

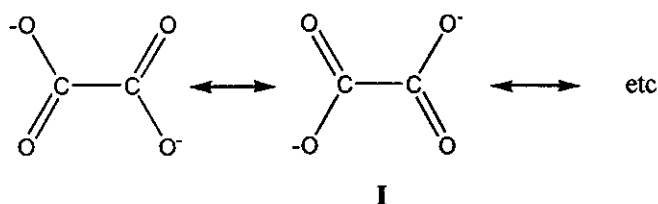
1. Introduction

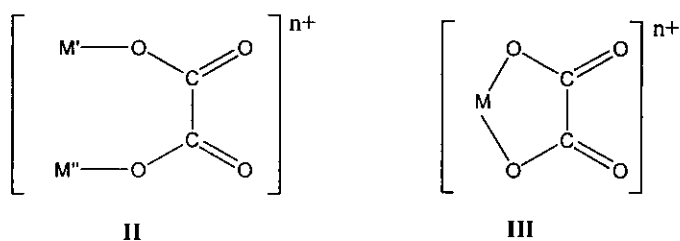
1.1 Introduction

Aluminium is a chemical element symbolized by Al with atomic number 13. The element is a hard, strong, and white metal. Elemental aluminium itself is clearly metallic and ionic in their character. It is the group IIIA element in the Periodic Table. The electronic configuration is $[\text{Ne}]3s^23p^1$ as a result the trivalent state is its most important state. It is the commonest metallic element in the earth's crust and occurs widely in nature in silicates such as micas and feldspars.

Chromium is a chemical element symbolized by Cr with atomic number 24. The electronic configuration is $[\text{Ar}]3d^54s^1$. The highest oxidation state is that corresponding to the total number of 3d and 4s electrons. The oxidation states are -II, -I, 0, I, II, III, IV, V, and VI. The most stable and important state is Cr^{III} , d^3 , which in an octahedral complex has each t_{2g} level singly occupied, giving a sort of half-filled shell stability (Cotton et al., 1972).

The dicarboxylic ($\text{C}_2\text{O}_4^{2-}$) or oxalato anion (ox^{2-}) or ethanedioate ion has σ -donor properties. The appearance of conjugated double bond show π electron delocalization of oxalate ligand (I) (Zhou., 1989). It can be an electron donor and often functions as bidentate bridging ligand. Complexes formed by the oxalate ion described below are of this type, with the possibility of π -bonding from the $2p$ orbitals on the oxygen making some contribution to the overall bond. The oxalate anion can coordinate to a metal as a monodentate (II) or bidentate (III) ligand : the bidentate chelate structure (III) is the most common one. (Nakamoto K., 1978).





The salts based on oxalate complexes are interesting materials, having technological applications as precursors to nanocrystalline metallic oxides, and to molecular-based magnetic materials (Tamaki et al., 1992). In these novel compounds, the oxalate ion can act as bridging ligand between metals and thus constructing one-, two- or three-dimensional honeycomb anionic networks $[\text{M}_2(\text{C}_2\text{O}_4)_3]_{\infty}^{n-}$ that behave as ferro, ferri or antiferro-magnets (Öhrström et al., 2000, Bérézovsky et al., 1999, Malézieux et al., 2001 and Armentano et al., 2001). The crystal structures of trioxalate metallate salts of general formula $\text{M}^{\text{I}}_3\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$, with $\text{M}^{\text{I}} = \text{K}, \text{Rb}, \text{NH}_4$ and $\text{M}^{\text{III}} = \text{Al}, \text{Cr}, \text{Ga}, \text{Fe}, \text{Mn}$ (Delgado et al., 2002) have been reported as monoclinic cells, space group $P2_1/c$, or as triclinic cells, space group $P\bar{1}$.

A large number of thermal studies on oxalate complexes have been reported (Haines P. J., 1999). The first step in the decomposition of solid oxalates is the loss of three moles of water. The second step is carbon monoxide to produce a carbonate and simple oxalates have been the subject of numerous studied by a variety of thermal techniques. The final product appears to be mixed oxides of metal and potassium (House J. E., 1980). So when aluminium oxalate decomposes it produces aluminium oxides.

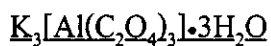
In some instances, aluminium oxides may contain trace of other metal ions. These include ruby (Cr^{III}) and blue sapphire (Fe^{II} , Fe^{III} , and Ti^{IV}). Ruby, natural or synthetic, is $\alpha\text{-Al}_2\text{O}_3$ containing occasional Cr^{III} ions in place of Al^{III} ions. The environment of the Cr^{III} in ruby is thus a slightly distorted (D_{3d}) octahedron of oxide ions. The frequencies of the spin-allowed bands of Cr^{III} in ruby indicate that the Cr^{III} ions are under considerable compression, since the value of Δ_0 calculated is

significantly higher than that in the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion or in other oxide lattices and glasses. In addition, in ruby, spin-forbidden transitions from the 4A_2 ground state to the doublet states the 2G state of the free ion are observed. The transitions to the 2E and 2T_1 states give rise to extremely sharp lines because the slopes of the energy lines for these are the same as that for the ground state (except in extremely weak fields) (Cotton et al., 1972).

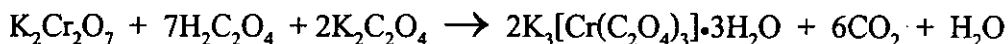
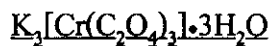
In this present work, oxalato complexes of chromium and aluminium with oxalate as bridging ligand were synthesized and characterized. The chemical properties of the complexes were studied by x-ray diffraction and spectroscopic techniques.

1.2 Literature reviews

Booth (1939) explained the preparations of $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ and $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ as followed.



A solution of 67 g (0.1 mol) of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ is treated with a solution of 24 g of NaOH. The precipitated aluminium hydroxide is filtered, washed, and boiled with a solution of 76.8 g of KHC_2O_4 (or a mixture of 55.2 g of $\text{K}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and 37.8 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) in about 800 ml. of water. Any $\text{Al}(\text{OH})_3$ which does not dissolve is filtered out and the filtrate is left to crystallization. The yield is nearly quantitative.



To a solution of 23 g. of $K_2C_2O_4$ and 55 g. of $H_2C_2O_4$ in 800 ml. of water is added 19 g. of powdered $K_2Cr_2O_7$ in small portions with vigorous stirring. At the end of the reaction, the solution is evaporated nearly to dryness and allows it to crystallize. $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ forms deep-green crystals with a brilliant blue iridescence. Yield 45 g (90 percent).

Palmer (1954) synthesized and characterized $K_3[Al(C_2O_4)_3] \cdot 3H_2O$, $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ and $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$. As indicated by the crystallographic constants in Table 1, the potassium trioxalato salts derived from the trivalent metals aluminium, chromium(III), and iron(III) are isomorphous and belong to the monoclinic system, but since the ration a/b is nearly unity, and the monoclinic angle β is nearly 90° , the crystals approach tetragonal symmetry. The percentage of oxalate group in $K_3[Al(C_2O_4)_3] \cdot 3H_2O$ complex was determined by titration technique.

Table 1 Isomorphous oxalate complexes, $K_3[M(C_2O_4)_3] \cdot 3H_2O$ (monoclinic system)

M	Ratio			β
	a	b	c	
Al	1.0061	1	0.3963	$93^\circ 23'$
Cr	1.0060	1	0.3989	$94^\circ 0'$
Fe	0.9916	1	0.3895	$94^\circ 13'$

$K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ complex can be prepared by dissolving potassium oxalate (6 g of the monohydrate) and oxalic acid (14 g of the dihydrate) in water (200 mL), adding potassium dichromate (5 g) slowly with continuous stirring. When the reaction is complete, evaporate the solution nearly to dryness and allow the product to

crystallize. Isolate the product by filtration, wash with acetone, and dry in a warm oven (Pass et al., 1974).

Taylor (1978) synthesized the complexes of $K_3[M(C_2O_4)_3] \cdot 3H_2O$ where M were Cr^{III} and Al^{III} and confirmed structure of two complexes. These complexes were characterized by x-ray crystallography. The two crystals are monoclinic, space group $P2_1/c$ with $Z = 4$. The structures comprised of discrete $M(C_2O_4)_3^{3-}$ anions, K^+ cation, and H_2O molecules.

House et al., (1980) studied the decomposition of solid $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ using TGA and DSC techniques. After dehydration, the chromium compound was found to decomposed by the loss of CO in two steps, the loss of CO_2 and CO, and finally the loss of CO_2 . The final product appeared to be either K_3CrO_3 or the mixed oxides of chromium and potassium. The decomposition of $K_3[Al(C_2O_4)_3] \cdot 3H_2O$ had been studied using TGA techniques (Keith et al., 1983). The dehydration occurs in the range $50-170^\circ C$ and decomposition of the anhydrous $K_3[Al(C_2O_4)_3]$ occurred in the range $380-525^\circ C$.

Doetschman (1974) studied electron paramagnetic resonance (EPR) of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ in $K_3[Al(C_2O_4)_3] \cdot 3H_2O$ and their photochemistry in singles crystals. The blue crystals were grown at room temperature from a saturated aqueous solution of 0.005 g $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ and 0.335 g $K_3[Al(C_2O_4)_3] \cdot 3H_2O$ by slowly evaporation of the solvent by passing N_2 through the flask containing the solution. The blue crystals degraded at temperature as low as 80 K due to the loss of H_2O .

Scaringe et al., (1977) reported the di- μ -hydroxobis[bis(oxalato)chromate(III)] hexahydrate, $Na_4[Cr(C_2O_4)_2OH]_2 \cdot 6H_2O$ by X-ray diffraction technique. The material

crystallized in the monoclinic space group $P2_1/c$. The structure consisted of two crystallographically independent dimeric $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{OH}]_2^{4-}$ anions which interacted with sodium cations and water molecules in the cell. There was extensive hydrogen bonding between the oxalate ligands and the water molecules. This complex was obtained by the reaction of aqueous ammonia with the monomeric complex $\text{cis-Na}_4[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2]$ and subsequent metathesis with sodium bromide. Suitable single crystals were obtained by slow evaporation of an aqueous solution of the powdered material.

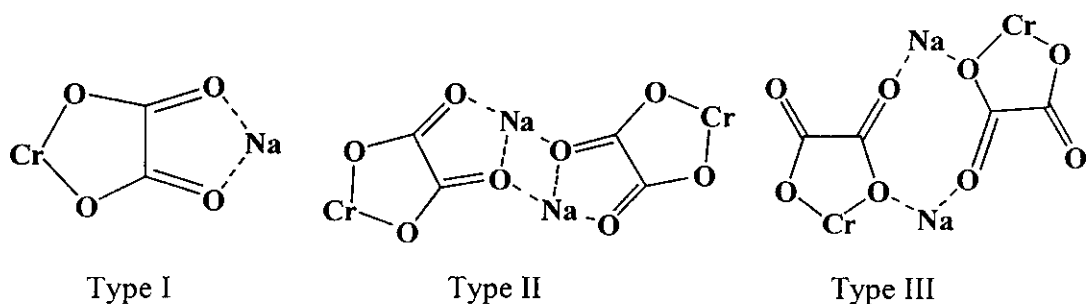
Daniele (1983) studied the formation and stability of Li^+ , Na^+ , and K^+ complexes with oxalate or dicarboxylate ligand potentiometrically at various temperature and ionic strengths. It was found that the protonation constants obtained in different background salts followed, almost invariably, the trend $\text{K}^+ > \text{Na}^+ \geq \text{Li}^+$, suggesting that they were weak complexes. The stabilities of the alkali metal complexes with dicarboxylate ligand were $\text{Li}^+ > \text{Na}^+ \geq \text{K}^+$.

Román et al., (1996) reported of $[\text{Ni}(\text{bipy})_3][\text{NaAl}(\text{ox})_3]$, where ox^{2-} was the oxalate dianion and bipy is 2,2'-bipyridine, was obtained by mixing of $\text{K}_2[\text{Ni}(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ and $[\text{H}_2\text{bipy}]\text{Cl}_2$ in silica hydrogel at room temperature. The complex, which incorporated Na and Al from the silica gel, was characterised by Fourier-transform IR spectroscopy, energy-dispersive X-ray analysis, thermogravimetric techniques and single-crystal X-ray diffraction. It crystallised in the cubic system, space group $P2_13$, with $a = 15.518(2) \text{ \AA}$, $U = 3736.9(8) \text{ \AA}^3$ and $Z = 4$. The crystal structure consisted of a chiral, three-dimensional polymeric network of Al^{3+} and Na^+ bridged by bis(bidentate oxalate) ligands, $[\text{NaAl}(\text{ox})_3]_n^{2n-}$, with the $[\text{Ni}(\text{bipy})_3]^{2+}$ cations inserted in the anionic network cavities. The cations and anionic network are held together by means of electrostatic forces and weak $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds.

Langford et al., (1999) studied the excitation energy transfer properties of $[\text{Cr}(\text{ox})_3]^{3-}$ chromophores in the three-dimensional network structure of $[\text{Rh}(\text{bpy})_3][\text{NaAlCr}(\text{ox})_3]\text{ClO}_4$ and $[\text{Rh}(\text{bpy})_3][\text{NaAl}_{1-x}\text{Cr}_x(\text{ox})_3]\text{ClO}_4$ ($x=0.05-0.9$). Two series of mixed crystal of nominal compositions $[\text{NaAl}_{1-x}\text{Cr}_x(\text{ox})_3][\text{Rh}_{0.99}\text{Cr}_{0.01}(\text{bpy})_3]\text{ClO}_4$ ($x = 0, 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, \text{ and } 1$) and $[\text{NaAl}_{0.09}\text{Cr}_{0.01}(\text{ox})_3][\text{Rh}_{1-y}\text{Cr}_y(\text{bpy})_3]\text{ClO}_4$ ($y = 0, 0.01, 0.02, 0.03, 0.04, \text{ and } 0.05$) were utilized. The method used for preparation of neat $[\text{NaCr}_x(\text{ox})_3][\text{Cr}(\text{bpy})_3]\text{ClO}_4$ crystals was applied to the preparation of $[\text{NaAl}_{1-x}\text{Cr}_x(\text{ox})_3][\text{Rh}_{1-y}\text{Cr}_y(\text{bpy})_3]\text{ClO}_4$ mixed crystals with some simple modifications. Appropriate nominal mole fractions in aqueous solution of $\text{K}_3[\text{Al}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ to $\text{K}_3[\text{Cr}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ and of $[\text{Rh}(\text{bpy})_3][\text{ClO}_4]_3$ to $[\text{Cr}(\text{bpy})_3][\text{ClO}_4]_3$ were used in place of $\text{K}_3[\text{Cr}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ and $[\text{Cr}(\text{bpy})_3][\text{ClO}_4]_3$ solutions, respectively.

Von Arx et al., (2002) studied the resonant energy transfer in the mixed crystal series $[\text{Rh}(\text{bpy})_3][\text{NaAl}_x\text{Cr}_{1-x}(\text{ox})_3]\text{ClO}_4$ ($x = 0.05-1$). Efficient resonant energy transfer occurred within the R_1 line of the ${}^4A_2 \rightarrow {}^2E$ transition of the $[\text{Cr}(\text{ox})_3]^{3-}$ chromophore in mixed crystal. The number of lines and their relative intensities depend critically upon the $[\text{Cr}(\text{ox})_3]^{3-}$ concentration and the excitation within the inhomogeneous distribution.

Sakagami et al., (1999) synthesized and characterized the complex of $\text{Na}[\text{Cr}(\text{ox})_2(\text{hm})]\cdot 3\text{H}_2\text{O}$ ($\text{hm} = \text{histamine}$) by single crystal X-ray diffraction technique and elemental analyses. This complex was obtained by QAE Sephadex column (Cl^- form) with 0.05 M NaCl solution as an eluent. The powder was obtained by adding ethanol to the aqueous solution. Crystals suitable for X-ray analyses was grown by slow evaporation of an alcoholic aqueous solution and refrigerated. When oxalato ions act as bridging ligands, there were many patterns of coordination modes but type I was the most popular bridging mode and was found in this compound.



Bérezovsky et al., (1999) synthesized and characterized a new polymeric two-dimensional compound of formula $[K(H_2O)Cr(C_2O_4)_2(bpym)]$ ($bpym = 2,2'$ -bipyridine) by infrared spectroscopy and x-ray structure determination. This complex crystallises in orthorhombic space group $P22_12_1$. They contained alternating Cr and K cations bounded through multi-bridging $bpym$ ligand and oxalate ligands which show unusual coordination mode. The Cr(III) had a slightly distorted octahedral geometry with two bidentate oxalate groups and one bidentate $bpym$ ligand. Each potassium cation was eight coordinated, this coordination arised from two bidentate and one monodentate oxalate groups, a $bpym$ bidentate ligand and a coordinated water molecule.

Andrés et al., (1999) synthesized and characterized of the enantiomeric forms of the two- and three-dimensional polymers: $\{[NBu_4][MnCr(ox)_3]\}_n$ (1) where $Bu = n$ -butyl, $ox = oxalate$), $\{[M(bpy)_3][LiCr(ox)_3]\}_n$ ($M = Ni$ (2), $Ru = (4)$), $\{[M(bpy)_3][Mn_2(ox)_3]\}_n$ ($M = Ni$ (3), $Ru = (5)$) using resolved $[Cr(ox)_3]^{3-}$ and $[M(bpy)_3]^{2+}$ species as chiral building blocks. The optical activity of these systems arised from the helical chirality of the tris-chelated sub-unit with Δ or Λ configurations. Bimetallic two-dimensional optically active network 1 results from the stacking of similar metallo-oxalate honeycomb like layers containing $[Cr(ox)_3]^{3-}$ unit of the same chirality. The assembly of homochiral species leads to optically active three-dimensional 3-connected 10-gon nets 2-5. Enantiomerically pure single crystals of the two

enantiomeric forms, 4Δ and 4Λ , had been obtained and the structures determined by x-ray diffraction studies (crystals data: cubic system, space group $P2_13$, $a = 15.293(8)$ (4Δ), $a = 15.289(2)$ (\AA) (4Λ)).

Bataille et al., (2000) studied the crystal structure of $\text{La}(\text{H}_2\text{O})_2\text{K}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ by powder x-ray diffraction. The symmetry was monoclinic, space group $C2/m$. The layers were formed by four-membered rings $[\text{La}(\text{C}_2\text{O}_4)]_4$. The potassium atom and two of the three water molecules were located between the layers. The lanthanum atom was tenfold-coordinated in a distorted bicapped square antiprism and the potassium atom was eightfold-coordinated in a dodecahedron.

Öhrström et al., (2000) synthesized $\text{cis-Cr}^{\text{III}}(\text{C}_2\text{O}_4)_2(\text{DMSO})_2\text{K}(\text{DMSO})_2$ which formed by $\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3$ in dimethylsulfoxide-THF mixtures. The structure was ribbon-like with $\text{cis-Cr}(\text{C}_2\text{O}_4)_2(\text{DMSO})_2^-$ complex ions bridged by oxalate to $(\text{DMSO})\text{K}(\text{DMSO})_2\text{K}(\text{DMSO})$ units forming interconnected rings of six metal complexes.

Hua et al., (2001) studied the compounds of $\Delta\text{-}[\text{Cr}(\text{en})_3]\Delta\text{-}[\text{Cr}(\text{ox})_3]$. Crystal of this compound was hexagonal. The susceptibility behavior suggested that magnetic interactions were strong in $\Delta\text{-}[\text{Cr}(\text{en})_3]\Delta\text{-}[\text{Cr}(\text{ox})_3]$ where both anion and cation were paramagnetic.

Coronado et al., (2001) reported the magnetic properties of the family of layered molecular magnets $\text{A}[\text{Fe}^{\text{III}}\text{M}^{\text{III}}(\text{ox})_3](\text{M}^{\text{III}} = \text{Cr, Fe, Ru; ox} = \text{oxalate; A}^+ = [\text{NBu}_4]^+, [\text{CoCp}^*_2]^+)$. The magnetic of the solid solution $\text{Fe}^{\text{II}}(\text{Ru}^{\text{III}}\text{Cr}^{\text{III}})$ was easily tuned by changing the chemical composition of the material within the magnetic layers and the type of cation A^+ inserted in between the layers.

Malézieux et al., (2001) investigated a series of (ferrocenylmethyl)trialkyl ammoniums: $\text{FcCH}_2\text{NR}_3^+$ with $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7, \text{n-C}_4\text{H}_9, \text{and n-C}_5\text{H}_{11}$. They planar chiral 1,2-disubstitued $\text{Fc}(\text{CH}_3)\text{CH}_2\text{NBu}_3^+$ used as template cation in order to synthesis bidimensional oxalate bridged molecule-based magnets of general formula $\{[\text{Cr}^{\text{III}}\text{M}^{\text{II}}(\text{ox})_3][\text{FcCH}_2\text{NR}_3]\}_n$ ($\text{M}^{\text{II}} = \text{Mn}^{2+}, \text{Ni}^{2+}$) and characterized by circular dichroism measurements. All these compounds were ferromagnets with a Curie-temperature close to 6 K when $\text{M} = \text{Mn}$ and to 17 K for Ni.

Delgado et al., (2002) studied magnetic susceptibility and crystal structure of $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$. It had been found that it crystallizes in the monoclinic space group $P2_1/c$. The crystal structure consisted of discrete $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ anions, K^+ cations and water molecules similar to chromium and aluminium oxalate. Six oxygen atoms from water molecules and oxalate anions surround each of the K^+ atoms distances varying from 2.60(6) to 2.90(9) Å.

Dinnebier et al., (2003) reviewed the molecular and crystal structure of solvent-free potassium oxalates from high-resolution synchrotron and x-ray laboratory powder patterns. It was orthorhombic system, the oxalate anion was planar.

1.3 Objectives

1.3.1 To prepare and study the chemistry of $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ and

$\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ complexes.

1.3.2 To prepare and study the chemistry of the products from the reaction of both complexes.