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SYNTHESIS AND CHARACTERIZATION OF TITANIUM(IV), VANADIUM(III), CHROMIUM(III), AND MANGANESE(II) MONOBROMOACETATES AND THEIR COMPLEXES WITH ORGANIC BASES

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SYNTHESIS AND CHARACTERIZATION OF TITANIUM(IV), VANADIUM(III), CHROMIUM(III), AND MANGANESE(II) MONOBROMOACETATES AND THEIR COMPLEXES WITH ORGANIC BASES

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ABSTRACT

Bromoacetates of the composition $MX_3(OOCCH_2Br)$, $MX_2(OOCCH_2Br)_2$, $MX(OOCCH_2Br)_3$, $M(OOCCH_2Br)_4$ (M = Ti), $M(OOCCH_2Br)_3$ (M = V, Cr), $M(OOCCH_2Br)_2$ (M = Mn) and their complexes of the types $MX_2(OOCCH_2Br)_2.2B$, $M(OOCCH_2Br)_4.2B$ (M = Ti, V), $M(OOCCH_2Br)_3.B$ (M = Cr) and $M(OOCCH_2Br)_2.2B$ (M = Mn) (X = Cl, B = pyridine, quinoline, triethylamine or 2-fluoroaniline) have been synthesized and characterized on the basis of elemental analyses, infrared spectra, reflectance, molar conductance and magnetic susceptibility studies.

INTRODUCTION

In continuation of our previous studies of solvolytic reactions in fused monobromoacetic acid (1–7), the present investigation reports the synthesis of

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monobromoacetates of titanium(IV), vanadium(III), chromium(III), manganese(II) and their complexes with various bases. The nature of these solid compounds has been established using physico-chemical methods.

The respective metal chlorides on refluxing in acetic acid gave anhydrous metal acetates (8–9) of the composition $OTi_2(OAc)_6$ and $[V_3(OAc)_8OH]$. Many contradictory reports exist in the literature (10–14) on the existence of vanadium(III) carboxylates of the compositions $V(OOCH)_3$, $V(OOCCH_3)_3.H_2O$, $V(OOCH)_4$, $V(OOCH)_3.HCOOH$, $V_2(OOCCH_3)_6$, $V_2(OOCC_6H_5)_6$, $[V_3(OH)(OOCCH_3)_8]$, $[V_3(OH)(OOCC_2H_5)_8]$, $H^+[V_3O(OOCCH_3)_8]^-$ and $H^+[V_3O(OOCC_2H_5)_8]^-$. The formation of the compounds $[Cr_3(OH)(OOCCH_3)_8]$ has also been reported (9). Spath (15) has prepared Cr(III) acetate by reacting chromium(III) nitrate with acetic anhydride but subsequent studies (16) showed this compound to be a trinuclear basic acetate, $[Cr_3(OH)_2(OOCCH_3)_6H_2O]^+$. The formation of manganese(II) acetates, $Mn(OOCCH_3)_2.4H_2O$, $Mn(OOCCF_3)_2$, $Mn(OOCCl_3)_2$ has also been reported in the literature (17–19).

RESULTS AND DISCUSSION

On solvolysis titanium(IV) chloride in monobromoacetic acid forms compounds of the types $TiCl_3(OOCCH_2Br)$, $TiCl_2(OOCCH_2Br)_2$, $TiCl(OOCCH_2Br)_3$ and $Ti(OOCCH_2Br)_4$, respectively. The solvolysis reactions may be proposed as follows

$$TiCl_4 + CH_2BrCOOH \xrightarrow[\text{Exothermic}]{\text{Fast Reaction}} TiCl_3(OOCCH_2Br) + HCl$$

$$TiCl_3(OOCCH_2Br) + CH_2BrCOOH \xrightarrow{\text{Fast Reaction}} TiCl_2(OOCCH_2Br)_2 + HCl$$

$$TiCl_2(OOCCH_2Br)_2 + CH_2BrCOOH \xrightarrow{\text{Slow Reaction}} TiCl(OOCCH_2Br)_3 + HCl$$

$$TiCl(OOCCH_2Br)_3 + CH_2BrCOOH \xrightarrow{\text{Reflux}} Ti(OOCCH_2Br)_4 + HCl$$

The stoichiometric compositions have been determined by elemental analyses (Table I). All of these compounds have fairly high melting points and are insoluble in most polar solvents with the exception of acetonitrile, dimethyl formamide and nitrobenzene. Molar conductance values of their millimolar solutions in these solvents exclude ionic dissociation.

Titanium Compounds

Infrared spectral studies of the solid monobromoacetates have been carried out to elucidate their structures. The position of the asymmetric and symmetric stretching modes in the region 1400–1600 cm^{-1} have been used to determine whether monobromoacetate behaves as monodentate or bidentate chelating bridging groups in a particular compound (20). In the case of $TiCl_2(OOCCH_2Br)_2$ no band has been observed in the region of 1720 cm^{-1} suggesting that no free carbonyl group is present. The intense absorption bands at 1585 and 1382 cm^{-1} suggest that the monobromoacetate groups in this compound are bidentate and the central metal atom is hexa-coordinated. The bands observed at 1635 and 1590 cm^{-1} for $TiCl_2(OOCCH_2Br)_2$, at 1645 and 1590 cm^{-1} for $TiCl_3(OOCCH_2Br)$, at 1640 and 1570 cm^{-1} for $TiCl(OOCCH_2Br)_3$ and at 1645 and 1575 cm^{-1} for $Ti(OOCCH_2Br)_4$, respectively, suggest that some of the monobromoacetate groups in all these compounds are acting as bridging groups as well (20). The other important bands present in the far-infrared spectra of the compounds are due to metal-oxygen stretching modes. They are found in the region 500–340 cm^{-1}. For the titanium compounds Ti-O and Ti-Cl bands are observed in the regions 500–350 cm^{-1} and 250–300 cm^{-1}, respectively, and are given in Table II.

Vanadium Compound

Vanadium(III) chloride undergoes solvolysis in pure anhydrous monobromoacetic acid on refluxing to form a dull-green crystalline compound of the composition $V(OOCCH_2Br)_3$. This compound is insoluble in most common organic solvents. Infrared spectral studies indicate bands at 1700, 1570 and 1260 cm^{-1} which may be assigned to asymmetric and symmetric COO^- absorption bands and which further indicate that the coordination of the metal atom is through both oxygen atoms of the carboxylate group. The band observed in the lower region *i.e.*, 500–300 cm^{-1} may be assigned to the vanadium-oxygen bond.

The electronic spectra of $V(OOCCH_2Br)_3$ have also been recorded to shed light on the nature of this compound. The electronic bands obtained at 11.11, 18.50 and 25.64 kK may be assigned to octahedral compounds of vanadium (III) in a manner as reported earlier in the literature (21–24).

The compound $V(OOCCH_2Br)_3$ has been found to have a μ_{eff} value of 2.75 B.M. at room temperature which is in agreement with the literature values (2.5 to 2.8 B.M.) for V^{3+} ion in a cubic field. Consequently, the structure in Fig. 1 may be proposed for this compound.

Chromium Compound

Similarly, a compound of the composition $Cr(OOCCH_2Br)_3$ has been prepared from the solvolysis of anhydrous chromium(III) chloride with fused monobromoacetic acid on refluxing. The new chromium(III) tris(monobromoacetate),

Table I. Elemental Analyses of the Metal Bromoacetates and Their Adducts with Bases

S. No.	Compound Molecular Formula (Empirical Formula)	Formula Weight	Colour	M.p. (°C)	%Metal Found (Requd)	%Br Found (Requd)	%Cl Found (Requd)	%C Found (Requd)	%H Found (Requd)	%N Found (Requd)	Molar Cond. Ohm^{-1} cm^{-1} $mole^{-1}$ in CH_3CN	Yield (%)
(**1**)	$TiCl_3(OOCCH_2Br)$ $(C_2H_2BrCl_3O_2Ti)$	292.11	Dull yellow	162–164	16.20 (16.38)	28.14 (27.35)	37.52 (36.43)	7.72 (8.21)	0.596 (0.684)		7.84	82
(**2**)	$TiCl_2(OOCCH_2Br)_2$ $(C_4H_4Br_2Cl_2O_4Ti)$	394.54	Dull yellow	167–169	12.92 (12.13)	41.21 (40.50)	18.01 (17.98)	12.83 (12.16)	1.14 (1.01)		10.21	80
(**3**)	$TiCl(OOCCH_2Br)_3$ $(C_6H_6Br_3ClO_9Ti)$	496.97	Dull yellow	173–174	10.00 (9.63)	47.94 (48.23)	8.16 (7.13)	13.92 (14.48)	0.984 (1.20)		6.98	75
(**4**)	$Ti(OOCCH_2Br)_4$ $(C_8H_8Br_4O_8Ti)$	599.40	Light yellow	41–42	7.44 (7.98)	52.48 (53.31)	—	15.90 (16.01)	1.29 (1.33)		9.83[b]	68
(**5**)	$V(OOCCH_2Br)_3$ $(C_6H_6Br_3O_6V)$	464.58	Dull green	113–114	9.92 (10.96)	49.23 (51.59)	—	14.29 (15.49)	1.20 (1.29)		23.45	65
(**6**)	$Cr(OOCCH_2Br)_3$ $(C_6H_6Br_3CrO_6)$	465.63	Dull green	210	11.04 (11.16)	50.13 (51.48)	—	15.39 (15.46)	1.23 (1.28)		—	70
(**7**)	$Mn(OOCCH_2Br)_2$ $(C_4H_4Br_2MnO_4)$	330.70	Buff	200	16.10 (16.61)	47.24 (48.32)	—	13.90 (14.51)	1.14 (1.20)		3.21	72
(**8**)	$TiCl_2(OOCCH_2Br)_2$- $NC_5H_5(C_9H_9Br_2Cl_2NO_4Ti)$	473.54	Dull yellow	167–168	10.04 (10.11)	32.93 (33.74)	14.82 (14.97)	21.93 (22.78)	1.78 (1.89)	2.79 (2.95)	94.43	75
(**9**)	$Ti(OOCCH_2Br)_4$- $2NC_5H_5(C_{18}H_{18}Br_4N_2O_8Ti)$	757.40	Light grey	181–182	6.19 (6.32)	42.08 (42.19)		28.29 (28.52)	2.25 (2.37)	3.28 (3.69)	78.64[a]	70

(10)	$V(OOCCH_2Br)_3$- $NC_5H_5(C_{11}H_{11}Br_3NO_6V)$	543.58	Light grey	103– 105	9.10 (9.37)	43.94 (44.09)	22.30 (24.28)	1.90 (2.03)	2.49 (2.57)	48.70[b]	72
(11)	$V(OOCCH_2Br)_3$- $NC_9H_7(C_{15}H_{13}Br_3NO_6V)$	593.58	Light grey	102– 104	8.50 (8.58)	39.27 (40.38)	29.91 (30.32)	2.14 (2.19)	2.30 (2.35)	39.41	68
(12)	$V(OOCCH_2Br)_3.N(C_2H_5)_3$ $(C_{12}H_{21}Br_3NO_6V)$	565.58	Grey	107	8.12 (8.99)	41.69 (42.38)	25.23 (25.46)	3.40 (3.71)	2.43 (2.47)	52.38	65
(13)	$Cr(OOCCH_2Br)_3.NC_5H_5$ $(C_{11}H_{11}Br_3CrNO_6)$	544.63	Grey	230	9.37 (9.54)	43.74 (44.01)	23.91 (24.23)	2.12 (2.02)	2.61 (2.57)	—	68
(14)	$Cr(OOCCH_2Br)_3.NC_9H_7$ $(C_{15}H_{13}Br_3CrNO_6)$	594.63	Grey	230	8.15 (8.74)	40.17 (40.31)	28.94 (30.27)	2.14 (2.18)	2.31 (2.35)	—	65
(15)	$Cr(OOCCH_2Br)_3.N(C_2H_5)_3$ $(C_{12}H_{21}Br_3CrNO_6)$	566.63	Dull green	210	9.10 (9.17)	41.18 (42.30)	24.92 (25.41)	3.67 (3.70)	2.42 (2.47)	—	65
(16)	$Mn(OOCCH_2Br)_2.2NC_5H_5$ $(C_{14}H_{14}Br_2MnN_2O_4)$	488.69	Buff	220	11.04 (11.24)	31.24 (32.69)	33.12 (34.38)	2.72 (2.86)	5.48 (5.73)	25.42	70
(17)	$Mn(OOCCH_2Br)_2.2NC_9H_7$ $(C_{22}H_{18}Br_2MnN_2O_4)$	588.69	Buff	220	9.20 (9.33)	26.98 (27.14)	43.97 (44.84)	3.01 (3.05)	4.43 (4.75)	16.02	68
(18)	$Mn(OOCCH_2Br)_2.2N(C_2H_5)_3$ $(C_{16}H_{34}Br_2MnN_2O_4)$	532.69	Buff	230	10.10 (10.31)	28.79 (29.99)	35.91 (36.04)	6.21 (6.38)	5.12 (5.25)	—	65
(19)	$V(OOCCH_2Br)_3$- $H_2NC_6H_4F$-2 $(C_{12}H_{12}Br_3FNO_6V)$		Greenish	125-27	8.44 (8.84)	40.92 (41.64)	24.92 (25.01)	2.01 (2.08)	2.40 (2.43)	—	62
(20)	$Cr(OOCCH_2Br)_3$- $H_2NC_6H_4F$-2 $(C_{12}H_{12}Br_3CrFNO_6)$		Brown	200	8.92 (9.01)	40.88 (41.56)	23.78 (24.96)	2.12 (2.08)	2.39 (2.42)	—	60
(21)	$Mn(OOCCH_2Br)_2$- $H_2NC_6H_4F$-2 $(C_{10}H_{10}Br_2FMnNO_4)$		Blackish	230	9.29 (9.47)	41.12 (41.36)	23.89 (24.84)	2.04 (2.07)	2.38 (2.41)	10.82	60

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[a] molar conductance in nitrobenzene.
[b] molar conductance in dimethylformamide.

Table II. Important Infrared Spectral Bands of Transition Metal Bromoacetates and Their Assignments in cm^{-1} Using Cesium Iodide Plates in Nujol

S.No.	Compound	$\nu_{asymm}(COO^-)$	$\nu_{symm}(COO^-)$	ν(M-O)	ν(M-Cl)
(**1**)	$TiCl_3(OOCCH_2Br)$	1645 sb, 1590 s, 1565 s, 1530 m	1385 m	335 m	270 s
(**2**)	$TiCl_2(OOCCH_2Br)_2$	1635 s, 1590 s, 1585 s	1382 s	405 s	280 s
(**3**)	$TiCl(OOCCH_2Br)_3$	1640 s, 1570 s, 1535 m	1400 w	490 s	280 s
(**4**)	$Ti(OOCCH_2Br)_4$	1645 s, 1575 s, 1540 m	1382 w	360 m	—
(**5**)	$V(OOCCH_2Br)_3$	1700 sb, 1570 s, 1555 m	1260 s	420 s	—
(**6**)	$Cr(OOCCH_2Br)_3$	1630 sb, 1550 s	1410 w	525 m	—
(**7**)	$Mn(OOCCH_2Br)_2$	1680 sb, 1595 s, 1565 m	1295 s	430 s	—

s = strong, sb = strong and broad, sh = shoulder, m = medium, w = weak.

$Cr(OOCCH_2Br)_3$, (d^{3}system) is green, slightly hygroscopic and insoluble in common organic solvents like carbon tetrachloride, benzene and nitromethane, although it is slightly soluble in acetonitrile and methanol.

The magnetic moment of the chromium(III) complex lies between 3.88 and 5.2 B.M. Since the $^4A_{2g}$(F) state is the ground term, there is no orbital contribution to the magnetic moment. Therefore, the μ_{eff} value should be close to the spin-only value of 3.88 B.M. The experimental value for $Cr(OOCCH_2Br)_3$, is 3.64 B.M. which is in the range expected for a d^3 system (23).

Infrared spectral studies of this compound were made to understand the nature of this compound in the solid state. The observed spectral bands along with their assignments are shown in Table III. Band assignments for the carboxylate group have been made by comparison with the spectra of the sodium salt of the parent carboxylic acid (24,25). The C–O stretching region of the compound is complex which may be due to the formation of a polymeric structure in the solid state.

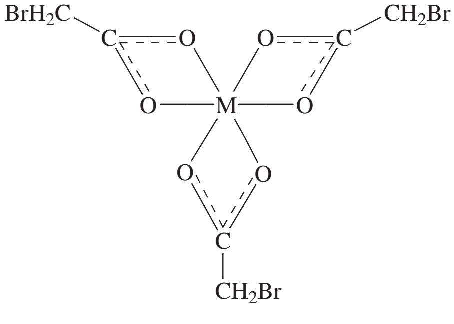


Figure 1. Suggested strucure of the complexes (M = V, Cr).

Table III. Important Infrared Spectral Bands of the Adducts of Transition Metal Bromoacetates in Nujol Using Cesium Iodide Plates

$M(OOCCH_2Br)_3.NC_5H_5$ (M = V, Cr)	$Mn(OOCCH_2Br)_2$ $.NC_9H_7$	$Mn(OOCCH_2Br)_2$ $.N(C_2H_5)_3$	$Mn(OOCCH_2Br)_2$ $.H_2NC_6H_4F\text{-}2$	Assignments
—	—	—	3420 s	ν(N-H)
—	—	—	3350 s	
3140 mb	3130 mb	—	3140 s	ν(C-H)(aromatic)
1295 m	—	—	—	
2940 s	2950 s	2920 s	2940 s	ν(C-H)(aliphatic)
2870 s	—	2830 s	—	
1630 s	1680 s	1660 s	1700 sb	ν(C=O)
1525 s	1560 s	1540 s	1580 s	
1455 sh	1440 sh	—	1450 w	ν(C-C)(skeletal)
1370 s	—	—	—	
—	—	1410 sb	—	δ(C-H)(aliphatic)
—	—	—	1420 sb	δ(N-H)
—	—	—	1280 s	ν(C-F)
1280 s	1240 s	1255 s	1250 s	ν(C-N)
1150 s	1155 w	1170 m	1160 m	ν(C-O)(aliphatic)
900 w	890 w	870 w	880 w	δ(C-C)(skeletal)
725 s	740 w	—	750 w	Aromatic
650 s	725 s	—	725 w	Ring

s = strong, sb = strong and broad, sh = shoulder, m = medium, w = weak.
IR frequencies for V, Cr Compounds are identical.

Infrared bands at 1630 cm^{-1} and 1550 cm^{-1} have been attributed to $\nu_{asymm}(COO^-)$ whereas an absorption band at 1410 cm^{-1} has been assigned to $\nu_{symm}(COO^-)$. The presence of more than one band due to the $\nu_{asymm}(COO^-)$ stretching mode suggests that the three carboxylato groups in this compound are non-equivalent and may be unsymmetrically coordinated in the solid state. The $\Delta\nu(COO^-)$ value of about 140 cm^{-1} may be attributed to the presence of bridging bidentate carboxylate groups and this is quite likely in view of the tendency of chromium(III) to aquire the coordination number six. Whereas the $\Delta\nu(COO^-)$ value of about 220 cm^{-1} is larger than the expected value for a bidentate carboxylato group, such a high value may either be due to unidentate or unsymmetrical bidentate carboxylato groups. Two structural possibilities may be considered,

(i) The chromium in this compound may be four-coordinated, where four of the six oxygen atoms of the three carboxylato groups are used to form bonds. The three carboxylato groups would then be non-equivalent (one-bidentate and two unidentate) and this would lead to the splitting of the $\nu_{asymm}(COO^-)$ band.

(ii) Or, alternatively, chromium in this compound may acquire six-coordination provided one of the carboxylato group is unsymmetrical with one Cr–O distance normal and the other significantly longer. The carbon-oxygen bond order in Fig. 1 is consistent with the high value of the $\nu_{asymm}(COO^-)$ bond. The other two carboxylato groups may act as symmetrical bidentate ligands probably exercising chelating or bridging action.

The second possibility that chromium in this compound is six coordinated seems more likely as Cr(III) is known to be always hexa-coordinated (26). This is supported by the UV and visible spectra of this compound, Table II, which are typical of an octahedral environment about the Cr atom (26–27). The appearance of a weak to medium intense band between 520-540 cm^{-1} in this compound has been assigned to the $\nu(Cr{-}O)$ stretching mode by analogy to a similar assignment in trinuclear iron(III) acetate (28). The possibility that there are two types of carboxylato groups is also consistent with the ^1H NMR spectrum of $Cr(OOCCH_2Br)_3$. It shows two peaks in the ratio 1:2 at δ10.1 and 12.1 ppm, respectively. The protons in $Cr(OOCCH_2Br)_3$ are highly shielded which may be attributed to the presence of unpaired electrons on the chromium metal. The ^1H NMR spectra of the other compounds could not be studied for lack of solubility in suitable solvents.

Manganese Compound

The compound $Mn(OOCCH_2Br)_2$ has been prepared similarly and studied by infrared spectral studies. The bands at 1680, 1595 and 1295 cm^{-1} are due to asymmetric and symmetric $\nu(COO^-)$ absorption bands which further indicate that the coordination of the metal atom is through the oxygen atoms of the COO group. The other important bands are given in Table II.

Electronic spectra have been recorded in support of the formation of the compound $Mn(OOCCH_2Br)_2$ and are shown in Table V. They show weak absorption bands in the region 5.0–15 kK. No bands have been observed in the region 15.0–30.0 kK which rules out the possibility of tetrahedral derivatives (29). A distinction between tetrahedral and octahedral complexes could best be made from the measurements of extinction coefficients. The octahedral complexes have a low extinction coefficient of the order of 10^{-2}–10^{-1} Lcm^{-1} $mole^{-1}$, whereas for the tetrahedral complexes, it lies between 1–10 $Lcm^{-1}mole^{-1}$.

The extinction coefficients of the 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 V) are suggestive of an octahedral environment around Mn(II) in an analogous manner as reported in the literature (29,30). A band is observed at 33.33 kK for the compound which may be assigned to charge transfer transitions.

The magnetic moment values for a high-spin octahedral derivative lie in the range 5.68–6.10 B.M. whereas the values for a low-spin octahedral derivative range from 1.8–2.1 B.M., the spin-only value for Mn(II) is expected to be 5.92 B.M. The tetrahedral Mn(II) system possesses magnetic moments quite close to that, but slightly higher than the spin-only value. The magnetic moment values calculated for the Mn(II) compound (Table V) indicate this system to be consisting of five unpaired electrons. It also rules out the possibility of a low-spin configuration.

Addition Compounds with Nitrogen Bases

Vanadium(III) and chromium(III) acetates are known to form complexes with ammonia, pyridine, piperidine and dimethyl sulfoxide (31,32). Complex derivatives of Mn(II) acetates have been reported with pyridine, γ-picoline, pyridine-N-oxide and γ-picoline-N-oxide etc. in the literature (18). In the present investigations, we have explored the possibility of the solvolysed products acting as Lewis acids by reacting them with pyridine at room temperature in carbon tetrachloride as a solvent, with continuous stirring for about 10 h using a magnetic bead in case of the titanium(IV) bromoacetates (Table I). The representative equations for the formation of the base adducts of these titanium bromoacetates may be suggested as:

$$TiCl_2(OOCCH_2Br)_2 + C_5H_5N \xrightarrow[\substack{\text{Stirring at}\\ \text{Room Temp.}\\ \text{for 10 h.}}]{CCl_4} TiCl_2(NC_5H_5)(OOCCH_2Br)_2$$

$$\mathrm{Ti(OOCCH_2Br)_4 + 2C_5H_5N \xrightarrow[\text{Stirring at Room Temp. for 10 h.}]{CCl_4} Ti(NC_5H_5)_2(OOCCH_2Br)_4}$$

These compounds are soluble in dimethyl formamide. Molar conductance value of their millimolar solutions are given in Table I. It is of interest to note that there is no substitution of the less basic bromoacetate group by the more basic pyridine and quinoline. In these compound, the separation of the symmetric and antisymmetric O–C–O band stretching frequencies and the shifts of the symmetric O–C–O stretching bands from the values in the parent compounds suggest that bromoacetate coordination becomes monodentate. The possibility of a five-coordinate structure for these compounds is ruled out as it would give two symmetric O–C–O stretching bands. The probability of a polymeric structure is low on complex formation with tertiary organic bases. The ν_{asymm}(O–C–O) and ν_{symm}(O–C–O) stretching frequencies shift to higher and lower frequency regions, respectively, which suggests nitrogen donation to the central metal atom. Similar observations have been reported by Kitchens and Bear (33).

Four vanadium complexes, $\mathrm{V(OOCCH_2Br)_3.N(C_2H_5)_3}$, $\mathrm{V(OOCCH_2Br)_3.NC_5H_5}$, $\mathrm{V(OOCCH_2Br)_3.NC_9H_7}$ and $\mathrm{V(OOCCH_2Br)_3.H_2NC_6H_4F\text{-}2}$, have been isolated in 1:1 molar ratio and characterised by elemental analyses. The representative equations for the formation of these complexes with bases may be shown as

$$\mathrm{V(OOCCH_2Br)_3 + B \xrightarrow[\text{in Benzene for 20 h}]{\text{Reflux}} V(OOCCH_2Br)_3.B}$$

$$\mathrm{[B{=}C_5H_5N,\ C_9H_7N,\ (C_2H_5)_3N,\ H_2NC_6H_4F\text{-}2]}$$

Their infrared spectra (Table III) contain all those bands which had been assigned to internal vibrations of these bromoacetate groups in parent compounds and are observed unperturbed. This may suggest that these bases are loosely solvated and do not enter the coordination sphere possibly vanadium metal in all these complexes has attained its highest coordination number. In case of the pyridine adduct of vanadium bromoacetate, its infrared spectra shows bands at 1650 s, 1615 m, 1480 m, 1440 m, 1410 s, 1360 w, 1320 w, 1215 m, 1065 m, 1045 m, 1015 m, 965 w, 820 m, 750 m, 720 m, 690 m, 640 m, 600 sb, 525 m, 435 s, 410 m, 330 s, 245 w. The shift to higher frequency in the pyridine ring vibrations (ν_{8a}; 1615 cm^{-1}, ν_1 1010 cm^{-1}, ν_{6a}; 640 cm^{-1} and ν_{16b}, 420 cm^{-1}) suggests the coordination of the pyridine ring nitrogen to vanadium. Bands which are assigned to bromoacetate group in the spectrum of $\mathrm{V(OOCCH_2Br)_3}$ are observed in the spectrum of its adduct without any significant change (Table III). It again suggest that the basic structure of this compound (Fig. 1) is not disturbed on coordination by pyridine or any other base. However the structure of a base adduct of the above metal bromoacetate with pyridine (B) in general may be suggested as:

All of these compounds are fairly soluble in most organic solvents. Electronic spectral studies of these addition compounds show bands at 10.8, 18.18, 26.31; 11.91, 17.98, 24.93; and 11.20, 18.34 and 27.62 kK, respectively which also support the octahedral arrangement of vanadium(III). A band has also been observed at 33.33 kK in these compounds, which may be assigned either to charge transfer or to ligand absorption (Table IV). The ligand field parameters 10Dq and β have also been evaluated employing energy ratio diagrams (34).

The addition compounds $Cr(OOCCH_2Br)_3.NC_5H_5$, $Cr(OOCCH_2Br)_3.N(C_2H_5)_3$, $Cr(OOCCH_2Br)_3.NC_9H_7$ and $Cr(OOCCH_2Br)_3.H_2NC_6H_4F\text{-}2$ have also been prepared in an analogous manner to that of the trinuclear basic Cr(III) acetate complexes (35). The mode of formation of these complexes may be represented as

$$Cr(OOCCH_2Br)_3 + B \xrightarrow[\text{in Benzene}\atop\text{for 20 h}]{\text{Reflux}} Cr(OOCCH_2Br)_3.B$$

$$[B{=}C_5H_5N,\ C_9H_7N,\ (C_2H_5)_3N,\ H_2NC_6H_4F\text{-}2]$$

Table IV. Electronic Spectral (in kK 1000 cm^{-1} Units), Molar Coefficients ϵ Values (in L cm^{-1} mole^{-1}) Given in Parentheses and Magnetic Moment Data of Vanadium(III) Bromoacetates and Chromium(III) Bromoacetates and Their Complexes

Compound	ν_1 (kK)	ν_2 (kK)	β' (kK)	ν_3[a] (kK)	10Dq (kK)	CT	μ_{eff} (B.M.)
$V(OOCCH_2Br)_3$	11.11	18.50(18)	0.560	25.64(12)	11.42	33.33	2.73
$V(OOCCH_2Br)_3.C_5H_5N$	11.91	17.98(26)	0.558	24.93(34)	10.93	—	2.80
$V(OOCCH_2Br)_3.C_9H_7N$	11.20	18.34(30)	0.554	27.62(36)	11.51	33.33	2.82
$V(OOCCH_2Br)_3.(C_2H_5)_3N$	10.80	18.18(34)	0.568	26.31(45)	11.47	33.33	2.71

	ν_1 (kK)	ν_2 (kK)	β' (kK)	ν_3[b] (kK)	10Dq (kK)	CT	μ_{eff} (B.M.)
$Cr(OOCCH_2Br)_3$	16.12(28)	22.72(16)	0.700	34.48(sh)	16.12		3.64
$Cr(OOCCH_2Br)_3.C_5H_5N$	15.98(43)	23.41(32)	0.723	35.22	15.98		3.67
$Cr(OOCCH_2Br)_3.C_9H_7N$	16.66(53)	22.72(43)	0.595	38.48(sh)	16.66		3.59

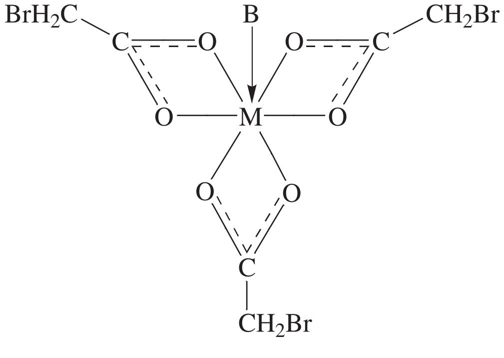
[a] Observed as shoulder on charge transfer band.

[b] Assignment obscured by charge transfer, ε molar value taken in methanol.

The infrared spectra of these addition compounds show all of the characteristic bands which had been observed in their structures in which the basic framework is not disturbed. Some new bands observed for $Cr(OOCCH_2Br)_3.NH_2C_6H_4F$-2 may be attributed to ν(N−H) stretching modes of the coordinated base. These bands are at significantly lower frequency in comparison to the N−H stretching frequencies in the free base (Table III). The electronic spectra of $Cr(OOCCH_2Br)_3$, $Cr(OOCCH_2Br)_3.NC_5H_5$, $Cr(OOCCH_2Br)_3.NC_9H_7$ have been studied and are recorded in Table IV. The spectra of these compounds have all the features requisite of an octahedral geometry.

Chromium(III) tris(monobromoacetate), $Cr(OOCCH_2Br)_3$, (d^3 system) absorbs at 16.12 kK due to $^4T_{2g} \leftarrow {}^4A_{2g}$ transitions (ν_1) and 22.72 kK due to $^4T_{1g} \leftarrow {}^4A_{2g}$ transitions (ν_2) which are characteristic of a Cr(III) compound in an octahedral ligand field (36). Unfortunately, the $^4T_{1g}(P) \leftarrow {}^4A_{2g}$ transition could not be observed unambiguously since it appears as a weak shoulder on the main charge transfer band. For chromium(III) bromoacetates, ν_1 vibrations is a direct measure of 10Dq. Also β^1 values have been calculated from the energy ratio diagrams and from these observations the structure of their addition compounds with bases may be suggested as shown in Fig. 2.

Similarly, the 10Dq values for $Cr(OOCCH_2Br)_3$, $Cr(OOCCH_2Br)_3.NC_5H_5$, $Cr(OOCCH_2Br)_3.NC_9H_7$ were obtained at 16.12, 15.98 and 16.16 kK, respectively. From the 10Dq values, β^1 values of 0.700, 0.723, 0.595 cm^{-1} were obtained for these compounds. The infrared spectra of the pyridine complex $Cr(OOCCH_2Br)_3.NC_5H_5$ is complicated as was observed in the case of the analogous vanadium(III) compounds. The important infrared absorption bands for the compound



[M = Vor Cr; B = C_5H_5N, C_9H_7N, $(C_2H_5)_3N$, $H_2NC_6H_4F$]

Figure 2. Suggested structure of addition complexes of $M(OOCCH_2Br)_3$.

$Cr(OOCCH_2Br)_3.NC_5H_5$ have been given in Table III. These bands may further be explained in an analogous manner as already explained in the case of vanadium(III) bromoacetates.

In the adduct $Cr(OOCCH_2Br)_3.NC_5H_5$ the same ν_{8a} mode of pyridine (as suggested earlier) cannot be distinguished clearly due to its overlapping with the ν_a (COO^-) stretching mode of the carboxylate group which occurs in the same region. The band at 1010 cm^{-1} corresponds to the 991 cm^{-1} (ν_1 mode) band of pyridine. Other significant changes involve shifts to higher frequencies in ring vibrations of the free pyridine at 601, 403 to 640 and 420 cm^{-1} in these complexes suggest the coordination of the pyridine ring nitrogen to chromium. Bands which are assigned to the monobromoacetate group in the spectrum of $Cr(OOCCH_2Br)_3$ are observed in the spectrum of $Cr(OOCCH_2Br)_3.NC_5H_5$ without any significant shift. It again suggest that the basic structure of this compound is not disturbed on coordination with pyridine. These above spectral changes (Table III) clearly show that pyridine is coordinated to the chromium atom. It is, therefore, inferred that monobromoacetato chelates of vanadium(III) and chromium(III) have pseudooctahedral geometries around the central metal ion. This is in agreement with the stereochemistry of trivalent compounds of titanium, vanadium and chromium as reportd by Gutmann and coworkers (37).

The adducts of $Mn(OOCCH_2Br)_2$ also have been prepared with pyridine, triethylamine, quinoline and 2-fluoroaniline. The stoichiometric composition of these adducts has been confirmed by their elemental analyses given in Table I. The mode of representative equations for the formation of these adducts may be shown as

$$Mn(OOCCH_2Br)_2 + 2B \xrightarrow[\substack{\text{in } CCl_4 \\ \text{for 12 h}}]{\text{Reflux}} [Mn(OOCCH_2Br)_2.B_2]$$

$$[B = C_5H_5N,\ C_9H_7N,\ (C_2H_5)_3N,\ NH_2C_6H_4 - F]$$

Their infrared spectra have also been recorded in the range 4000-200 cm^{-1} and the various bands and their assignments are recorded in Table III. The infrared spectra of the amine complexes do not give a great deal of information on the details of the structure. Octahedral pyridine metal halides give infrared bands in the region assigned to a metal amine mode (38) and the present band is considered to be derived from a variation of this type.

In the higher frequency region all the complexes gave strong absorption bands in the ranges 1400-1500 cm^{-1} and 1500-1700 cm^{-1} due to symmetric and asymmetric stretches, respectively, of the carboxylate group (Tables II and III). The frequency difference between these bands has been previously used to provide evidence for the bonding of the carboxylate group (39) but the results are

Table V. Electronic Spectral (in kK 1000 cm^{-1} Units) and Magnetic Moment Data of Manganese(II) Bromoacetate and Its Complexes

Compound	Band Positions d-d Transitions(kK)	Charge Transfer Transition (kK)	μ_{eff} (B.M.)
$Mn(OOCCH_2Br)_2$	5.88, 14.28	33.33	5.41
$Mn(OOCCH_2Br)_2.2C_5H_5N$	6.41, 7.53 (12)	33.33	5.69
$Mn(OOCCH_2Br)_2.2C_9H_7N$	6.83, 13.21 (22)	33.33	5.81
$Mn(OOCCH_2Br)_{2s}.(C_2H_5)_3N$	6.91, 14.20 (28)	33.33	5.72

Molar values ε in L cm^{-1} $mole^{-1}$ taken in methanol are given in parenthesis.

conflicting and are also sensitive to the nature of the substituents (40,25). From these complexes it is clear that a group of complexes with similar stoichiometry and presumably similar structure shows very similar values of $\Delta\nu$(difference in ν_{asymm} and ν_{symm} vibrations). The band near 860 cm^{-1}, which has been described (41) as a pseudosymmetric C–C stretching mode, also seems to be metal sensitive. Similar results to those previously reported (42,43) for copper pyridine complexes were found for the other amine complexes.

The evidence in support of the formation of the above complexes has been given by the electronic spectral studies. They show weak absorption bands in the region 5.0-15.0 kK (Table V). No bands have been observed in the region 15.0 to 30.0 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. The magnetic susceptibility measurements gave values for the compounds $Mn(OOCCH_2Br)_2$, $Mn(OOCCH_2Br)_2.2NC_5H_5$, $Mn(OOCCH_2Br)_2.2NC_9H_7$ and $Mn(OOCCH_2Br)_2.2N(C_2H_5)_3$ complexes as 5.41, 5.69, 5.81, and 5.72 B.M., respectively (Table V), which further support the octahedral arrangement around the metal atom in these complexes (Fig. 3)

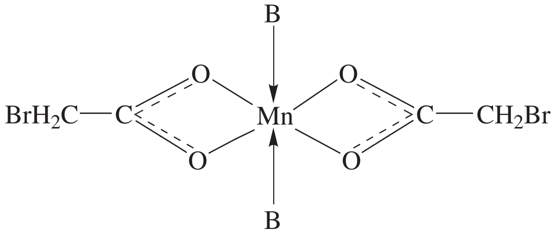


Figure 3. Suggested structure for the addition complex.

EXPERIMENTAL

Materials and Methods

Monobromoacetic acid (Riedel, Germany) was crystallized in pure anhydrous benzene. The acid was then distilled under vacuum. Bromine was determined by the standard method known in the literature and its specific conductance was found to be 1.35×10^{-3} $\text{ohm}^{-1}\text{cm}^{-1}$ which confirmed the purity of the bromoacetic acid. The melting point was also determined and bromoacetic acid with m.p. 47–50 ^{0}C was used for all preparations.

A commercially available sample of titanium(IV) chloride was purified by the standard method before use. Anhydrous vanadium(III) chloride was prepared by refluxing powdered V_2O_5 (18.0 g, 0.1 mole) in 40 mL of sulfur monochloride for 8 h in the absence of moisture. Excess sulfur monochloride, which contained dissolved sulfur, was decanted off and VCl_3 thus formed was washed with carbon disulfide. The violet product was filtered and dried under vacuum at room temperature and analysed (Analysis % V: found 32.2; required 32.4 %; Cl found 67.4; required 67.6; yield obtained 13.55 g (65%).

Anhydrous chromium(III) chloride was prepared and purified by the method reported in the literature (44). The bromoacetates of titanium(IV) were prepared by taking pure anhydrous samples of titanium(IV) chloride (2 g, 10.52 mmol) in a standard joint flask fitted with a reflux condenser equipped with a silica gel guard tube. To that was added pure anhydrous monobromoacetic acid (10 g, 71.94 mmol). The mixture was then refluxed in an oil bath maintained at the desired temperature of the reaction for a period ranging from 24 h to a few days to obtain maximum yields. The product thus formed was filtered under vacuum and washed with anhydrous dichloromethane to completely remove excess of monobromoacetic acid. The solvolysed product was dried under vacuum and analysed (Table I).

Molar conductances of millimolar solutions were determined in acetonitrile, nitrobenzene or dimethyl formamide using a cell having a cell constant of 0.5996 cm^{-1} and a Beckmann RC-18 conductivity bridge.

Infrared and electronic spectra of the new compounds were measured in nujol mull between cesium iodide plates using Perkin- Elmer 337 and 225 spectrophotometers. Solution spectra were obtained by using specially designed cells with a 225 Analat-6160 FTIR system at St. Catherines University, Ontario, Canada. Analyses of metals and halogens were carried out at the Chemistry Department, Panjab University, Chandigarh, India, while the analyses of carbon, hydrogen and nitrogen, were made by the Central Instrumental Laboratory at Panjab University, Chandigarh, India.

Preparation of Bromoacetates

The bromoacetates $V(OOCCH_2Br)_3$, $Cr(OOCCH_2Br)_3$ and $Mn(OOCCH_2Br)_2$ were prepared from VCl_3 (5 g, 31.76 mmol) and monobromoacetic acid (13.23 g, 31.76 mmol); $CrCl_3$ (45.0 g, 28.4 mmol) and monobromoacetic acid (11.83 g, 28.38 mmol); anhydrous $MnCl_2$ (3 g, 23.79 mmol) and monobromoacetic acid (6.61 g, 23.79 mmol), respectively, in separate round-bottomed flasks containing 30 mL of carbon tetrachloride and fitted with a condensor and a guard tube. The respective reaction mixtures were then refluxed in an oil bath for 30–40 h. The green coloured product in case of the bromoacetates of vanadium and chromium and the buff-coloured product obtained in case of manganese were then filtered through a sintered glass filtration unit in a dry nitrogen atmosphere under vacuum. The product was then washed with anhydrous hot benzene to remove excess of bromoacetic acid from the product. Finally, the products were washed with anhydrous dichloromethane and dried under vacuum and analysed (Table I).

Preparation of Adducts of Metal Bromoacetates with Bases

The addition compounds $V(OOCCH_2Br)_3.NC_5H_5$; $V(OOCCH_2Br)_3.N(C_2H_5)_3$; $V(OOCCH_2Br)_3.NC_9H_7$ and $V(OOCCH_2Br)_3.H_2NC_6H_4F$-2 were prepared by taking (1.5 g, 3.22 mmol) of $V(OOCCH_2Br)_3$ and (0.255 g, 3.22 mmol) of C_5H_5N; $V(OOCCH_2Br)_3$ (1 g, 2.15 mmol) and $(C_2H_5)_3N$ (0.217 g, 2.15 mmol) and $V(OOCCH_2Br)_3$ (1.0 g, 2.15 mmol) and C_9H_7N (0.277 g, 2.15 mmol); $V(OOCCH_2Br)_3$ (1.2 g, 2.58 mmol) and $H_2NC_6H_4F$-2 (0.286 g, 2.58 mmol), respectively, in separate round-bottomed flasks containing 20 mL of benzene and equipped with a guard tube. The respective bases were then added slowly to the respective bromoacetates with continuous stirring using a magnetic stirrer. After complete addition of the bases, the reaction mixture was allowed to reflux for about 20 h between 70-75^0 C. The products were then filtered through a filtration unit in an atmosphere of dry nitrogen under vacuum and finally the products were washed with anhydrous dichloromethane and dried under vacuum[13] and analysed (Table I).

The compound $Cr(OOCCH_2Br)_3.NC_5H_5$, $Cr(OOCCH_2Br)_3.N(C_2H_5)_3$ and $Cr(OOCCH_2Br)_3.NC_9H_7$, $Cr(OOCCH_2Br)_3.H_2NC_6H_4F$-2, $Mn(OOCCH_2Br)_2.NC_5H_5$, $Mn(OOCCH_2Br)_2.N(C_2H_5)_3$, $Mn(OOCCH_2Br)_3.NC_9H_7$ and $Mn(OOCCH_2Br)_3.H_2NC_6H_4F$-2 were prepared by taking $Cr(OOCCH_2Br)_3$ (1.2 g, 2.57 mmol), C_5H_5N (0.203 g, 2.57 mmol); $Cr(OOCCH_2Br)_3$ (1.4 g, 3.11 mmol), $(C_2H_5)_3N$ (0.314 g, 3.1 mmol); $Cr(OOCCH_2Br)_3$ (1.2 g, 2.57 mmol), C_9H_7N (0.286 g, 2.57 mmol); $Cr(OOCCH_2Br)_3$ (1.5 g, 3.22 mmol), $H_2NC_6H_4F$-2 (0.357 g, 3.22 mmol); $Mn(OOCCH_2Br)_2$ (1.0 g, 3.62 mmol), C_5H_5N (0.573 g, 3.62 mmol); $Mn(OOCCH_2Br)_2$ (1.35 g, 4.08 mmol), $(C_2H_5)_3N$ (0.824 g, 4.08 mmol); $Mn(OOCCH_2Br)_2$ (1.3 g, 3.93 mmol), C_9H_7N (1.01 g, 3.93 mmol) and $Mn(OOCCH_2Br)_2$ (1.4 g, 4.23 mmol), $H_2NC_6H_4F$-2 (0.469 g, 4.23 mmol) were prepared by reacting the respective bromoacetate and the base as described for the vanadium adducts.

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