

Synthesis and Characterization of Iron(III), Manganese(III) and Chromium(III) Complexes with *N,N'*-Propylene-bis(3-carboxypropenamide)

C.G. RADHAKRISHNAN NAMBOORI* and G. KRISHNAN†

Department of Chemistry, Mahatma Gandhi College

Thiruvananthapuram-695 004, India

E-mail: chettoormana@eth.net

A series of thirteen complexes of trivalent transition metal ions, viz., Fe(III), Mn(III) and Cr(III) with a polydentate ligand *N,N'*-propylene-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, 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'*-Propylene-bis(3-carboxypropenamide).

INTRODUCTION

A number of complexes of 1,3-diaminopropane and its derivatives have been reported in literature¹⁻³. However, studies on metal complexes of maleic anhydride derivative of this diamine, *N,N'*-propylene-bis(3-carboxypropenamide) have not been carried out so far. Therefore, we considered it worthwhile to synthesize and characterize some trivalent transition metal complexes with *N,N'*-propylene-bis(3-carboxypropenamide) (PBCPH₂) 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.

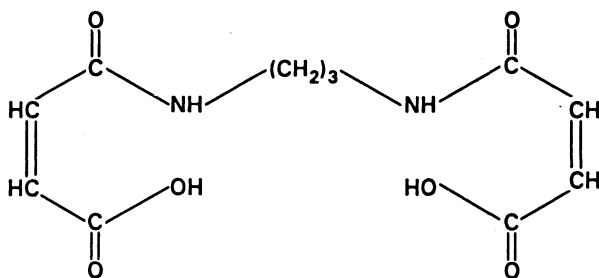


Fig. 1. Structure of *N,N'*-propylene-bis(3-carboxypropenamide)

†Department of Chemistry, University College, Thiruvananthapuram-695 034, India.

EXPERIMENTAL

The ligand PBCPH₂ was prepared by literature method⁴. Maleic anhydride (9.8 g, 0.1 mol) was dissolved in glacial acetic acid (50 mL) and kept overnight. Propylenediamine (3.75 g, 0.05 mol) was then added dropwise with constant stirring under ice-cold condition. The white crystals of the amido acid (PBCPH₂) formed was filtered, washed several times with acetone, dried in air and recrystallized from aqueous ethanol (m.p. 163°C).

Iron(III) chloro, bromo, perchlorato and nitrate complexes were prepared by mixing equal volumes (20 cm³) of solutions of ferric salt and sodium salt of the ligand (PBCPH₂) 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 PBCPH₂ 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 P₄O₁₀.

The acetato complex of manganese(III) was prepared by refluxing equal volumes of the solutions of manganese(III) acetate dihydrate and sodium salt of the ligand (PBCPH₂) in the molar ratio 1 : 1 in methanol. Manganese(III) chloro, bromo, perchlorato, nitrate 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 with methanol and dried over P₄O₁₀.

The chloro complex of chromium(III) was prepared by mixing equal volume of solutions of chromium(III) chloride and sodium salt of the PBCPH₂ 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 acetonitrile, DMF and DMSO.

Iron content was obtained by direct pyrolysis of the complex to its oxide, Fe₂O₃. Manganese was estimated by spectrophotometric method⁵. The chromium content of the complexes was obtained by standard gravimetric procedures. 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 employed⁶. The anion content was estimated gravimetrically. Kurz's method was employed to estimate perchlorate⁷.

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 10–27, 4–24 and 4–25 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ of 10^{-3} M solutions in DMF, acetonitrile and methanol respectively at room temperatures.⁸

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF M(PBCP)X COMPLEXES

Compound (Colour)	Analysis %: Found (Calcd.)						μ_{eff} (B.M.)
	M	C	H	N	Cl/Br	S/ClO ₄	
PBCPH ₂ (White)	—	48.82 (48.89)	5.02 (5.19)	10.26 (10.37)	—	—	—
Fe(PBCP)Cl (Deep brown)	14.97 (15.54)	36.57 (36.74)	3.13 (3.34)	7.88 (7.79)	9.48 (9.87)	—	3.78
Fe(PBCP)Br (Dark brown)	13.52 (13.83)	32.76 (32.69)	2.64 (2.97)	6.55 (6.93)	19.68 (19.79)	—	4.30
Fe(PBCP)NCS (Reddish brown)	14.63 (14.63)	37.62 (37.71)	3.02 (3.14)	11.18 (11.00)	—	8.28 (8.38)	4.09
Fe(PBCP)NO ₃ (Brown)	14.28 (14.47)	34.42 (34.21)	2.98 (3.11)	10.56 (10.89)	—	—	3.68
Fe(PBCP)ClO ₄ (Reddish brown)	13.34 (13.19)	30.97 (31.18)	2.67 (2.83)	6.48 (6.62)	—	23.38 (23.49)	3.60
Cr(PBCP)Cl (Grey)	14.86 (14.63)	36.98 (37.14)	3.24 (3.38)	7.63 (7.88)	9.72 (9.97)	—	3.81
Cr(PBCP)NCS (Violet)	13.88 (13.76)	37.95 (38.09)	3.08 (3.17)	11.25 (11.11)	—	8.18 (8.47)	3.86
Mn(PBCP)Cl (Brownish black)	15.28 (15.33)	36.67 (36.83)	3.21 (3.35)	7.67 (7.81)	9.97 (9.89)	—	4.70
Mn(PBCP)Br (Brownish black)	13.52 (13.64)	32.62 (32.77)	2.76 (2.98)	6.78 (6.95)	19.72 (19.83)	—	4.56
Mn(PBCP)NCS (Brownish black)	14.25 (14.42)	37.63 (37.80)	3.22 (3.15)	11.15 (11.03)	—	8.32 (8.40)	4.74
Mn(PBCP)NO ₃ (Brownish black)	13.98 (14.27)	34.07 (34.29)	2.96 (3.12)	10.82 (10.91)	—	—	4.59
Mn(PBCP)ClO ₄ (Brownish black)	12.94 (13.01)	30.99 (31.25)	2.70 (2.84)	6.55 (6.63)	—	23.26 (23.54)	4.98
Mn(PBCP)CH ₃ COO (Brownish black)	14.12 (14.38)	40.64 (40.84)	3.78 (3.93)	7.10 (7.33)	—	—	4.65

The observed magnetic moment values of Fe(III) and Mn(III) complexes are in the ranges 3.60–4.30 B.M. and 4.56–4.98 B.M. respectively. The deviation from the expected value (5.92 BM for Fe(III) and 4.90 BM for Mn(III)) may be

due to metal-metal interaction, as reported for many five coordinate high-spin complexes^{9,10}. The magnetic moment values observed for the chromium(III) complexes correspond to three unpaired electrons. The magnetic moments of [Cr(PBCP)Cl] (3.81 B.M.) is slightly less than the spin only value (3.88 BM) as is generally the case with octahedral chromium(III) complexes¹¹ due to very small spin orbit coupling constant of Cr³⁺

TABLE-2
MOLAR CONDUCTANCE VALUES ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) OF Fe(III), Mn(III) AND Cr(III) COMPLEXES OF PBCPH₂

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(PBCP)Cl]	1.02	20.1	1.08	23.1	1.06	19.0	Non-electrolyte
[Fe(PBCP)Br]	1.04	28.7	1.12	25.5	1.05	17.6	Non-electrolyte
[Fe(PBCP)NCS]	0.99	22.3	1.18	3.9	1.10	4.5	Non-electrolyte
[Fe(PBCP)NO ₃]	1.01	30.0	1.04	29.3	0.95	24.9	Non-electrolyte
[Fe(PBCP)ClO ₄]	1.03	27.5	1.06	15.8	1.13	25.3	Non-electrolyte
[Cr(PBCP)Cl]	1.06	19.6	1.26	9.3	1.19	11.5	Non-electrolyte
[Cr(PBCP)NCS]	1.19	29.6	1.04	7.7	0.99	12.0	Non-electrolyte
[Mn(PBCP)Cl]	1.08	30.7	1.16	15.2	1.08	15.3	Non-electrolyte
[Mn(PBCP)Br]	1.11	30.8	0.97	21.7	1.13	20.1	Non-electrolyte
[Mn(PBCP)NCS]	1.09	10.8	0.97	14.3	1.18	10.8	Non-electrolyte
[Mn(PBCP)NO ₃]	1.02	35.3	1.09	24.5	1.14	22.8	Non-electrolyte
[Mn(PBCP)ClO ₄]	0.97	30.8	1.06	19.1	1.10	24.4	Non-electrolyte
[Mn(PBCP)CH ₃ COO]	1.28	18.9	1.07	12.6	1.12	19.0	Non-electrolyte

The electronic spectra of Cr(III) complexes show bands at around 33,330 and 26,315 cm^{-1} , which are due to charge transfer. The ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (P) transition is most probably obscure by the charge transition band at 26,315 cm^{-1} . The weak bands with maxima appearing at 20,410 cm^{-1} and near 15,385 cm^{-1} are assigned to the ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F) and ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (F) transitions respectively¹². Electronic spectra of Fe(III) and Mn(III) complexes show bands with maxima at 33,330 cm^{-1} and 27,700–27,400 cm^{-1} region respectively, 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 maxima at *ca.* 21,000 cm^{-1} may be due to spin forbidden transition ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (F)¹³. The broad band with maxima at 19,800 cm^{-1} for the Mn(III) complexes is due to ${}^5E_g \rightarrow {}^5T_{2g}$ transition. The thiocyanato complex, [Mn(PBCP)NCS], shows an additional shoulder at 18,520 cm^{-1} . This absorption may be due to the electronic transition between the split components of the 5E_g state of the distorted octahedral complex¹⁴.

The strong band at 3300 cm^{-1} in free ligand is assigned to the NH stretching frequency of secondary amide groups¹⁵. This frequency is observed around $3250\text{--}3235\text{ cm}^{-1}$ after complexation indicating that coordination has occurred through nitrogen atoms of both the amide groups. Another strong band observed at 1710 cm^{-1} in the spectrum of the free ligand, due to $\nu_{\text{as}}(\text{C}=\text{O})$ of carboxylic groups, disappears and two new bands observed at $1600\text{--}1585\text{ cm}^{-1}$ and $1420\text{--}1410\text{ cm}^{-1}$ regions in complexes are assigned to $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ respectively of the coordinated carboxylate groups¹⁶⁻¹⁸. The energy separation between the two bands is *ca.* 190 cm^{-1} . The strong band observed at 1625 cm^{-1} in free ligand, assigned to $\nu(\text{C}=\text{O})$ of the secondary amide groups does not undergo significant shift in the infrared spectra of the complexes. This ruled out 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 $580\text{--}545\text{ cm}^{-1}$ and $480\text{--}455\text{ cm}^{-1}$ in the infrared spectra of the complexes are assigned to $\nu(\text{M}\text{--}\text{N})$ and $\nu(\text{M}\text{--}\text{O})$ respectively^{16, 20}. The coordination of chloride and bromide in the complexes is supported by infrared spectra, conductance and analytical data.

The position of bands in the region $1110\text{--}1085\text{ cm}^{-1}$ (ν_4 and ν_1) and $700\text{--}620\text{ cm}^{-1}$ (ν_3 and ν_5) and the magnitude of separation between them suggests the monodentate nature for the coordinated perchlorate group (tetrahedral symmetry has changed to C_{3v})²¹. The weak band at 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 to the metal ion.

In the nitrate complexes, the strong band observed at 1385 cm^{-1} and medium band in $1460\text{--}1445\text{ cm}^{-1}$ region 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 $1800\text{--}1700\text{ cm}^{-1}$ 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 $2095\text{--}2070\text{ cm}^{-1}$ and medium band at $490\text{--}480\text{ cm}^{-1}$ regions in the thiocyanate complexes are assigned to $\nu(\text{C}\text{--}\text{N})$ and $\delta(\text{NCS})$ 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 ($860\text{--}780\text{ cm}^{-1}$). Hence the NCS bending vibration is used for ascertaining the coordination through nitrogen.

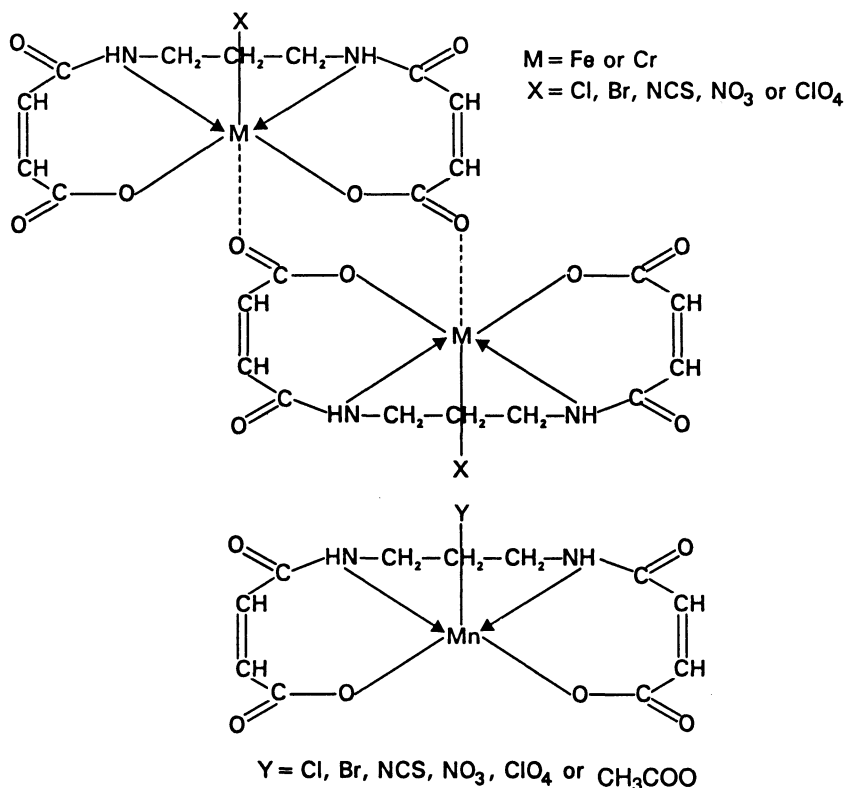
The nature of the acetate group in the manganese(III) acetate complex cannot be predicted from the infrared spectrum because there are ligand vibrations in the same region where carbonyl group vibrations are also expected. However, the coordinated nature of the acetate ion is evidenced from the conductance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

TABLE-3
 INFRARED SPECTRAL BANDS (cm^{-1}) OF PBCP H_2 AND ITS Fe(III), Cr(III) AND Mn(III) COMPLEXES

Compounds	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{CO})$	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{s}}(\text{OCO})$	$\nu(\text{NH})$	$\nu(\text{CN} + \text{NH})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
Ligand(PBCP H_2)	3300	1710	1625	—	—	1580	1365	—	—
[Fe(PBCP)Cl]	3250	—	1624	1595	1410	1540	1310	570	460
[Fe(PBCP)Br]	3240	—	1623	1600	1415	1535	1315	565	455
[Fe(PBCP)NCS]	3245	—	1626	1590	1415	1540	1310	565	465
[Fe(PBCP)NO $_3$]	3250	—	1625	1595	1420	1530	1310	560	455
[Fe(PBCP)ClO $_4$]	3240	—	1622	1585	1415	1535	1315	560	455
[Cr(PBCP)Cl]	3235	—	1625	1600	1415	1565	1315	545	470
[Cr(PBCP)NCS]	3240	—	1623	1595	1410	1555	1315	550	465
[Mn(PBCP)Cl]	3245	—	1622	1590	1415	1555	1310	575	465
[Mn(PBCP)Br]	3240	—	1623	1595	1410	1535	1335	565	475
[Mn(PBCP)NCS]	3240	—	1622	1585	1410	1550	1315	580	470
[Mn(PBCP)NO $_3$]	3245	—	1622	1585	1410	1540	1345	570	465
[Mn(PBCP)ClO $_4$]	3240	—	1624	1595	1410	1550	1355	580	460
[Mn(PBCP)CH $_3$ COO]	3235	—	1623	1570	1410	1535	1335	570	455

The X-ray powder pattern of the iron(III) chloro and chromium(III) thiocyanate complexes were 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 $\text{CoK}\alpha$ or $\text{CuK}\alpha$ radiation using 40 kV 20 MA. All the 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, $a = 18.2712 \text{ \AA}$, $b = 14.9184 \text{ \AA}$ and $c = 10.69863 \text{ \AA}$ for the Fe(III) complex and $a = 21.3810 \text{ \AA}$, $b = 18.6971 \text{ \AA}$ and $c = 13.6278 \text{ \AA}$ for the Cr(III) complex. The density of the complexes 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 for both the complexes.

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



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