

# Synthesis and Reactivity of Chromium and Manganese Dibromoacetates and Their Complexes with Organic Bases

Jugal Kishore Puri and Rajni Chhoker

**Abstract**—Complexes of composition  $\text{CrCl}(\text{Br}_2\text{CHCOO})_2$ ,  $\text{Cr}_3\text{O}(\text{Br}_2\text{CHCOO})_6\text{Cl}$ ,  $[\text{Cr}_3\text{O}(\text{Br}_2\text{CHCOO})_6(\text{Br}_2\text{CHCOOH})_3\text{Cl}]$ ,  $\text{Cr}(\text{Br}_2\text{CHCOO})_3$ ,  $\text{Cr}(\text{Br}_2\text{CHCOO})_3\cdot\text{Py}$ ,  $\text{Cr}(\text{Br}_2\text{CHCOO})_3\cdot\text{Q}$ ,  $\text{Cr}(\text{Br}_2\text{CHCOO})_3(\text{C}_2\text{H}_5)_3\text{N}$ ,  $[\text{Cr}_3\text{O}(\text{Br}_2\text{CHCOO})_6(\text{NH}_3)_3]\text{Cl}\cdot 5\text{NH}_3$ ,  $\text{Mn}(\text{Br}_2\text{CHCOO})_2$ ,  $\text{Mn}(\text{Br}_2\text{CHCOO})_2\cdot 2\text{Py}$ ,  $\text{Mn}(\text{Br}_2\text{CHCOO})_2\cdot 2\text{Q}$ ,  $\text{Mn}(\text{Br}_2\text{CHCOO})_2\cdot 2(\text{C}_2\text{H}_5)_3\text{N}$  and  $(\text{Me}_4\text{N})_2\text{Mn}(\text{Br}_2\text{CHCOO})_4$  have been synthesized. All these compounds have been characterized by elemental analysis, molar conductance, infra-red, reflectance and thermo-gravimetric studies. These studies indicate the hexa co-ordination of chromium and manganese in these compounds having octahedral geometry and suggest the formation of polymeric structures. Further attempts are in progress to isolate the single crystal of these complexes in order to throw more light on the structure of these complexes from single crystal x-ray studies.

**Index Terms**—Chromium and manganese dibromoacetates and their adducts, spectroscopic techniques, TGA studies.

## 1 INTRODUCTION

IN the recent past, we have published few papers on the synthesis of metal bromoacetates and their complexes with bases [1-9].

Now in the present investigation we report the formation of some new Chromium (III) and Manganese (II) dibromoacetates and their complexation with various bases. These resulting dibromoacetates have been characterized by using physico-chemical methods. These new compounds may be having good insecticidal properties due to the presence of bromine.

Compound of composition  $[\text{Cr}_3(\text{OH})(\text{OOCCH}_3)_8]$  has been reported [10]. Chromium (III) acetate has been synthesized by reacting chromium (III) nitrate with acetic anhydride [11] but later studies showed the formation of a trinuclear basic acetate  $[\text{Cr}_3(\text{OH})_2(\text{OOCCH}_3)_6\cdot 6\text{H}_2\text{O}]^+$  [12]. Further the trimeric structure for this compound has been proposed on the basis of magnetic and X-ray diffraction studies [13-15]. Adducts of these compounds with ammonia, dimethylsulphoxide and pyridine have been reported [16]. Dubicki and Martin [17] have interpreted the visible spectra of the trinuclear chromium (III) acetate  $[(\text{Cr}_3\text{O})(\text{OOCCH}_3)_6]\text{Cl}$  in terms of the ligand field theory. Krauss [18] has isolated a compound by reacting chromium oxide and acetic anhydride and has formulated it as  $\text{Cr}_2\text{O}(\text{OOCCH}_3)_2$ .

Compounds of manganese (II) acetate of type  $\text{Mn}(\text{OCOCH}_3)_2\cdot 2\text{H}_2\text{O}$ ,  $\text{Mn}(\text{OOCCH}_3)_2\cdot 4\text{H}_2\text{O}$ ,  $\text{Mn}(\text{OOCF}_3)_2$  and  $\text{Mn}(\text{OOCCH}_3)_2$  have also been reported in literature [19-21]. It has been suggested that complex  $\text{Mn}(\text{OCOCH}_3)_2\cdot (\text{C}_6\text{H}_5\text{NHNH}_2)_2$  may have a similar structure.

The adducts  $\text{Mn}(\text{OCOCX}_3)_2\cdot \text{L}_4$  where  $\text{X} = \text{Cl}$ ,  $\text{L} = \text{Pyridine}$  or  $\gamma$ -picoline,  $\text{Mn}(\text{OCOCX}_3)_2\text{L}_2$  and  $\text{Mn}(\text{OCOCX}_3)_2\text{L}$  where  $\text{L} = \text{pyridine-N-oxide}$  or  $\gamma$ -picoline-N-oxide have also been prepared and characterized by infra red, electronic and magnetic studies. All these compounds have been shown to possess octahedral manganese (II)

(loc.cit).

## 2 MATERIALS AND METHOD

### 2.1 Preparation of Dibromoacetates of Chromium and Manganese

The dibromoacetates  $\text{Cr}(\text{Br}_2\text{CHCOO})_3$  and  $\text{Mn}(\text{Br}_2\text{CHCOO})_2$  were prepared from  $\text{CrCl}_3$  (anhydrous) (4.5 g, 28.40 mmole) and  $\text{MnCl}_2$  (anhydrous) (1g, 7.94 mmole) and dibromoacetic acid (18.58 g, 85.23 mmole); (3.46 g, 15.88 mmole) respectively which were taken in separate round bottomed flask containing 30 ml of carbon tetrachloride and fitted with the condenser and a guard tube. The respective reaction mixtures were then refluxed in an oil bath for 30-35 hrs. The green coloured product in case of chromium and the buff coloured product obtained in case of manganese were then filtered through sintered glass filtration unit in a dry nitrogen atmosphere under vacuum. The products were washed with anhydrous hot benzene to remove any excess of dibromoacetic acid. Finally the products were washed with anhydrous dichloromethane and dried under vacuum and analysed (Table I).

The compound corresponds to the composition  $\text{CrCl}(\text{Br}_2\text{CHCOO})_2$  was prepared by anhydrous chromium(III) chloride (1.5g, 8.90 mmole) on refluxing with dibromoacetic acid (3.88g, 17.81 mmole) for 8-10 hrs in carbon tetrachloride. The final green coloured product was obtained after washing with carbon tetrachloride and on drying under vacuum.

Solution of excess of dibromoacetic acid in carbon tetrachloride was when added dropwise to chromyl chloride diluted in the same solvent, colour changed from red to green which further on refluxing for nearly 20 hrs. gave the product which was after washing with petroleum ether (40-60°) and dried under vacuum and analysed was found to correspond to composition  $[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{COO})_6(\text{CHBr}_2\text{COOH})_3]\text{Cl}$  (Table I).

### 2.2 Preparation of adducts of dibromoacetates of Chromium & Manganese with bases

- Prof. Jugal Kishore Puri, (Corresponding Author) Centre of Advanced Studies and Department of Chemistry, Panjab University, Chandigarh 160014, India, Email : [prof\\_jkpuri@yahoo.com](mailto:prof_jkpuri@yahoo.com)
- Rajni Chhoker, Chemistry Department, Mewar University, Chittorgarh, Rajasthan, India, Email : [rajni68123@gmail.com](mailto:rajni68123@gmail.com)

The addition compounds  $\text{Cr}(\text{Br}_2\text{CHCOO})_3\cdot\text{Py}$ ,  $\text{Cr}(\text{Br}_2\text{CHCOO})_3\cdot\text{Q}$ ,  $\text{Cr}(\text{Br}_2\text{CHCOO})_3\cdot(\text{C}_2\text{H}_5)_3\text{N}$ ,  $\text{Mn}(\text{O}_2\text{CCHBr}_2)_2\cdot 2\text{C}_5\text{H}_5\text{N}$ ,  $\text{Mn}(\text{O}_2\text{CCHBr}_2)_2\cdot 2\text{C}_9\text{H}_7\text{N}$ ,  $\text{Mn}(\text{O}_2\text{CCHBr}_2)_2\cdot 2(\text{C}_2\text{H}_5)_3\text{N}$  were prepared by taking  $\text{Cr}(\text{Br}_2\text{CHCOO})_3$  (1.2 g, 1.70 mmole) and Pyridine (0.134 g, 1.70 mmole);  $\text{Cr}(\text{Br}_2\text{CHCOO})_3$  (1.45 g, 2.06 mmole) and Quinoline (0.162 g, 2.06 mmole);  $\text{Cr}(\text{Br}_2\text{CHCOO})_3$  (1.45 g, 2.06 mmole) and Triethylamine (0.208 g, 2.06 mmole);  $\text{Mn}(\text{Br}_2\text{CHCOO})_2$  (2g, 4.09 mmole) and Pyridine (0.65 g, 8.18 mmole);  $\text{Mn}(\text{Br}_2\text{CHCOO})_2$  (2g, 4.09 mmole) and quinoline (1.06g, 8.18mmole);  $\text{Mn}(\text{Br}_2\text{CHCOO})_2$  (2g, 4.09 mmole) and Triethylamine (0.208 g, 2.06 mmole) respectively in round bottomed flask separately equipped with calcium chloride guard tube in each case. The contents were mixed together and stirred for about 10-12 hrs. The corresponding products were washed with anhydrous dichloromethane and dried under nitrogen atmosphere. Their analyses are shown in Table I. The products were slightly hygroscopic and are insoluble in all the conventional organic solvents except are sparingly soluble in dimethyl formamide and acetonitrile.

### 2.3 Preparation of $[\text{Cr}_3\text{O}(\text{CHBr}_2\text{COO})_6]\text{Cl}$ & adduct $[\text{Cr}_3\text{O}(\text{CHBr}_2\text{COO})_6(\text{NH}_3)_3]\text{Cl}\cdot 5\text{NH}_3$

When excess of dibromoacetic acid in  $\text{CCl}_4$  was added to anhydrous chromium(III) chloride diluted in the same solvent and kept under 36 hrs refluxing, a green coloured product was formed. The analytical result corresponds to  $[\text{Cr}_3\text{O}(\text{CHBr}_2\text{COO})_6]\text{Cl}$ . Excess of ammonia (10-12 folds) diluted with 20 ml  $\text{CCl}_4$  was added to a suspension containing known weight (~10mmol) of the anhydrous trinuclear  $[\text{Cr}_3\text{O}(\text{CHBr}_2\text{COO})_6]\text{Cl}$  in 25ml  $\text{CCl}_4$ . The content was stirred at room temperature for 4 hrs. Solid formed was filtered under dry nitrogen atmosphere, washed with  $\text{CCL}_4$  & finally dried in vacuum. Analytical result corresponds to  $[\text{Cr}_3\text{O}(\text{CHBr}_2\text{COO})_6(\text{NH}_3)_3]\text{Cl}\cdot 5\text{NH}_3$  (Table I).

### 2.4 Preparation of $(\text{Me}_4\text{N})_2[\text{Mn}(\text{O}_2\text{CCHBr}_2)_4]$

In a typical preparation, manganese chloride,  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  (1.98g, 10.00 mmol) and tetramethyl ammonium chloride (2.19g, 20.00 mmol) in 1:2 molar ratio were separately dissolved in absolute ethanol. On mixing the two solutions, a light green solid of composition  $(\text{Me}_4\text{N})_2[\text{MnCl}_4]$  was precipitated which was filtered and dried under vacuum. The analysis and yield confirmed the formation of Bis(tetramethylammonium) tetrachloromanganese(II) i.e;  $(\text{Me}_4\text{N})_2[\text{MnCl}_4]$  (Yield- 78% ; Manganese- Observed 15.72%, Calculated 15.94% ; Chlorine- Observed 40.90%, Calculated 41.16%).

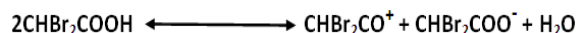
Bis(tetramethylammonium)tetrabromoacetatomanganese(II) was prepared by mixing Bis(tetramethylammonium) tetrachloromanganese(II) (1.03g, 2.98mmol) with silver dibromoacetate (3.88g, 11.94mmol) in nitromethane in stoichiometric amounts. Silver chloride formed after stirring for 5 hrs was filtered under dry nitrogen atmosphere. Filtrate was evaporated to dryness which gave a light green product with yield of 85%.

## 3 RESULTS AND DISCUSSION

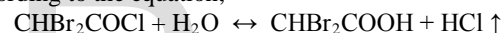
In the present studies we have explored the possibility of the synthetic reactions and the formation of some new dibromoacetates of Chromium and Manganese from the reaction of anhydrous metal chlorides in dibromoacetic acid.

### 3.1.1 Chemistry of Chromium with dibromoacetic acid

Chromium(III) chloride undergoes substitution reaction when reacts with excess of dibromoacetic acid in carbon tetrachloride as solvent at room temperature with the steady evolution of HCl gas. On refluxing at a moderate temperature solvolysed products of composition  $[\text{Cr}_3\text{O}(\text{CHBr}_2\text{COO})_6]\text{Cl}$  is obtained (Table-I). Our analytical data clearly indicates that chlorine in  $\text{CrCl}_3$  is not completely solvolysed at moderate temperature, even on further refluxing this resulting compound with fresh dibromoacetic acid. The product still contain chlorine and agrees with the composition of starting dibromoacetate. Such type of analogous compound containing trinuclear chromium(III) acetates are already known in literature (loc.cit). As suggested previously dibromoacetic acid undergoes self dissociation as [1, 4];



It is further assumed that water generated in the above equilibrium is taken up by the chromium(III) chloride and  $\text{CHBr}_2\text{CO}^+$  ions are removed as  $\text{CHBr}_2\text{COCl}$ . Bromoacetyl chloride and water occur together are known to combine with each other to form dibromoacetic acid and HCl according to the equation;



The mode of solvolytic reaction may thus be represented as ;



The compound formed is green solid, slightly hygroscopic and is insoluble in common organic solvents such as benzene, nitrobenzene, nitromethane and acetonitrile except this is fairly soluble in methanol. Molar conductance value of its milimolar solution indicate it to be a monomer.

This compound is paramagnetic having magnetic moment in the range 2.45 to 2.8 BM at room temperature. This value is significantly lower from the spin only value of 3.88 BM which is experimentally observed for Cr(III) complexes [22] and fall in the same range as is observed for similar basic trinuclear chromium(III) carboxylates. The low value suggests the presence of some antiferromagnetic exchange interaction between chromium atoms and also point to the polymeric nature of the compound in solid state.

Infra red spectral studies of this compound was carried out to understand the nature of the compound. The bands assignments have been made by comparison with the spectra of sodium dibromoacetates [23, 24]. The difference ( $\Delta\nu$ ) between  $\nu_{\text{asymCOO}}$ -stretching and  $\nu_{\text{symCOO}}$ -frequencies has been extensively used in the structure elucidation of metal carboxylates since  $\text{COO}^-$  stretching frequencies have been observed to be sensitive to co-ordination to a metal. The compound show bands at  $1660\text{ cm}^{-1}$  and  $1415\text{ cm}^{-1}$  which have been assigned to  $\nu_{\text{asymCOO}}$ - and  $\nu_{\text{symCOO}}$ - stretching vibration, respectively.

TABLE - I  
PHYSICAL AND ANALYTICAL DATA OF DIBROMOACETATES OF Cr(III) & Mn(II) AND THEIR COORDINATION COMPLEXES WITH VARIOUS BASES

Compound	Colour	M.Pt. °C	Analysis (%) Found (Calculated)						Molar Conductance cm <sup>2</sup> ohm <sup>-1</sup> mole <sup>-1</sup> in CH <sub>3</sub> CN
			M	Br	Cl	C	H	N	
Cr(Br <sub>2</sub> CHCOO) <sub>3</sub>	Green	>260	07.01 (07.38)	65.44 (68.28)	-	09.65 (10.24)	00.41 (00.43)	-	33.8
CrCl(Br <sub>2</sub> CHCOO) <sub>2</sub>	Green	195	09.28 (09.95)	29.18 (30.69)	06.68 (06.81)	08.45 (09.21)	00.36 (00.38)	-	7.8
Cr <sub>3</sub> O(Br <sub>2</sub> CHCOO) <sub>6</sub> Cl	Green	-	09.87 (10.32)	66.15 (63.61)	02.21 (02.35)	08.97 (09.54)	02.24 (02.35)	-	70.0 <sup>a</sup>
[Cr <sub>3</sub> O(Br <sub>2</sub> CHCOO) <sub>6</sub> (Br <sub>2</sub> CHCOO) <sub>3</sub> Cl]	Green	-	06.78 (07.20)	63.87 (66.55)	01.58 (01.64)	05.28 (05.55)	01.38 (01.44)	-	22.12
Cr(Br <sub>2</sub> CHCOO) <sub>3</sub> .Py	Greenish Grey	>210(d)	06.28 (06.63)	59.12 (61.38)	-	16.04 (16.88)	00.96 (01.02)	01.48 (01.79)	42.26
Cr(Br <sub>2</sub> CHCOO) <sub>3</sub> .Q	Green	>230(d)	05.89 (06.24)	55.09 (57.69)	-	20.76 (21.63)	01.14 (01.20)	01.46 (01.68)	37.18
Cr(Br <sub>2</sub> CHCOO) <sub>3</sub> .(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	Dull Green	220-222	06.21 (06.46)	57.18 (59.70)	-	17.08 (17.91)	02.18 (02.24)	01.42 (01.74)	49.24
[Cr <sub>3</sub> O(Br <sub>2</sub> CHCOO) <sub>6</sub> (NH <sub>3</sub> ) <sub>3</sub> Cl.5NH <sub>3</sub> ]	Violet	-	09.18 (09.46)	56.12 (58.35)	02.02 (02.15)	08.24 (08.75)	01.82 (01.72)	06.12 (06.31)	-
Mn(O <sub>2</sub> CCHBr <sub>2</sub> ) <sub>2</sub>	Buff	>200	10.62 (11.22)	62.66 (65.45)	-	9.09 (9.81)	0.38 (0.41)	-	3.54
Mn(O <sub>2</sub> CCHBr <sub>2</sub> ) <sub>2</sub> .2C <sub>2</sub> H <sub>5</sub> N	Buff	222-224	8.09 (8.48)	47.62 (49.46)	-	24.39 (25.97)	1.44 (1.85)	4.14 (4.32)	28.42
Mn(O <sub>2</sub> CCHBr <sub>2</sub> ) <sub>2</sub> .2C <sub>5</sub> H <sub>7</sub> N	Buff	218-220	7.02 (7.35)	40.28 (42.84)	-	33.28 (35.34)	1.98 (2.14)	3.52 (3.75)	27.64
Mn(O <sub>2</sub> CCHBr <sub>2</sub> ) <sub>2</sub> .2(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	Buff	230-232	7.62 (7.95)	44.12 (46.32)	-	26.04 (27.79)	4.34 (4.63)	3.85 (4.05)	18.46
[(Me <sub>2</sub> N) <sub>2</sub> ][Mn(O <sub>2</sub> CCHBr <sub>2</sub> ) <sub>2</sub> ]	Light Green	-	4.92 (5.13)	57.14 (59.76)	-	16.85 (17.93)	2.48 (2.61)	2.49 (2.61)	6.14

a = methanol

TABLE - II  
INFRARED VIBRATIONAL FREQUENCIES (cm<sup>-1</sup>) Of CHROMIUM COMPLEXES

Assignment	CrCl(OOCCHBr <sub>2</sub> ) <sub>2</sub>	[Cr <sub>3</sub> O(OOCCHBr <sub>2</sub> ) <sub>6</sub> ]Cl	[Cr <sub>3</sub> O(OOCCHBr <sub>2</sub> ) <sub>6</sub> (HOOCCHBr <sub>2</sub> ) <sub>3</sub> Cl]	Cr(OOCCHBr <sub>2</sub> ) <sub>2</sub>
COO asym str	1665(s), 1582(s)	1660(s), 1625(s), 1555(s)	1665(s), 1625(s), 1555(s)	1655(s), 1505(s)
COO sym str	1425(sh)	1415(s)	1415(s)	1410(s)
CH <sub>2</sub> sym bend deform	-	-	-	-
-CH <sub>2</sub> COO (adj. to COO)	-	1445(m)	1440(m)	-
CH <sub>2</sub> bend deform	-	-	-	-
CH <sub>2</sub> wagging	-	1270(m)	1272(m)	-
-CH bend	1225(s)	1230(s)	-	1235(m)
CH <sub>2</sub> rock	-	970(m)	972(m)	-
C-C skeletal	965(s)	-	-	970(s)
CBr asym str	825(s)	825(s)	830(s)	-
CBr sym str	785(s)	785(s)	785(s)	830(s)
COO in plane bend	-	730(sh)	730(sh)	792(m)
COO deform	682(s)	605(s)	605(s)	720(m), 680(w)
CH or COO out of plane	535(m)	545(m)	540(m)	625(m)
CH deform or COO rock	-	545(m)	540(m)	545(m)
(Cr <sub>3</sub> O) modes	-	455, 425(m)	460, 450(s)	-
(Cr-O) modes	455, 445(m), 330(m)	285(m)	350, 285(m)	265(m)
(Cr-Cl) mode	310(s)	-	-	-

s=strong, m=medium, sh=sharp

The presence of more than one band which has been assigned to V<sub>asymCOO</sub>- stretching mode may suggest that the carboxylato groups may be unsymmetrically coordinated in the solid state. The ΔV values of 160-210 and 120 cm<sup>-1</sup> may be attributed to the presence of bridging bidentate carboxylato groups and this is quite likely in view of the tendency of chromium(III) to acquire six co-ordination bonds are shown in Table-II. The appearance of a weak to medium intensity band between 510 to 545 cm<sup>-1</sup> have been assigned to (Cr<sub>3</sub>O) stretching mode by analogy to a similar assignment in a trinuclear iron(III) acetate [25]. Bands below 500 cm<sup>-1</sup> have been tentatively assigned to Cr<sub>3</sub>O and modes of Cr-O arising due to the bonding of dibromoacetate groups to chromium atom.

TG-DTG curve of this compound indicate that their decomposition takes place in a single step.

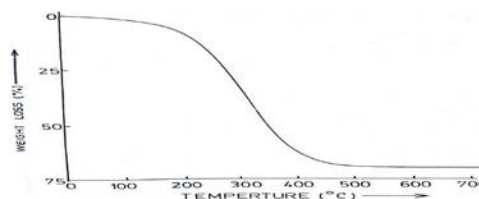


FIGURE : I THERMOGRAVIMETRIC CURVE OF [Cr<sub>3</sub>O(OOCCHBr<sub>2</sub>)<sub>6</sub>]Cl

This begins to lose weight on heating above 60 °C. The weight loss is quite slow at the beginning but becomes rapid above 260 °C. The formation of the final residue, Cr<sub>2</sub>O<sub>3</sub> is complete near 580 °C. The total weight loss is in agreement with the value calculated on the basis of their proposed formulae. TG curve for the compound is given in Figure-I. The observed weight loss, near 70% agrees well with the theoretically required weight loss value 72%.

This compound further forms complex with ammonia and the resulting complex corresponds to the composition [Cr<sub>3</sub>O(OOCCHBr<sub>2</sub>)<sub>6</sub>(NH<sub>3</sub>)<sub>3</sub>]Cl.5NH<sub>3</sub>. This compound has been made in analogy to some known adducts of trinuclear basic chromium(III) acetate [16]. Its infra red spectra indicate all the characteristic bands which had been observed in the parent compound and this is in agreement with its proposed structure in which the basic framework is not disturbed. Some new bands obtained at 3250 cm<sup>-1</sup> and 3130 cm<sup>-1</sup> are observed which may be attributed to (NH) stretching mode of co-ordinated NH<sub>3</sub>. These bands are significantly lowered as compared to the NH stretching frequencies in free ammonia [26] which are observed at 3414 and 3336 cm<sup>-1</sup> have shown that bands owing to symmetrical bending vibration (δ<sub>s</sub>) and rocking vibrations (δ<sub>v</sub>) of ammonia are of diagnostic importance in compound where it forms stable coordinate bonds. In the spectra of this compound, the NH<sub>3</sub> band could not be clearly identified due to the overlap of other vibrations such as V<sub>sym</sub>(COO<sup>-</sup>) in the same region. The band due to NH<sub>3</sub> (δ<sub>v</sub>) vibrations has been observed at 780 cm<sup>-1</sup> in this compound.

Chromium(III) chloride when reacts with dibromoacetic acid in the 1:2 stoichiometric ratio and refluxed in carbon tetrachloride, it forms CrCl(OOCCHBr<sub>2</sub>)<sub>2</sub> as shown in Table-I. This compound is green solid, soluble in most of the organic solvents like nitrobenzene, nitromethane, acetonitrile etc. The molar conductance values (Table-I) of its millimolar solution suggest that it behaves as non-electrolyte. Molecular weight determinations of this compound corresponds to its monomeric nature. Compound is paramagnetic in nature and has effective magnetic moment value which is below the spin only value of 3.88 BM [22] (Table-IV) thereby suggesting antiferromagnetic coupling between chromium atoms. The spectra of Cr(III) complexes are well understood [loc.cit]. The UV-visible spectra of the compound is given in Table-III. If we consider an energy level diagram for a d<sup>3</sup> ion in an octahedral field, it is seen that three spin allowed transitions;

${}^4T_{2g}(F) \leftarrow {}^4A_{2g}$  ;  ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$  ;  ${}^4T_{1g}(P) \leftarrow {}^4A_{2g}$   
are expected (loc.cit) and these have been observed.

TABLE - III  
ULTRAVIOLET SPECTRAL DATA AND MAGNETIC  
MOMENT OF CrCl(OOCCHBr<sub>2</sub>)<sub>2</sub>

COMPOUND	${}^4T_{2g}(F)$	${}^4T_{1g}(F)$	${}^4T_{1g}(P)$	Solvent	$\mu_{eff}$ (B.M.)
CrCl(OOCCHBr <sub>2</sub> ) <sub>2</sub>	16560	22720	40000	Methanol	5.42
Cr(OOCCHBr <sub>2</sub> ) <sub>3</sub>	15560	22425	45452	Diethyl ether	5.70

Some important infrared bands and their assignments for this compound are reported in Table-II. This compound shows more than one band which may be assigned to V<sub>asym</sub>(COO<sup>-</sup>) stretching vibrations, thus suggesting the presence of more than

one type of carboxylate groups. The ΔV(COO<sup>-</sup>) value of 185 cm<sup>-1</sup> may be attributed to ionic or bridging carboxylate groups. However molar conductance measurements rule out the presence of ionic carboxylate ligands. Other important bands due to carboxylate groups are also recorded in Table-II. This compound shows a strong band around 300 cm<sup>-1</sup> which by analogy with literature [27] and by comparison with the spectra of Cr(OOCCHBr<sub>2</sub>)<sub>3</sub> compound may be attributed to Cr-Cl mode. A strong band between 425-450 cm<sup>-1</sup> is assigned to Cr-O modes. Their observed physical properties, UV-Visible spectra and infra red data favour bidentate bridging carboxylate groups over bidentate chelating arrangement, resulting in polymeric structures.

TABLE - IV  
ELECTRONIC SPECTRAL AND MAGNETIC MOMENT  
DATA OF COMPLEXES OF Cr(III) DIBROMOACETATES

COMPOUND	V <sub>1</sub> (KK)	V <sub>2</sub> (KK)	β' (KK)	V <sub>3</sub> * (KK)	10 Dq (KK)	μ <sub>eff</sub> (B.M.)
Cr(O <sub>2</sub> CCHBr <sub>2</sub> ) <sub>3</sub>	16.22	22.81	0.704	34.49 (sh)	16.22	3.65
Cr(O <sub>2</sub> CCHBr <sub>2</sub> ) <sub>3</sub> .Py	15.99	23.48	0.721	35.23	15.99	3.69
Cr(O <sub>2</sub> CCHBr <sub>2</sub> ) <sub>3</sub> .Q	16.68	22.76	0.595	34.48 (sh)	16.68	3.62

\*assignment observed by charge transfer

Chromyl chloride reacts with dibromoacetic acid exothermally to form green solid (Table-I). This compound contains chromium in +3 oxidation state. This is suggested by its green colour and also by the inability of this compound to oxidize KI to free iodine. The compound is better represented as [Cr<sub>3</sub>O(OOCCHBr<sub>2</sub>)<sub>6</sub>(CHBr<sub>2</sub>COOH)<sub>3</sub>]Cl. This green coloured compound is fairly soluble in nitrobenzene, methanol and acetonitrile. The molar conductance value of its millimolar concentration in acetonitrile suggests the non-ionic nature of the compound. This compound is paramagnetic in nature and its magnetic moment value falls in the range of 3.1-3.5 BM at room temperature. The value is significantly below the spin only value of 3.88 BM (loc.cit) and suggests that this compound is magnetically concentrated.

Infra red spectra of this compound (Table-II) do not show any band between the region 3300-3100 cm<sup>-1</sup> which are characteristic of (OH) band. Bands between the regions 1600-1680 and 1400-1440 cm<sup>-1</sup> are assigned to V<sub>asym</sub>(COO<sup>-</sup>) and V<sub>sym</sub>(COO<sup>-</sup>) stretching frequencies, respectively of the bridging carboxylate group (loc.cit). The large V<sub>COO</sub> values of the order of approximately 215 cm<sup>-1</sup> are comparable to those observed for bridging carboxylate groups. Other bands due to carboxylate group are assigned at their usual position. The appearance of a weak to medium band at 540 cm<sup>-1</sup> is assigned to Cr<sub>3</sub>O group [25]. These observations combined with physical properties like lack of volatility, insoluble nature, intercluster hydrogen bonding concludes trinuclear formulation resulting in polymeric structure.

Compound of type Cr(OOCCHBr<sub>2</sub>)<sub>3</sub> has also been prepared by refluxing anhydrous Cr(III) chloride with anhydrous dibromoacetic acid in carbon tetrachloride. The green compound formed which is slightly hygroscopic. The compound is insoluble in common organic solvents such as carbon tetrachloride, benzene, nitrobenzene, nitromethane and except it is slightly soluble in acetonitrile and methanol. At this moment owing to its low solubility in acetonitrile, it is very difficult to predict its nature.

The magnetic moment of a Cr(III) complex lies be-

tween 3.88 BM and 5.2 BM. Since  ${}^4A_{2g}$  (F) is the ground term, there is no orbital contribution to the magnetic moment (loc.cit), therefore the magnetic moment value should be close to spin only value of 3.88 BM. The experimental value has been found to be in range as expected for a  $d^3$  system (loc.cit).

This compound has been further supported by its infra red spectral studies. The difference between  $V_{\text{asym}}(\text{COO})$  and  $V_{\text{sym}}(\text{COO})$  frequencies has been extensively used in the structure elucidation of the metal carboxylates since  $\text{COO}^-$  stretching frequencies have been observed to be sensitive to co-ordination to a metal. This compound show bands at 1600-1660, 1550, 1555  $\text{cm}^{-1}$  and 1410, 1415  $\text{cm}^{-1}$  which have been assigned to  $V_{\text{asym}}(\text{COO})$  and  $V_{\text{sym}}(\text{COO})$  stretching vibrations respectively. The presence of more than one band has been assigned to  $V_{\text{asym}}(\text{COO})$  stretching mode and suggest that the carboxylate group may be unsymmetrically co-ordinated in this solid state. The  $\Delta V(\text{COO}^-)$  value 140  $\text{cm}^{-1}$  may be attributed to the presence of bridging bidentate carboxylate groups and this is quite likely in view of the tendency of Cr(III) to acquire six co-ordination. The appearance of a weak to medium intensity band between 520 to 540  $\text{cm}^{-1}$  in this compound has been assigned to  $V_{\text{Cr-O}}$  stretching mode by analogy to similar assignment in trinuclear iron(III) acetate.

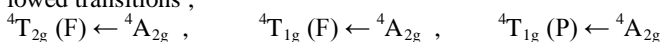
### 3.1.2 Adducts of Dibromoacetates of Chromium with Pyridine, Quinoline and Triethylamine

We have prepared the adducts of the type  $\text{Cr}(\text{CHBr}_2\text{COO})_3$ .Py,  $\text{Cr}(\text{CHBr}_2\text{COO})_3$ .( $\text{C}_2\text{H}_5$ ) $_3$ N and  $\text{Cr}(\text{CHBr}_2\text{COO})_3$ .Q in a manner analogous to some known adducts of trinuclear basic chromium(III) acetate (16). Their infra red spectra show all the characteristic bands which had been observed in their proposed structures in which the basic frame work is not disturbed. Some new bands observed may be attributed to  $V_{\text{N-H}}$  stretching modes of co-ordinated base. These bands are significantly lower in comparison to the  $V_{\text{N-H}}$  stretching frequencies in the free base (Table-V).

TABLE - V  
INFRARED VIBRATIONAL FREQUENCIES ( $\text{cm}^{-1}$ ) OF  
ADDUCTS OF CHROMIUM(III) DIBROMOACETATES  
WITH PYRIDINE, QUINOLINE AND TRIETHYLAMINE

$\text{Cr}(\text{O}_2\text{CCHBr}_2)_3$ .Py	$\text{Cr}(\text{O}_2\text{CCHBr}_2)_3$ .Q	$\text{Cr}(\text{O}_2\text{CCHBr}_2)_2$ .( $\text{C}_2\text{H}_5$ ) $_3$ N	Assignments
3145	3134	-	$V_{\text{C-H}}$ (aromatic)
1298, 2945, 2874	2955	2925, 2832	$V_{\text{C-H}}$ (aliphatic)
1632, 1529	1682, 1565	1665, 1542	$V_{\text{C=O}}$
1448, 1372	1442, 1412	-	$V_{\text{C-H}}$ (skeletal)
1285	1258	1252	$V_{\text{C-N}}$
1152	1158	1175	$V_{\text{C-O}}$ (aliphatic)
902	892	872	$V_{\text{C-C}}$ (skeletal)
727, 655	745, 728	-	Aromatic ring

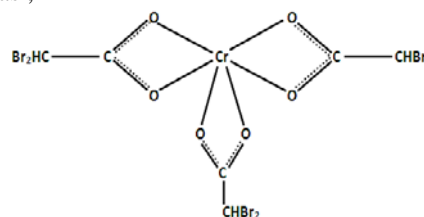
The ultraviolet and visible spectra of these compounds are given in Table-III. If we consider an energy level diagram for a  $d^3$  ion in an octahedral field, it is observed that these spin allowed transitions ;



are expected and these have been observed in the region 13.0-39.0 KK. The  $V_3$  transitions which is observed above 30.0 KK is obscured if ligand absorb in the ultra violet region.

The electronic spectra of  $\text{Cr}(\text{CHBr}_2\text{COO})_3$ ,  $\text{Cr}(\text{CHBr}_2\text{COO})_3$ .Py and  $\text{Cr}(\text{CHBr}_2\text{COO})_3$ .Q have been studied and recorded in Table-IV. The spectra of all these compounds have all the features requisite of a octahedral geometry.

Tris(dibromoacetato)chromium(III) i.e.  $\text{Cr}(\text{CHBr}_2\text{COO})_3$  ( $d^3$  system) compound absorbs at 16-22 KK respectively are due to  ${}^4T_{1g}(\text{F}) \leftarrow {}^4A_{2g}$  transitions ( $V_2$ ) which is characteristics of a  $\text{Cr}^{3+}$  compound in an octahedral ligand field. Unfortunately,  ${}^4T_{1g}(\text{P}) \leftarrow {}^4A_{2g}$  could not be observed unambiguously since it appears as a weak shoulder on the main charge transfer for chromium(III), and  $V_1$  is a direct measure of 10 Dq. Also  $\beta'$  value has been calculated from energy ratio diagrams. From these observations a structure may be assigned to these compound as ;



Similarly the 10 Dq values for  $\text{Cr}(\text{CHBr}_2\text{COO})_3$ ,  $\text{Cr}(\text{CHBr}_2\text{COO})_3$ .Py and  $\text{Cr}(\text{CHBr}_2\text{COO})_3$ .Q are obtained at 16.22, 15.99 and 16.68 KK, respectively. From the 10 Dq values a  $\beta'$  values of 0.709, 0.72 and 0.595  $\text{cm}^{-1}$  are obtained for these compounds.

The infra red spectra of pyridine complex  $\text{Cr}(\text{CHBr}_2\text{COO})_3$ .Py is complicated as was observed in case of analogous vanadium(III) compounds. The important infra red absorption bands for these compounds have been tabulated in Table-V.

In the adduct  $\text{Cr}(\text{CHBr}_2\text{COO})_3$ .Py, the  $V_{\text{sa}}$  modes of pyridine could not be distinguished clearly due to its overlapping with the  $V_{\text{COO}}$  stretching mode of the carboxylate group which occurs in the same region. The bands at 1010  $\text{cm}^{-1}$  and 1015  $\text{cm}^{-1}$  corresponds to the 991  $\text{cm}^{-1}$  ( $V_1$  mode) band of pyridine. Other significant changes involve shift to higher frequencies in amine ring vibrations of free pyridine at 601, 605 and 403, 406 to 640, 420  $\text{cm}^{-1}$  in these complexes. These changes show that pyridine is co-ordinated to Cr-atoms.

### 3.2.1 Chemistry of Manganese with dibromoacetic acid

A few acetates of manganese(II) and their addition complexes have already been prepared and characterized by infrared, electronic spectral and magnetic susceptibility studies and appear to contain octahedral manganese(II) [28-29]. In the present studies the compound  $\text{Mn}(\text{OOCCHBr}_2)_2$  has been prepared by the solvolysis of anhydrous Mn (II) chloride with fused dibromoacetic acid under reflux. The stoichiometry of this compound is further confirmed by its analysis (Table-I).

The infra-red spectral studies of the compound  $\text{Mn}(\text{OOCCHBr}_2)_2$  have been recorded in the range 4000-200 $\text{cm}^{-1}$ . The bands at 1690, 1590, 1290 are marked to asymmetric and symmetric  $V(\text{COO}^-)$  absorption bands which further indicate that the co-ordination of metal atom is through the carboxyl atom.

Electronic spectra has been recorded in support of the formation of the compound  $\text{Mn}(\text{OOCCHBr}_2)_2$  in Table- VI. It shows weak absorption bands in the region 5.0-15.0 KK. No

bands have been observed in the region 15.0-30.0 KK which rules out the possibility of tetrahedral derivative. A distinction between the tetrahedral and octahedral complexes could best be made from the measurements of extinction coefficients. The octahedral complexes have a low extinction coefficient in order of  $10^{-2}$  -  $10^{-1}$   $Lcm^{-1}mole^{-1}$  whereas for the tetrahedral complexes it ranges between 1-10  $Lcm^{-1}mole^{-1}$ . The extinction coefficient of Mn(II) compound could not be evaluated owing to their very low solubility in all conventional solvents. However, very weak absorption bands obtained for the compound (Table-VI) are suggestive of an octahedral environment around manganese(II). A band is observed at 33.35 KK in all these compounds may be assigned to the charge transfer spectra.

The magnetic moment values for a high spin octahedral derivative exist in the range 5.68 - 6.10 B.M. whereas the value for a low spin octahedral derivatives ranges from 1.8 - 2.1B.M. The spin only value for Mn(II) is expected to be 5.92 B.M. Compound posses magnetic moment values calculated for the Mn(II) compounds (Table-VI) indicate these systems to be consisting of five unpaired electrons. It also rules out the possibility of a low spin configuration.

### 3.2.2 Adducts of Manganese dibromoacetates with Pyridine, Quinoline and Triethylamine

Adducts of  $Mn(OOCCHBr_2)_2$  have been prepared with pyridine, triethylamine and quioline. Their stoichiometric compositions have been confirmed by their elemental analyses, given in Table-I. Their infra red spectra have also been recorded in the range 4000-200  $cm^{-1}$ . The various bands and their assignments are shown in Table-VII. The infra red spectra of the amine complexes does not give great deal of information on the details of its structure. Octahedral pyridine metal halides give information on the details of the structure.

TABLE – VI  
ELECTRONIC SPECTRAL AND MAGNETIC MOMENT DATA OF Mn(II) DIBROMOACETATES AND ITS COMPLEXES WITH BASES

COMPOUND	BAND POSITION d-d TRANSITIONS (kk)	CHARGE TRANSFER TRANSITIONS (kk)	$\mu_{eff}$ (B.M.)
$Mn(O_2CCHBr_2)_2$	5.90, 14.32	33.35	5.42
$Mn(O_2CCHBr_2)_2 \cdot 2Py$	6.42, 7.55	33.35	5.70
$Mn(O_2CCHBr_2)_2 \cdot 2Q$	6.85, 13.25	33.33	5.82
$Mn(O_2CCHBr_2)_2 \cdot 2(C_2H_5)_3N$	6.92, 14.25	33.33	5.74

TABLE - VII  
INFRARED VIBRATIONAL FREQUENCIES ( $cm^{-1}$ ) OF ADDITION COMPLEXES OF Mn (II) DIBROMOACETATES WITH PYRIDINE, QUINOLINE AND TRIETHYLAMINE

$Mn(O_2CCHBr_2)_2 \cdot Py$	$Mn(O_2CCHBr_2)_2 \cdot Q$	$Mn(O_2CCHBr_2)_2 \cdot (C_2H_5)_3N$	Assignments
-	-	-	N-H
3145	3135	-	C-H aromatic
2960, 2870	2955	2925, 2835	C-H aliphatic
1610, 1530	1635, 1555	1660, 1540	C=O
1455, 1370	1440	-	C=C skeletal
-	-	1410	C-H aliphatic
1290	1240	1260	C-N
1155	1160	1175	C-O aliphatic
905	890	875	C-C skeletal
730, 650	740, 725	-	Aromatic ring

In the higher frequency region all the complexes give strong absorption bands in the range 1400-1500 and 1500-1700  $cm^{-1}$  marked to the symmetric and asymmetric stretching bands respectively of the carboxylate group (Table-VII). The frequency difference between these bands has been previously used to provide evidence for the bonding of the carboxylate group [30] but the results are conflicting and are also sensitive to the nature of the substituent [23]. From these complexes it is clear that group of complexes with similar stoichiometry and most probably similar structure show very similar values of  $\Delta V$ . The band which occurs near 865  $cm^{-1}$  has been described as a pseudo symmetric  $V_{C-C}$  stretching mode also seems to be metal sensitive. Similar results to those previously reported for copper pyridine complexes [23] were found for other amine complexes.

The evidence in favour of the formation of above complexes has been given by the electronic spectral studies. They show weak bands in the region 5.0-15.0 KK. No bands have been observed in the region 15.00-30.00 KK, which rules out the possibility of a tetrahedral derivative and suggest an octahedral arrangement in these complexes. A band obtained at 33.33 KK in these complexes may be assigned to charge transfer spectra. [31-32]

The magnetic susceptibility measurements gave the value of  $Mn(OOCCHBr_2)_2$ ,  $Mn(OOCCHBr_2)_2 \cdot 2Q$ ,  $Mn(OOCCHBr_2)_2 \cdot 2Py$  and  $Mn(OOCCHBr_2)_2 \cdot 2(C_2H_5)_3N$  complexes at 5.42-5.82, 5.70 and 5.74 B.M. respectively (Table-VI) which further support the octahedral arrangement around the metal atom in these complexes.

Metathetical reactions of  $[Me_4N]_2[MnCl_4]$  with silver dibromoacetates in nitromethane has further been carried out which yields corresponding dibromoacetate in nitromethane. This solution on evaporation to dryness gives the dibromoacetate complex. The analytical data of compound is presented in Table-I. This compound is solid, hygroscopic in nature and soluble in polar organic solvents like acetonitrile and nitromethane but insoluble in non polar organic solvents. The reaction of  $[Me_4N]_2[MnCl_4]$  with dibromoacetic acid do not give completely substituted product and the mathematical reaction in absolute ethanol are not promising. The molar conductance value of its millimolar solution in acetonitrile (i.e. 230  $ohm^{-1} mole^{-1} cm^2$ ) is well in the range expected for ionic formulations.

The infra red spectra of this compound has been recorded in the range 2000-200  $cm^{-1}$  (Table -VIII). The characteristic features of the spectra are appearance of  $V_{asymCOO}$  between the region 1680-1650  $cm^{-1}$ . The bands between the region 1435-1415  $cm^{-1}$  have been assigned to  $V_{symCOO}$ . The  $\Delta V_{COO}$  values of the range 250  $cm^{-1}$  comparable well with that of 270  $cm^{-1}$  as reported earlier which suggest that the compound contain uniden-

tate dibromoacetate groups. Strong bands between the regions 1470-1485  $\text{cm}^{-1}$  and 940-950  $\text{cm}^{-1}$  are assigned to tetramethyl ammonium group.

TABLE – VIII  
INFRARED VIBRATIONAL FREQUENCIES ( $\text{cm}^{-1}$ ) OF  
[(Me<sub>4</sub>N)<sub>2</sub>][Mn(O<sub>2</sub>CCHBr<sub>2</sub>)<sub>4</sub>]

[(Me <sub>4</sub> N) <sub>2</sub> ][Mn(O <sub>2</sub> CCHBr <sub>2</sub> ) <sub>4</sub> ]	Assignments
1675 s	COO asym str
1425 m	COO sym str
1180 m	CHBr <sub>2</sub> str
1160 w, 1110 w	CHBr <sub>2</sub> str
1470 s, 940 s	Bands due to Me <sub>4</sub> N group
840 s	C-C str
800	OCO deform
730 s	CHBr <sub>2</sub> bend
625 w	CHBr <sub>2</sub> bend
460 vw	M-O
260 m	CHBr <sub>2</sub> wag

The electronic spectra of this complex has also been studied. Octahedral field energy level diagram for Mn (II) (d<sup>5</sup> configuration) is the same as tetrahedral field energy level sequence. It follows that same energy level diagram may be used for octahedral, tetrahedral or cubic fields. In octahedral field, this configuration gives spin forbidden as well as partly forbidden transitions and thus extremely pale yellow colour of the compounds [4]. In tetrahedral environment, the transitions are still spin forbidden, but no longer partly forbidden, thus the compound has yellowish green colour. The light green colour and very weak bands at 315, 400, 540 and 680  $\text{cm}^{-1}$  in diffused reflectance spectrum of manganese complex favour a tetrahedral environment around manganese atom. These bands are similar to other tetrahedral manganese(II) complexes [33]. The band at 250  $\text{cm}^{-1}$  is assigned to charge transfer band.

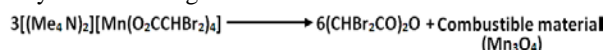
High spin manganese(II) compounds are expected to indicate magnetic moment very close to spin only value of 5.92 B.M. and are independent of temperature, irrespective of whether the ligand arrangement is octahedral, tetrahedral or is of lower symmetry. Magnetic moment of [(Me<sub>4</sub>N)<sub>2</sub>][Mn(O<sub>2</sub>CCHBr<sub>2</sub>)<sub>4</sub>] is 6.14 B.M. which is very close to spin only value as reported in literature for other Mn(II) tetrahedral complexes [34-35].

Thus on the basis of infra red, electronic spectra and magnetic moments of [(Me<sub>4</sub>N)<sub>2</sub>][Mn(O<sub>2</sub>CCHBr<sub>2</sub>)<sub>4</sub>], it may be

concluded that unlike tetranitrato metal(II) complexes, this has tetrahedral environment around central metal atom.

TG-DTG curves of [(Me<sub>4</sub>N)<sub>2</sub>][Mn(O<sub>2</sub>CCHBr<sub>2</sub>)<sub>4</sub>] show that it decompose in two stages. However, these steps overlap (indicated by DTG curves). They began to loose weight on heating above 45°C. The weight loss is slow at the beginning but becomes rapid around 140°C. The formation of the final residue, metal oxide, is complete above 400°C. Total loss in weight is in agreement with the value calculated on the basis of their proposed formula. Curve for [(Me<sub>4</sub>N)<sub>2</sub>][Mn(O<sub>2</sub>CCHBr<sub>2</sub>)<sub>4</sub>] is shown in Figure-II. In the first step there is a loss of two molecules of dibromoacetic anhydride part as combustible material (Weight loss 88.68%, Calculated 88.34%).

Overall thermal decomposition mode of this complex may be shown as given below.



The presence of dibromoacetic anhydride was characterized from the infra-red spectrum of the trapped volatile material in separate experiment.

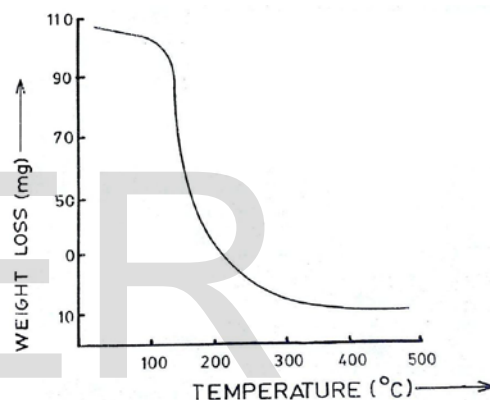


FIGURE : II Thermogravimetric Curve of  
[(ME<sub>4</sub>N)<sub>2</sub>][Mn(OOCCHBr<sub>2</sub>)<sub>4</sub>]

## 7.2 Acknowledgments

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