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Synthesis and Characterization of Iron(III), Manganese(III) and Chromium(III) Complexes with N,N′-ethylene-bis-(3-carboxypropenamide)

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A series of thirteen complexes of trivalent transition metal ions *viz.*, Fe(III), Mn(III) and Cr(III) with a polydentate ligand N,N′-ethylene-bis(3-carboxypropenamide) and various anions such as chloride, bromide, nitrate, thiocyanate, perchlorate and acetate have been synthesized and characterized. The analytical data include elemental analysis, molecular weight determinations, molar conductance, magnetic moment, infrared spectra and X-ray diffraction. The spectral studies suggest that ligand behaves as divalent tetradentate ligand, coordinating through two-amido nitrogen and two oxygen atoms of the carboxylate groups and the anions act as unidentate ligand.

Key Words: Iron(III), Manganese(III), Chromium(III), Polydentate ligand, Complexes, N,N′-Ethylene-bis(3-carboxypropenamide).

INTRODUCTION

A survey of the literature showed that there have been numerous studies on metal complexes with the derivatives of ethylenediamine[1–3]. However, little information is available on transition metal complexes of the maleic anhydride derivative of ethylenediamine. Except for the synthesis of Co(II), Ni(II) and Pd(II) complexes of N,N′-ethylene-bis(3-carboxypropenamide) ($EBCPH_2$)[4], no other studies on synthesis and characterization of transition metal complexes of this ligand have been carried out so far. Therefore, we considered worthwhile to synthesize and characterize some trivalent transition metal complexes with N,N′-ethylene-bis(3-carboxypropenamide) ($EBCPH_2$) in presence of coordinating anions such as chloride, bromide, nitrate, thiocyanate, perchlorate and acetate. The structure of the ligand can be represented as Fig. 1.

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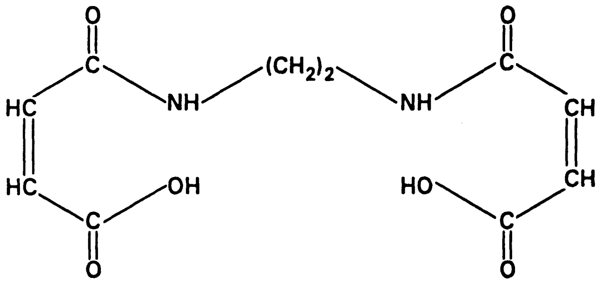


Structure of N,N′-ethylene-bis(3-carboxypropenamide)

Fig. 1

EXPERIMENTAL

The ligand $EBCPH_2$ was prepared by literature method[4]. Maleic anhydride (9.8 g, 0.1 mol) was dissolved in glacial acetic acid (50 mL) and kept overnight. Ethylenediamine (3.05 g, 0.05 mole) was then added dropwise with constant stirring under ice-cold condition. The white crystals of the amido acid ($EBCPH_2$) formed were filtered, washed several times with acetone, dried in air and recrystallized from aqueous ethanol (m.p. 161°C).

Iron(III) chloro, bromo, perchlorato and nitrato complexes were prepared by mixing equal volumes (20 cm^3) of solutions of ferric salt and sodium salt of the ligand ($EBCPH_2$) in the molar ratio 1 : 1 in methanol. In the case of thiocyanato complex, ferric thiocyanate solution in ether was mixed with equal volume of sodium salt of the $EBCPH_2$ in methanol. The perchlorato complex is obtained only after refluxing on a water bath. The brown coloured solid complex formed was filtered, washed several times with methanol and dried in a desiccator over P_4O_{10}.

The acetato complex of mangancse(III) was prepared by refluxing equal volumes of the solutions of manganese(III) acetate dihydrate and sodium salt of the ligand ($EBCPH_2$) in the molar ratio 1 : 1 in methanol. The manganese(III) chloro, bromo, perchlorato, nitrato and thiocyanato complexes were prepared from this acetato complex by refluxing with 0.01 mole solution of lithium chloride, bromide, perchlorate, nitrate or ammonium thiocyanate in methanol. The brownish black coloured solid complex formed was filtered, washed several times with methanol and dried over P_4O_{10}.

The chloro complex of chromium(III) was prepared by mixing equal volume of solutions of chromium(III) chloride and sodium salt of the $EBCPH_2$ in methanol in the molar ratio 1 : 1 and refluxed on a water bath for about 2 h. The grey coloured solid complex formed was filtered, washed several times with methanol and dried. The solid violet coloured thiocyanate complex was prepared from this chloro complex by substitution using ammonium thiocyanate.

All the complexes are stable at room temperature and non-hygroscopic. They are only slightly soluble in methanol and ethanol; insoluble in common organic solvents like ether, acetone, benzene, carbon tetrachloride, petroleum ether and nitrobenzene but are freely soluble in DMF, acetonitrile and DMSO.

Iron content was obtained by direct pyrolysis of the complex to its oxide, Fe_2O_3. Manganese was estimated by spectrophotometric method[5]. The chromium content of the complexes was obtained by standard gravimetric procedure[5]. The molar conductivities of the complex in DMF, acetonitrile and methanol were measured at room temperature. The IR spectra of the ligand and complexes were recorded in KBr in the range 4000–400 cm^{-1}. The complexes were analysed for carbon, hydrogen and nitrogen using a Heraeus CHN rapid analyser. For the estimation of iron in perchlorato complex, peaceful pyrolysis was employed[6]. The anion content was estimated gravimetrically. Kurz's method was employed to estimate perchlorate[7]

RESULTS AND DISCUSSION

The analytical data of the complexes along with some physical properties are summarized in Table-1. The microanalytical data of the metal complexes reveal the formation of 1 : 1 (metal : ligand) complexes. They are non-electrolytes with low molar conductance values 8–27, 17–37 and 14–37 ohm^{-1} cm^2 mol^{-1} of 10^{-3} M solutions in DMF, acetonitrile and methanol respectively at room temperature[8].

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF [M(EBCP)X] COMPLEXES

Complex (Colour)	Analysis %: Found (Calcd.)						μ_{eff} (B.M.)
	M	C	H	N	Cl/Br	S/ClO_4	
Fe(EBCP)Cl (Deep brown)	16.02 (16.17)	34.28 (34.75)	2.81 (2.90)	8.18 (8.11)	9.97 (10.27)	—	4.67
Fe(EBCP)Br (Dark brown)	13.88 (14.33)	31.15 (30.79)	2.32 (2.57)	7.10 (7.18)	20.84 (20.50)	—	4.10
Fe(EBCP)NCS (Reddish brown)	14.87 (15.18)	35.56 (35.88)	2.63 (2.72)	11.75 (11.42)	—	8.84 (8.70)	3.77
Fe(EBCP)NO_3 (Dark brown)	14.76 (15.02)	32.63 (32.27)	2.52 (2.69)	11.02 (11.29)	—	—	4.53
Fe(EBCP)ClO_4 (Reddish brown)	13.88 (13.65)	29.14 (29.32)	2.36 (2.44)	6.75 (6.84)	—	24.49 (24.30)	4.37
Cr(EBCP)Cl (Grey)	15.99 (15.23)	35.28 (35.14)	2.74 (2.93)	8.38 (8.20)	10.45 (10.38)	—	3.85
Cr(EBCP)NCS (Violet)	14.38 (14.29)	36.43 (36.26)	2.66 (2.75)	11.71 (11.54)	—	8.55 (8.79)	3.76
Mn(EBCP)Cl (Brownish black)	16.15 (15.95)	34.58 (34.84)	2.73 (2.90)	8.25 (8.13)	10.53 (10.29)	—	4.80
Mn(EBCP)Br (Brownish black)	14.42 (14.13)	30.56 (30.86)	2.45 (2.57)	7.51 (7.20)	20.26 (20.55)	—	4.86
Mn(EBCP)NCS (Brownish black)	14.82 (14.97)	35.73 (35.97)	2.91 (2.73)	11.09 (11.45)	—	8.91 (8.72)	4.95
Mn(EBCP)NO_3 (Brownish black)	15.10 (14.81)	32.06 (32.35)	2.57 (2.70)	11.52 (11.32)	—	—	4.94
Mn(EBCP)ClO_4 (Brownish black)	13.23 (13.45)	29.54 (29.38)	2.61 (2.45)	6.93 (6.86)	—	24.84 (24.35)	4.92
Mn(EBCP)CH_3COO (Brownish black)	15.25 (14.93)	38.87 (39.14)	3.45 (3.53)	7.83 (7.61)	—	—	4.89

The magnetic moment values observed for the chromium(III) complexes correspond to three unpaired electrons. The magnetic moments of [Cr(EBCP)NCS] (3.76 B.M.) is slightly less than the spin only value as is generally the case with octahedral chromium(III) complexes[9] due to very small spin-orbit coupling constant of. Cr^{3+}. The observed magnetic moment values of Fe(III) and Mn(III) complexes are in the ranges 3.77–4.66 B.M. and 4.80–4.95 B.M. respectively. The deviation from the expected value may be due to metal- metal interaction, as reported for many five coordinate high-spin complexes[10, 11]

TABLE-2
MOLAR CONDUCTANCE VALUES (ohm^{-1} cm^{-1} mol^{-1}) OF Fe(III), Mn(III) AND Cr(III) COMPLEXES OF $EBCPH_2$

Complex	DMF		Acetonitrile		Methanol		Electrolytic nature
	Concn. $\times 10^{-3}$ M	Ω_m	Concn. $\times 10^{-3}$ M	Ω_m	Concn. $\times 10^{-3}$ M	Ω_m	
[Fe(EBCP)Cl]	1.02	14.6	1.11	20.8	1.09	19.1	Non-electrolyte
[Fe(EBCP)Br]	1.05	24.7	0.96	26.0	1.00	25.7	Non-electrolyte
[Fe(EBCP)NCS]	1.06	16.2	0.99	30.4	1.23	14.6	Non-electrolyte
[Fe(EBCP)NO_3]	1.03	27.8	1.06	37.3	1.10	35.7	Non-electrolyte
[Fe(EBCP)ClO_4]	0.97	20.8	1.04	21.5	1.01	27.6	Non-electrolyte
[Cr(EBCP)Cl]	1.12	8.9	1.24	12.7	1.22	14.3	Non-electrolyte
[Cr(EBCP)NCS]	1.07	12.9	1.14	20.5	1.01	20.9	Non-electrolyte
[Mn(EBCP)Cl]	1.09	18.5	1.10	22.4	1.07	23.2	Non-electrolyte
[Mn(EBCP)Br]	1.07	22.1	1.02	26.4	0.98	21.6	Non-electrolyte
[Mn(EBCP)NCS]	1.05	16.5	1.13	28.0	1.11	23.9	Non-electrolyte
[Mn(EBCP)NO_3]	0.99	21.7	1.05	36.4	1.07	32.9	Non-electrolyte
[Mn(EBCP)ClO_4]	1.03	16.2	1.00	17.4	1.06	29.7	Non-electrolyte
[Mn(EBCP)CH_3COO]	1.17	10.3	1.01	21.9	1.13	25.0	Non-electrolyte

The electronic spectra of Cr(III) complexes show bands at around 33,170 and 26,660 cm^{-1}, which are due to charge transfer. The $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) transition is most probably obscured by the charge transition band at 26,660 cm^{-1}. The weak bands with maxima appearing at 21,670 cm^{-1} and at 15,500 cm^{-1}, for the chloro complex, are assigned to the $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{2g}(F)$ transitions respectively. The broad band with maximum at 17575 cm^{-1} in the thiocyanato complex is assigned to the $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transition. The $^4A_{2g} \rightarrow {}^4T_{2g}(F)$ transition in this case may be overlapped by $^4A_{2g} \rightarrow {}^4T_{1g}(F)$[12]. Electronic spectra of Fe(III) and Mn(III) complexes show bands with maxima at 33,330 cm^{-1} and around 27,700 cm^{-1} which are due to charge transfer transition. Since the ground state for Fe(III) high-spin complexes is $^6A_{1g}$, all the transitions are spin forbidden. For the Fe(III) complexes, a comparatively weak broad band observed with maximum at *ca.* 20,000 cm^{-1} may be due to spin forbidden transition $^6A_{1g} \rightarrow {}^4T_{1g}$ (F)[13]. The broad band with maxima at *ca.* 19,850 cm^{-1} for the Mn(III) complexes is due to $^5E_g \rightarrow 5T_{2g}$ transition. The thiocyanato complex, [Mn(EBCP)NCS), shows an additional shoulder at 18,350 cm^{-1}. This absorption may be due to the electronic transition between the split components of the $^5T_{2g}$ and ^5E_g levels of the distorted octahedral complex[14].

The strong band at 3300 cm^{-1} in free ligand is assigned to the NH stretching frequency of secondary amide groups[15]. This frequency is observed around 3245–3230 cm^{-1} after complexation indicating that coordination has occurred through nitrogen atoms of both the amide groups. Another strong band observed at 1700 cm^{-1} in the spectrum of the free ligand, due to ν_{as}(C═O) of carboxylic groups, disappears and two new bands observed at 1608–1565 cm^{-1} and 1420–1385 cm^{-1} regions in complexes are assigned to ν_{as}(OCO) and ν_s(OCO) respectively of the coordinated carboxylate groups[16–18]. The energy separation between the two bands is *ca.* 190 cm^{-1} (Table-3). The strong band observed at 1620 cm^{-1} in free ligand assigned to ν(C═O) of the secondary amide groups does not undergo significant shift in the infrared spectra of the complexes. This observation precludes the possibility of complexation at this group[4, 19].

From the above observations it may be concluded that in these complexes the ligand behaves as divalent tetradentate, coordination sites being the two-amide nitrogen and two oxygen atoms of carboxylate groups. The bands observed in the regions 585–565 cm^{-1} and 475–455 cm^{-1} in the infrared spectra of the complexes are assigned to ν(M—N) and ν(M—O) respectively[16, 20]. The coordination of chloride and bromide in complexes is supported by infrared spectra, conductance and analytical data.

The position of bands in the region 1150–1080 cm^{-1} (ν_4 and ν_1) and 700–620 cm^{-1} (ν_3 and ν_5) and the magnitude of separation between them suggest the monodentate nature for the coordinated perchlorato group (tetrahedral symmetry has changed to C_{3V})[21]. The weak band in the region 940–930 cm^{-1} is assigned to ν_2 of the coordinated ClO_4^- group. The ν_6 vibrations expected around 480 cm^{-1} for coordinated perchlorate could not be located since the metal-ligand stretching frequency is also expected in this region. The conductance data is also in support of the non-ionic nature of the perchlorate group and is therefore coordinated.

In the nitrato complexes, the strong band observed at 1385 cm^{-1} and medium band at 1460 cm^{-1} regions are assigned to the split components of ν_3. The magnitude of separation suggests monodentate nature of the nitrate group[22, 23]. The weak bands observed in the region 1800–1700 cm^{-1} are attributed to the combination bands ($\nu_1 + \nu_4$). The non-planar rocking ν_6 vibration is observed at around 840 cm^{-1}.

The strong band at 2090–2060 cm^{-1} and medium band at 490–480 cm^{-1} regions in the thiocyanate complexes are assigned to ν(C—N) and ν(NCS) bending respectively of coordinated thiocyanate group[24, 25]. The C—S stretch could not be identified since the ligand itself has bands in that region (860–780 cm^{-1}). Hence the NCS bending vibration is used for ascertaining the coordination through nitrogen.

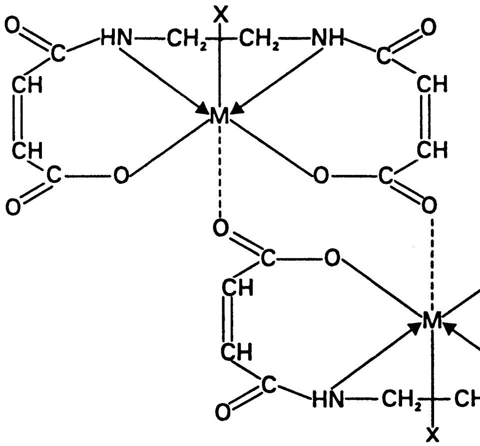
TABLE-3
INFRARED SPECTRAL BANDS (cm^{-1}) OF $EBCPH_2$ AND ITS Fe(III), Cr(III) AND Mn(III) COMPLEXES

Compounds	ν(NH)	ν(C=O)	ν(CO)	ν_{as}(OCO)	ν_s(OCO)	ν(NH)	ν(CN + NH)	ν(M—N)	ν(M—O)
Ligand($EBCPH_2$)	3300	1700	1620	—	—	1560	1375	—	—
[Fe(EBCP)Cl]	3230	—	1624	1605	1413	1550	1315	565	455
[Fe(EBCP)Br]	3245	—	1623	1605	1415	1540	1320	570	460
[Fe(EBCP)NCS]	3240	—	1624	1595	1410	1540	1315	570	455
[Fe(EBCP)NO_3]	3243	—	1625	1605	1420	1540	1315	570	460
[Fe(EBCP)ClO_4]	3230	—	1625	1600	1415	1540	1320	570	450
[Cr(EBCP)Cl]	3235	—	1624	1605	1420	1555	1315	580	460
[Cr(EBCP)NCS]	3245	—	1624	1600	1410	1555	1320	595	470
[Mn(EBCP)Cl]	3245	—	1622	1608	1415	1555	1310	585	465
[Mn(EBCP)Br]	3240	—	1622	1605	1410	1535	1335	565	475
[Mn(EBCP)NCS]	3240	—	1624	1605	1415	1550	1315	580	470
[Mn(EBCP)NO_3]	3245	—	1620	1585	1405	1540	1345	600	465
[Mn(EBCP)ClO_4]	3240	—	1622	1565	1384	1550	1355	580	460
[Mn(EBCP)CH_3COO]	3235	—	1623	1590	1405	1535	1335	570	455

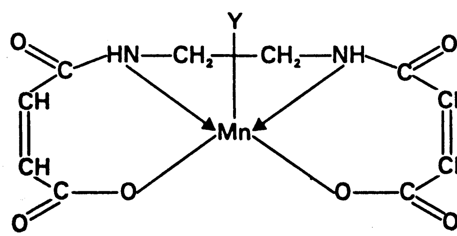
The nature of the acetate group in the manganese(III) acetate complex cannot be predicted from the infrared spectrum because there are ligand vibrations in the same region where carbonyl group vibrations are also expected. However, the coordinated nature of the acetate ion is evidenced from the conductance and analytical data.

The X-ray powder pattern of the iron(III) chloro complex was recorded on a Rigaku (Japan) PW 1710 X-ray powder diffractometer on chart recorder. Reflections from various sets of planes have been recorded for 5–70° at a sample rotation 0.05°/sec. with CoK_α radiation using 40 kV 20MA. All the 41 lines on the XRD powder pattern, by employing Hesse and Lipson's procedure[26, 27], could be indexed successfully for the orthorhombic system with the unit cell dimensions, a = 17.5544 Å, b = 14.9184 Å and c = 11.9613 Å. The density of the complex was determined with specific gravity bottle using petroleum ether as the displacing liquid. The number of molecules per unit cell was found to be four.

Analytical, magnetic and spectral studies suggest that the possible structures of the complexes are as given below.



M = Fe or Cr
X = Cl, Br, NCS, NO_3 or ClO_4



Y = Cl, Br, NCS, NO_3, ClO_4 or CH_3COO

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