble in ethanol, water, acetone, diethyl ether and DMSO. The general reaction for the preparation of these Mn(III) mixed ligand complexes may be given as follows:

$$KMnO_4 + \beta\text{-diketone} \rightarrow Mn(\beta\text{-diketone})_3$$
$$Mn(\beta\text{-diketone})_3 + HX \rightarrow [Mn(\beta\text{-diketone})_2X]$$
$$[Mn(\beta\text{-diketone})_2X] + en \rightarrow [Mn(\beta\text{-diketone})_2X]_2[en]$$

The non electrolytic nature for all these Mn(III) mixed ligand complexes is shown by the electrical conductivity and electronic conductivity data. The values for these Mn(III) complexes obtained have been found to be very close to the electronic and molar conductivity values reported for other Mn(III) complexes[36,37]. The molar conductivity value for the complexes **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11** and **12** in *n*-propanol is 0.136, 0.133, 0.131, 0.129, 0.133, 0.131, 0.128, 1.25, 0.129, 0.127, 0.125 and 0.124 $\Lambda sm^2\ mol^{-1}$, respectively. The electronic conductivity value for the above complexes are 1.93×10^{-4}, 1.91×10^{-4}, 1.89×10^{-4}, 1.88×10^{-4}, 1.91×10^{-4}, 1.89×10^{-4}, 1.87×10^{-4}, 1.85×10^{-4}, 1.89×10^{-4}, 1.87×10^{-4}, 1.85×10^{-4} and $1.83 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$, respectively.

Infrared spectra for all these mixed ligand complexes exhibit two very strong peaks appearing at 1011 and 1080 cm^{-1}, which is assigned as $\delta(NH_2)$ and δ(C-N), respectively for the bridging ethylenediamine. The ligand ethylenediamine is present as a bridging group between the two Mn(III) ions, this is shown by the IR spectra of these complexes as the spectra are extremely simple. Because if the amino group would have been in the *cis* position or as the equatorial chelating ligand then the IR spectra would have been more complicated[38]. The simplicity in the IR spectra for these complexes where only one absorption peak is found for the amino group confirms that the ligand (en) is in the *trans* (or only slightly perturbed -*trans*) configuration[38]. Another significant peak appearing at 1713-1680 cm^{-1} is assigned as ν(C=O), the ketonic group present in the β-diketonic ligand which has coordinated with the metal ion. The π-resonance is also observed in this group therefore the shifting of ν(C=O) has taken place from the absolute range 1638-1538 cm^{-1}. Two other significant peaks appearing at 1640 and 2065 cm^{-1} can be assigned to the ν(C=C) and ν(C=H), respectively. These peaks are in accordance with the reported values[39], thus confirming the non coordinating situation for these two groups with central metal. A significant IR band in the spectrum of thiocyanato complexes appears in the range of 2243-2230 cm^{-1}. It is due to the stretching vibration for C≡N group, which usually appears in the range of 2260-2240 cm^{-1}. This band has suffered a downward shift of about 17 cm^{-1} indicating the coordination of nitrogen present in NCS group with the Mn(III). Here the coordination through N has taken place as N is more electronegative donor atom than S. Therefore N is coordinate to the metal ion rather than S, this fact is evident in the spectra also. The IR spectra of the azido complexes exhibit a significant peak in the range of 1278-1259 cm^{-1} assigned to the stretching vibration for azido group present in these complexes, which usually appears in the range of 1340-1180 cm^{-1}. This band has also suffered a downward shift of about 62 cm^{-1}, due to the coordination. The spectra of the chloro complexes exhibit a significant IR band in the range of 721-715 cm^{-1} assigned to ν(Cl), the stretching vibrations for the chloro group which usually appears in the range of 800-600 cm^{-1}. A downwards shift of about 79 cm^{-1} is due to the coordination of chloro group with the Mn(III) ion. The IR spectra of the bromo complexes exhibit a significant peak in the range of 525-515 cm^{-1} due to the stretching vibration of bromo group present in this complex. This band usually appears in the range of 600-500 cm^{-1} a down word shift of about 75 cm^{-1} is due to coordination of the bromo group with the central metal.

The electronic spectra of all these Mn(III) complexes exhibit bands in the region 18000-21000 cm^{-1} attributing to the $^5T_{2g} \rightarrow {}^5E_g$ transitions suggesting octahedral geometry for these Mn(III) complexes. The ligand field parameters such as 10Dq, B and β have been calculated for all these Mn(III) mixed ligand complexes using the procedure given by Drago. The value of 10Dq for the complexes **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11** and **12** are 1879, 1989, 2019, 1900, 1981, 2005, 2015, 1989, 1979, 2001, 2013 and 1097 cm^{-1} while the value of B is 1085, 1100, 1120, 1095, 1095, 1115, 1125, 1105, 1080, 1109, 1121 and 1097 cm^{-1}, respectively. β- value is 0.76, 0.85, 0.87, 0.80, 0.76, 0.84, 0.88, 0.80, 0.75, 0.84, 0.87 and 0.79, respectively. The magnetic moments for all these complexes are in the range of 4.50-4.70 BM indicating the presence of four unpaired electrons in these weak field high-spin complexes confirming the octahedral geometry for these complexes.

The TG curves for Mn(III) complexes show only exothermic peaks above 200 ºC corresponding to the loss of organic moieties. The absence of endothermic peak below 200 ºC indicates the absence of coordinated water in all these complexes. In case of thiocyanato*bis*(β-diketone)manganese(III)ethylenediamine taking the loss of organic moieties ethylenediamine, thiocyanate, four methyl groups, two C-H groups at 0-200, 200-400, 400-600 and 600-800 ºC, respectively at last the formation of manganese oxide at 800-1000 ºC. In the case of azido*bis*(β-diketone) manganese(III)-ethylenediamine the loss of organic moieties ethylenediamine, azide, four methyl groups, two C-H groups at 0-200, 200-400, 400-600, 600-800 ºC, respectively the formation of manganese oxide at 800-1000 ºC takes place. In the chloro and bromo complexes the chloride and bromide moieties are lost at 200-400 ºC. The TG curves for all the Mn(III) mixed ligand complexes indicate four clear stages of decomposition corresponding to the loss of organic and inorganic moieties leading to the formation of metal oxide.

Antifungal activity: These complexes are screened for their fungi toxic proprieties against six fungal strains namely *A. niger*, *C. falcatum*, *C. lunata*, *F. oxysporum*, *F. moniliforme*, *C. saccharii*. The screening data for the mycelial growth of these fungi at 10, 100 and 1000 ppm concentrations are calculated. The values obtained suggest that the thiocyanato complexes are the most fungi toxic than rest of the mixed ligand complexes of Mn(III) which may be attributed to the presence of NCS group in these complexes[40]. The azido complexes show the least fungi toxic property in compression to the rest of the newly synthesised Mn(III) complexes, azido complex is the least fungi toxic than the rest of the complex due to the presence of bridging azido group.

Antibacterial activity: All these Mn(III) mixed ligand complexes are also screened for their bacteriological properties against five bacterial strains namely *Bacillus subtilis*, *Thiobacillus thixidans*, *Agrobacterium temefaciens*, *Xanthomonas oryzae*, *Xanthomonas citr*. Thus obtained data for the percentage inhabitation of the bacteria at 10, 100 and 1000 ppm concentrations are compared. The values suggest that the thiocyanato complexes are the most antibacterial than rest of the Mn(III) complexes, due to the presence of thiocyanato group in this complex[40]. Azido complexes are the least antibacterial in comparison to the rest of the newly synthesised Mn(III) complexes. These novel complexes containing substituted chalcogens showed promising results in the inhabitation at the colony growth.

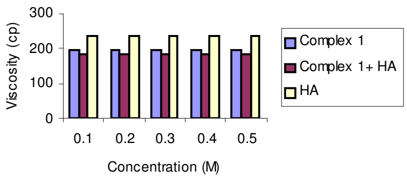
Delignification properties: On the basis of the viscosity measurement data (Table-1) and the Figs. (1-12) obtained by plotting concentrations *versus* viscosity, it can be suggested that these Mn(III) complexes are able to break the humic acid into it's lower molecular weights fractions. As the viscosity of humic acid when taken along with these complexes is found to be lesser than the viscosity of humic acid alone or the viscosity of these Mn(III) complexes alone. This decrease in viscosity of humic acid when taken along with these Mn(III) complexes indicates the breaking of humic acid into its lower molecular weight components. These findings are well supported by the other workers[41]. Azido mixed ligand complexes show the maximum catalytic property while the bromo mixed ligand complexes show the minimum catalytic property by comparing the graphs and the data obtained. The catalytic properties of these novel mixed ligand complexes of Mn(III) can be explored for industrial applications also. This is the beginning only because as the way in which humic acid is broken by these Mn(III) mixed ligand complexes has yet to be proposed. Different model complexes of this type can be prepared according to the need of breaking the humic acid portions and then applying for industrial purposes.

Structure: These structures fulfill all the characterization data obtained during the present investigations. On the basis of elemental analyses, molecular weights, molar conductivities, electronic conductivities, magnetic moments and spectral (UV-visible, IR) data the probable structures for these complexes can be proposed as distorted octahedral with bridging ethylenediamine between the two Mn(III) units as shown in Figs. 13-15. The coordination number of central Mn(III) is six; which is satisfied by two bidentate ligands, one monodentate ligand and one bridging bidantate ligand between the two Mn(III) distorted octahedral units.

TABLE-1
VISCOSITIES OF COMPLEXES AND COMPLEXES WITH HUMIC ACID

S. No.	Strength complex	0.1 M	0.2 M	0.3 M	0.4 M	0.5 M
		(1 = complex 1, 1a = complex 1 with humic acid)				
1	**1**	196.3541×10^{-5}	196.4554×10^{-5}	196.5512×10^{-5}	196.6011×10^{-5}	196.7513×10^{-5}
2	**1a**	185.4510×10^{-5}	185.4001×10^{-5}	185.3511×10^{-5}	185.3000×10^{-5}	185.2509×10^{-5}
3	**2**	199.1041×10^{-5}	199.1501×10^{-5}	199.2002×10^{-5}	199.2509×10^{-5}	199.3008×10^{-5}
4	**2a**	186.4500×10^{-5}	186.4009×10^{-5}	186.3511×10^{-5}	186.3019×10^{-5}	186.2520×10^{-5}
5	**3**	190.2514×10^{-5}	190.3005×10^{-5}	190.3511×10^{-5}	190.4031×10^{-5}	190.4511×10^{-5}
6	**3a**	181.4501×10^{-5}	181.4001×10^{-5}	181.3511×10^{-5}	181.3021×10^{-5}	181.2500×10^{-5}
7	**4**	185.2500×10^{-5}	185.3019×10^{-5}	185.3513×10^{-5}	185.4017×10^{-5}	185.4515×10^{-5}
8	**4a**	179.3511×10^{-5}	179.3019×10^{-5}	179.2511×10^{-5}	179.2000×10^{-5}	179.1509×10^{-5}
9	**5**	199.1517×10^{-5}	199.2018×10^{-5}	199.2519×10^{-5}	199.3020×10^{-5}	199.3521×10^{-5}
10	**5a**	186.3517×10^{-5}	186.3016×10^{-5}	186.2515×10^{-5}	186.2514×10^{-5}	186.1523×10^{-5}
11	**6**	205.0519×10^{-5}	205.1020×10^{-5}	205.1521×10^{-5}	205.2022×10^{-5}	205.2523×10^{-5}
12	**6a**	187.2501×10^{-5}	187.2002×10^{-5}	187.1503×10^{-5}	187.1004×10^{-5}	187.0505×10^{-5}
13	**7**	195.0711×10^{-5}	195.1212×10^{-5}	195.1713×10^{-5}	195.2214×10^{-5}	195.2715×10^{-5}
14	**7a**	184.4515×10^{-5}	184.4014×10^{-5}	184.3513×10^{-5}	184.3012×10^{-5}	184.2511×10^{-5}
15	**8**	190.1511×10^{-5}	190.2012×10^{-5}	190.2513×10^{-5}	190.3014×10^{-5}	190.3515×10^{-5}
16	**8a**	183.4516×10^{-5}	183.4015×10^{-5}	183.3014×10^{-5}	183.3513×10^{-5}	183.3012×10^{-5}
17	**9**	204.1511×10^{-5}	204.2010×10^{-5}	204.2513×10^{-5}	204.3013×10^{-5}	204.3516×10^{-5}
18	**9a**	195.4511×10^{-5}	195.4013×10^{-5}	195.3512×10^{-5}	195.3015×10^{-5}	195.2517×10^{-5}
19	**10**	209.0513×10^{-5}	209.1019×10^{-5}	209.1516×10^{-5}	209.2015×10^{-5}	209.2513×10^{-5}
20	**10a**	196.3515×10^{-5}	196.3016×10^{-5}	196.2517×10^{-5}	196.2018×10^{-5}	196.1519×10^{-5}
21	**11**	200.1019×10^{-5}	200.1520×10^{-5}	200.2021×10^{-5}	200.2522×10^{-5}	200.3023×10^{-5}
22	**11a**	193.2515×10^{-5}	193.2014×10^{-5}	193.1513×10^{-5}	193.1012×10^{-5}	193.0511×10^{-5}
23	**12**	193.0711×10^{-5}	193.1212×10^{-5}	193.1719×10^{-5}	193.2220×10^{-5}	193.2719×10^{-5}
24	**12a**	189.3911×10^{-5}	189.3413×10^{-5}	189.2913×10^{-5}	189.2417×10^{-5}	189.1918×10^{-5}

1



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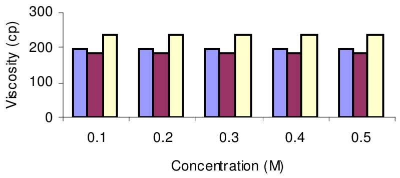

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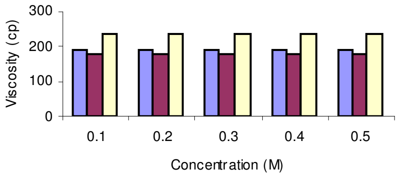

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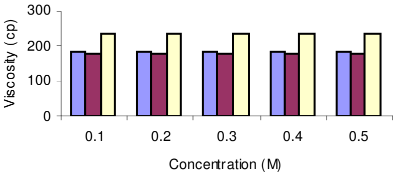

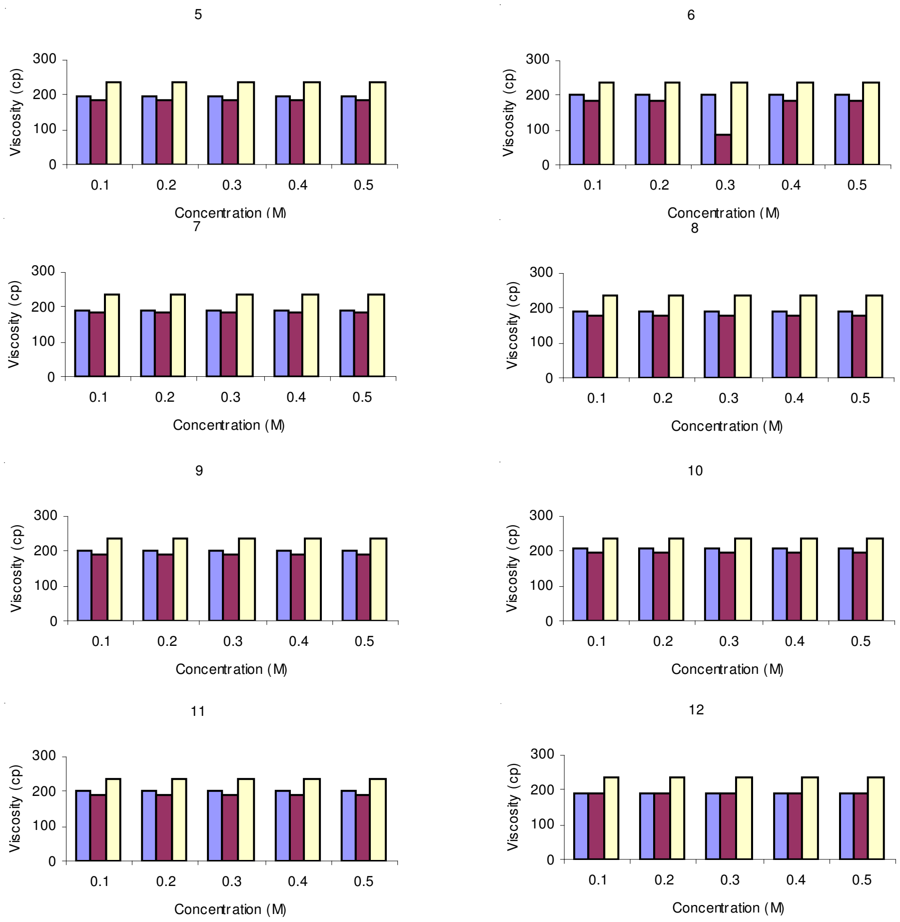

Figs. 1-12

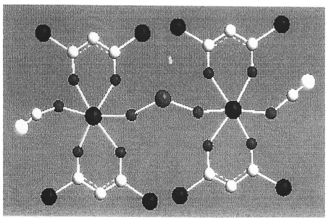

Fig. 13. [Mn(β-diketonato)$_2$ NCS]$_2$diamine

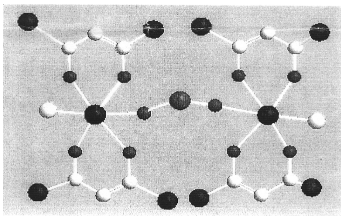

Fig. 14. [Mn(β- diketonato)$_2$X]$_2$ diamine, X= Cl$^-$ or Br$^-$

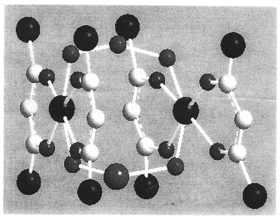

Fig. 15. [Mn(β-diketonato)$_2$ N$_3$]$_2$diamine

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