

portance. Many of these complexes are of high-spin type. Very few low-spin Mn(III) complexes are known¹. Many high-spin Mn(III) complexes containing biguanide have been reported by us previously². We report here one low-spin Mn(III) complex, (hydroxoquoopiperazine-di-biguanido)Mn(III), [Mn^{III}(OH)(H₂O)(pipzbig)] (where pipzbig = dianion of piperazine-di-biguanide).

Piperazine-di-biguanide was obtained by the reaction of piperazine-di-biguanide sulphate (2 g) with stoichiometric amount of ethanolic sodium ethoxide solution and filtering off the precipitated sodium sulphate.

The complex was prepared by adding an ethanolic solution of freshly prepared Mn(III) acetate (1.5 g) to an ice-cold ethanolic solution of piperazine-di-biguanide obtained above. A brown crystalline compound was precipitated which was filtered, washed with ethanol and dried *in vacuo* over fused CaCl₂ and solid KOH [Found: C, 28.21; H, 5.60; N, 40.76; Mn, 15.88. Calc. for Mn(III)(OH)(H₂O)(C₈H₁₆N₁₀): C, 28.08; H, 5.55; N, 40.94; Mn 16.08%].

The complex is insoluble in water and common organic solvents. It is neutral to litmus. There is no loss in weight when the complex is heated up to 110°. It is stable in contact with water. The oxidation state of the metal ion in the complex was determined by oxidimetric titration.

The magnetic moment value of 2.88 BM (at 27°) for the present Mn(III) complex is quite close to the spin-only value (2.83 BM) for a low-spin *d*⁴ system. A value of 2.92 BM has been reported previously for a low-spin Mn(III) complex, K₃[Mn(CN)₅OH]³. However, other low-spin Mn(III) complexes, K₃[Mn(CN)₆] and K₃MnF₅·H₂O have been reported to have considerably higher μ_{eff} values of 3.80 and 3.32 BM respectively⁴. Nevertheless, the μ_{eff} value of the complex and the results of the oxidimetric titration support the presence of low-spin Mn(III) species in the present complex.

Following tentative assignments of the electronic spectral bands (*nujol*) of the complex are based on those made for Mn(CN)₆²⁻ and Mn(CN)₅OH³⁻. The absorption bands at ~43,000, 40,000 and 20,000 cm⁻¹ are charge-transfer in origin. However, it may be mentioned that biguanide $\pi \rightarrow \pi^*$ transition also appears at ~43,000 cm⁻¹ (ref. 5). The bands at ~25,500 and at ~24,500 cm⁻¹ may be due to splitting of the spin-allowed transition ${}^3T_{1g} \rightarrow {}^3E_g$, because of the reduction in the symmetry of the complex from *O_h* to *C_{4v}*. The band due to this spin-allowed transition has been observed around 27,000 cm⁻¹ in the complex Mn(CN)₆²⁻. In the present complex spin-forbidden transitions are responsible for the bands at 13,000 (${}^3T_{1g} \rightarrow {}^1E_g$), 11,800 (${}^3T_{1g} \rightarrow {}^1T_{2g}$), and 11,000 cm⁻¹ (${}^3T_{1g} \rightarrow {}^5E_g$). It is difficult to give definite assignment of shoulders appearing at 34,000 and 30,500 cm⁻¹. However, these bands may probably be due to other spin-allowed transitions [${}^3T_{1g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g}$, 3E_g (2) and ${}^3T_{1g} \rightarrow {}^3A_{1g}$, ${}^3T_{1g}$ respectively].

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Complexes of Co(II), Ni(II) & Cu(II) with 4-Methyl-2-aminothiazole & 4-Phenyl-2-aminothiazole

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Complexes of the type $ML_n X_m \cdot mH_2O$ [where $n = 2$ and $m = 0$ for $M = \text{Co(II)}$ or Ni(II) , $X = \text{Cl}^-$ or OAc^- and $L = 4\text{-methyl-2-aminothiazole (MAT)}$ or $4\text{-phenyl-2-aminothiazole (PhAT)}$; $n = 4$ and $m = 0$ for $M = \text{Cu(II)}$, $X = \text{Cl}^-$ and $L = \text{PhAT}$; $n = 2$ and $m = 2$ for $M = \text{Cu(II)}$, $X = \text{Cl}^-$ or OAc^- and $L = \text{MAT}$] have been isolated and characterized on the basis of IR and electronic spectral data. Distorted tetrahedral and distorted octahedral structures have been proposed for the complexes of Co(II) and Ni(II) respectively. Cu(II) complexes have been assigned either a square planar or an octahedral stereochemistry. In 4-methyl/phenyl-2-aminothiazole coordination takes place through ring nitrogen atom.

IN continuation of our earlier work¹ on the complexes of 2-aminothiazole with Ni(II), Cu(II) and Cd(II), we report here isolation and characterization of complexes of Co(II), Ni(II), and Cu(II) with 4-methyl-2-aminothiazole (MAT) and 4-phenyl-2-aminothiazole (PhAT). It is found that substitution at 4-position in 2-aminothiazole changes the stoichiometry of all the complexes formed, except that of the complex of CuCl₂ with PhAT.

MAT (Aldrich Chemicals) was used without further purification. PhAT was prepared by the literature method². IR spectra (4000-300 cm⁻¹) were recorded on a Perkin-Elmer spectrophotometer. Electronic reflectance spectra were recorded on a Unicam SP-700 spectrophotometer. Magnetic susceptibility was measured at room temperature using Gouy's method and Hg[Co(NCS)₄] as the calibrant.

The method used for the preparation of complexes with 2-aminothiazole¹ was not successful for the preparation of present complexes. Complexes with MAT were prepared by adding solid ligand to an ethanolic solution of metal salt in 4:1 (ligand: metal)

TABLE 1 — COLOUR, ELEMENTAL ANALYSIS*, AND ELECTRONIC REFLECTANCE SPECTRAL AND MAGNETIC SUSCEPTIBILITY DATA FOR COMPLEXES

Complex	Colour	Calc. (%)		Found (%)		μ_{eff} (BM)	Electronic spectral maxima (cm^{-1})		
		M	N	M	N				
$\text{Co}(\text{MAT})_2\text{Cl}_2$	Pinkish blue	16.5	15.64	16.3	15.25	4.7	17540,	15900,	7630
$\text{Co}(\text{MAT})_2(\text{OAc})_2$	Blue	14.6	14.0	14.7	13.95	4.6	17140,	16000,	7630
$\text{Co}(\text{PhAT})_2\text{Cl}_2$	Blue	12.2	11.6	12.4	11.09	4.7	17540,	15970,	7955
$\text{Ni}(\text{PhAT})_2\text{Cl}_2$	Light green	12.2	11.6	12.5	11.1	3.07	20834,	15380,	8700,
							6580	5158	
$\text{Ni}(\text{MAT})_2\text{Cl}_2$	Dark green	16.5	15.64	16.1	15.2	2.9	21660,	15380,	9170,
							6500,	5200	
$\text{Cu}(\text{MAT})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	Green	13.7	14.0	13.9	14.5	1.84	18860,	16670,	15970
$\text{Cu}(\text{MAT})_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	Green	14.5	12.5	14.8	12.87	1.72	19220,	15900	
$\text{Cu}(\text{PhAT})_4\text{Cl}_2$	Dark green	7.7	13.4	7.2	12.86	1.88	21000,	17500	

MAT = 4-Methyl-2-aminothiazole; PhAT = 4-Phenyl-2-aminothiazole.

*Satisfactory C and H analyses were also obtained.

ratio. A solid separated on shaking. The contents were refluxed on a steam-bath for 30 min and the precipitate filtered, washed with ethanol and diethyl ether and finally dried *in vacuo*. The complexes of PhAT were prepared by refluxing the ethanolic solutions of the ligand and metal salt (4:1 ratio) for 2 hr. The solution was concentrated by distilling off the solvent to yield the solid product, which was filtered, washed with diethyl ether and dried *in vacuo*. Except for the complex of CuCl_2 with PhAT, where ligand to metal ratio is 4:1, maximum ligand: metal ratio attained is 2:1 in all the complexes.

Elemental analysis, colour and electronic reflectance spectral and magnetic susceptibility data of the complexes are given in Table 1. The complexes have negligible solubility in common organic solvents. These are non-conducting in nitrobenzene.

The IR spectra of free thiazoles show bands due to stretching ($1600\text{--}1550\text{ cm}^{-1}$) and pulsating ($900\text{--}850\text{ cm}^{-1}$) vibrations of thiazole ring³. In the present complexes, an upward shift (30 cm^{-1}) in these frequencies is observed, which may be attributed to coordination through the ring nitrogen of thiazole. The positions of these bands are found to remain unchanged in the complexes where bonding through exocyclic nitrogen of amino group has been proposed⁴. Further, no noticeable change in the frequency of $\beta\text{-C-NH}_2$ vibration of the ligands (360 cm^{-1}) is observed.

The cobalt complexes, CoL_2X_2 (where $\text{L}=\text{MAT}$ or PhAT and $\text{X}=\text{Cl}^-$ or OAc^-) may be proposed to have distorted tetrahedral structure as the electronic reflectance spectra (Table 1) of these complexes resemble those of $\text{Co}(\text{2-aminothiazole})_2\text{Cl}_2$ and $\text{Co}(\text{2-bromothiazole})_2\text{Cl}_2$ (ref. 5), where a pseudotetrahedral structure has been suggested. This proposal is further supported by magnetic moment values of the complexes at room temperature⁶ (Table 1) and appearance of a new band around 330 cm^{-1} which is characteristic for $\nu_{\text{Co-Cl}}$ in tetrahedral $\text{Co}(\text{II})$ complexes⁶.

$\text{Ni}(\text{II})$ forms complexes of the type NiL_2Cl_2 irrespective of the nature of the ligand. The magnetic moment and electronic reflectance spectra of these complexes are characteristic of distorted octahedral $\text{Ni}(\text{II})$ complexes⁸. Distorted octahedral

structure may be attained through polymerization in the present cases.

With PhAT, $\text{Cu}(\text{II})$ forms a complex having the stoichiometry $\text{Cu}(\text{PhAT})_4\text{Cl}_2$ whereas the corresponding complex with MAT contains only two ligand molecules. However, in the latter case, two molecules of water are also present to yield complexes of the type $\text{Cu}(\text{MAT})_2\text{X}_2 \cdot 2\text{H}_2\text{O}$ (where $\text{X}=\text{Cl}^-$ or OAc^-). The electronic reflectance spectrum of the $\text{Cu}(\text{II})$ complex of PhAT is consistent with octahedral stereochemistry⁹ which is also indicated by its magnetic moment value⁷. Electronic reflectance spectra are suggestive of a heavily distorted octahedral stereochemistry in the case of $\text{Cu}(\text{MAT})_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and almost a square-planar stereochemistry in the case of $\text{Cu}(\text{MAT})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (ref. 8). From the IR spectrum of $\text{Cu}(\text{MAT})_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, the value of ν_{asCOO} (1580 cm^{-1}) is found to be about the same as that observed in CH_3COONa ¹⁰, whereas ν_{sCOO} at 1460 cm^{-1} is considerably higher. This is indicative of the acetate acting as a bidentate ligand, with both oxygens coordinating almost equally to the metal ion. There are no bands characteristic of coordinated water in the region $1000\text{--}800\text{ cm}^{-1}$ in the IR spectra of these complexes, implying thereby that water molecules are weakly coordinated. A band at 300 cm^{-1} in the far IR spectrum of the complex $\text{Cu}(\text{MAT})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ is assigned to $\nu_{\text{Cu-Cl}}$; this value is nearer to that for a trans square planar structure as bands for bridging $\nu_{\text{Cu-Cl}}$ modes expected to be present in a polymerized octahedral structure are found at lower value¹¹.

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Oxy-Ti(IV) Dicarboxylates

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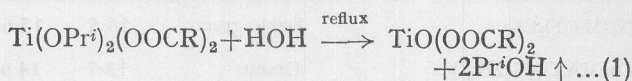
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Oxy-titanium(IV) carboxylates of composition $TiO(OOCR)_2$ have been synthesized by controlled hydrolysis of dialkoxy titanium dicarboxylates. These are obtained as viscous liquids, semisolids or solids, depending upon the chain length of carboxylic acids. Their refractive indices, melting points, molecular weights, thermal decomposition and IR data are reported.

TITANYL compounds possess different types of metal-oxygen linkages¹⁻³ depending upon the routes of their synthesis and molecular association. Some of these derivatives find extensive industrial applications⁴. The possibility of the formation of oxycarboxylates has been indicated by Mehrotra

and Pandey⁵ during their attempts to synthesize titanium tetra soaps. In the present note we report the synthesis of some oxy-titanium dicarboxylates. Their refractive indices, melting points, molecular weights, IR spectra and thermal decomposition data are also being reported.

Oxy-titanium dicarboxylates were synthesized by controlled hydrolysis of dialkoxy-titanium dicarboxylates in benzene solution (Eq. 1).



Pr^iOH produced in the reaction was removed azeotropically using benzene and estimated quantitatively. The excess solvent was distilled out under reduced pressure and the products obtained were finally dried at $50^\circ/0.5$ mm.

The products are viscous liquids, semisolids or solids depending upon the number of carbon atoms in the carboxylic acid chain. The liquid derivatives have very little difference in their refractive indices (Table 1).

The ebullioscopic and osmometric molecular weight determinations in benzene solution show little tendency of association. The molecular complexities fall in the range 1.2-1.4. The plot of the weight of compound added to a measured quantity of benzene against the change in resistance is always linear showing that the molecular complexity is independent of concentration of the solute within the measured range.

The IR spectra of $TiO(OOCR)_2$ derivatives (in nujol or neat) show the presence of two types of

TABLE 1 — ANALYTICAL AND PHYSICO-CHEMICAL DATA OF OXY-TITANIUM CARBOXYLATES

Reactants (g)	Isopropanol (g) Found (calc.)	Product	Yield (g) Found (calc.)	Ti (%) Found (calc.)	Mol. wt. Found (calc.)
$Ti(OPr^i)_2(OOCC_7H_{15})_2$ (2.10) H_2O (0.10)	0.24 (0.28)	$TiO(OOCC_7H_{15})_2^*$ $\eta_D^{35} = 1.4975$	1.70 (1.63)	13.52 (13.68)	451 (350)
$Ti(OPr^i)_2(OOCC_{11}H_{23})_2$ (3.36) H_2O (0.11)	0.30 (0.33)	$TiO(OOCC_{11}H_{23})_2^*$ $\eta_D^{35} = 1.4902$	2.82 (2.73)	10.05 (10.35)	592 (462)
$Ti(OPr^i)_2(OOCC_{13}H_{27})_2$ (1.36) H_2O (0.04)	0.10 (0.13)	$TiO(OOCC_{13}H_{27})_2^*$ $\eta_D^{35} = 1.4882$	1.23 (1.14)	9.02 (9.23)	662 (519)
$Ti(OPr^i)_2(OOCC_{15}H_{31})_2$ (4.21) H_2O (0.20)	0.36 (0.37)	$TiO(OOCC_{15}H_{31})_2^\dagger$	3.69 (3.58)	8.23 (8.34)	733 (575)
$Ti(OPr^i)_2(OOCC_{17}H_{35})_2$ (5.51) H_2O (0.14)	0.43 (0.45)	$TiO(OOCC_{17}H_{35})_2^*$ $\eta_D^{35} = 1.4978$	4.72 (4.74)	7.78 (7.65)	751 (626)
$Ti(OPr^i)_2(OOCC_{17}H_{35})_2$ (4.41) H_2O (0.12)	0.33 (0.36)	$TiO(OOCC_{17}H_{35})_2^\ddagger$ (m.p. $58-9^\circ$)	3.85 (3.79)	7.50 (7.59)	857 (630) (886)§
$Ti(OPr^i)_2(OOCC_{21}H_{43})_2$ (3.04) H_2O (0.07)	0.21 (0.22)	$TiO(OOCC_{21}H_{43})_2^\ddagger$ (m.p. $65-6^\circ$)	2.81 (2.68)	6.38 (6.45)	908 (743) (1038)§

*Viscous liquid.

†Semisolid.

‡White solid.

§Molecular weight determined by osmometry.