



Synthesis and characterization of pure Nickel, Copper and Magnesium Cobaltite using hydrazinium compounds as precursors

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ABSTRACT

Hydrazinium mixed metal hydrogenethylenediaminetetraacetate mono hydrates such as $[N_2H_5M_{1/3}Co_{2/3}(HEDTA)].H_2O$ where M: Ni, Cu or Mg have been prepared by the aqueous reaction between the ligand, dihydrazinium dihydrogenethylenediaminetetraacetate and a mixture of respective metal nitrate hydrates in appropriate and accurate ratio. The complexes were characterized by hydrazine and metal analyses, infrared spectra, thermal analysis and X-ray powder diffraction techniques. From the conclusions derived from TG-DTA analyses, attempt were made to prepare mixed metal oxides, metal cobaltites such as magnesium cobaltite ($MgCo_2O_4$), nickel cobaltite ($NiCo_2O_4$) and copper cobaltite ($CuCo_2O_4$) by decomposing the respective pure crystalline complexes at $600^\circ C$. The products obtained were characterized and confirmed by chemical analysis, infrared spectra, X-ray powder diffraction and SEM techniques.

Key Words: Hydrazinium complexes, metalcobaltites, IR spectra, TG-DTA, X-ray powder diffraction, SEM.

INTRODUCTION

Hydrazine complexes, as low temperature precursors to metal oxides and mixed metal oxides have been studied and exploited for different applications during the last two decades [1-9]. The endothermic nature of N-N bond and crystalline nature of the hydrazinium complexes play a vital role in the preparation of metal cobaltites and ferrites in pure form at lower temperatures than the similar non-hydrazine complexes. In spite of a large number of hydrazine mixed metal precursors have been reported and characterized, the hydrazinium ($N_2H_5^+$) derivatives are far more limited in the literature [1-10]. The hydrazine adducts as starting materials to fine particle oxides have limitation for the purity reasons because of their rapid precipitations from aqueous solutions due to their water insoluble nature. However, hydrazinium complexes are water soluble and hence isolated by crystallization from aqueous solutions and hence are highly crystalline in nature and almost 100% pure. Hence, efforts have been made to synthesis such water soluble hydrazinium metal carboxylates and to utilize them for the synthesis of pure metal oxide and mixed metal oxides. Furthermore, so far the hydrazinium mixed metal complexes containing copper has not been reported in the literature due to the ease of reduction of Cu^{2+} to Cu^0 in the presence of weak bases like hydrazine. In the present case due to the strong chelating ability of $EDTA^{4-}$, the copper is very much stabilized even in the presence of base and surprisingly form hydrazinium complexes. During the course of our research work we have reported few hydrazinium metal ethylenediaminetetraacetate hydrates and determined the crystal structures of manganese(II)[11], iron(III)[12], nickel(II)[12], copper(II)[13] and cadmium(II) complexes. The work has been extended for the preparation of mixed metal complexes and in this paper, we report the preparation and characterization of such mixed metal complexes and mixed metal oxides. As far we are aware of the

literature this is the first report of the hydrazinium mixed metal carboxylate which has been utilized to prepare copper cobaltite.

EXPERIMENTAL SECTION

Preparation of the Complexes

The ligand $(N_2H_5)_2H_2EDTA$ was prepared by the method described elsewhere [14]. The cobalt-nickel mixed metal complexes was prepared by slowly adding an aqueous solution (50ml) of ligand (21.36g, 0.06mol) to an aqueous solution (50ml) containing a mixture of cobalt nitrate hexahydrate (5.82g, 0.02mol) and nickel nitrate hexahydrate (2.97g 0.01mol) with constant stirring. The clear solution obtained was kept at room temperature for about 2hr. The white precipitate, H_4EDTA thrown out from the solution was filtered using wattmann filter paper and the clear solution was refluxed on a mantle for 1hr using water condenser. The resulting solution was concentrated on a water bath to one third of its original volume and allowed to crystallize at room temperature in dust free clean atmosphere. The crystalline complex formed after 3-4 days was filtered using a Buckner funnel, washed with ice cold distilled water, dried and stored in vacuum desiccator.

The cobalt-copper mixed metal complex is also prepared by the above procedure using copper nitrate tetrahydrate(2.42g, 0.01mol) and cobalt-magnesium mixed metal complex by using magnesium nitrate hexahydrate (2.56g, 0.01mol) instead of nickel nitrate hexahydrate. All the complexes are highly crystalline, soluble in water, insoluble in alcohol and decompose in dilute hydrochloric acid.

Physio-Chemical Techniques

Commercially available chemicals of Analar or equivalent grade were used as received from SD fine chemicals without further purification. Hydrazine hydrate (99-100%) and ethylenediaminetetraacetate(99%) were used for the preparation of salts and complexes. For the preparation of complexes and analyses doubly distilled water was used. Organic solvents such as alcohol, chloroform and carbon tetrachloride were distilled before use.

The CHN analyses of the complexes were recorded on a Perkin-Elmer 1240 CHN analyzer. The hydrazine content present in the samples were determined by Andrew's method [14]. The metal contents were determined by the method described earlier [15]. The conductivity at room temperature of 0.01 mol of the aqueous solution of the mixed metal complexes were measured using a Centaury digital conductivity meter model cc 601 and dip type cell with a smooth platinum electrode. The infrared spectra of the solid complexes and the metal cobaltites were recorded in the range $4000-200cm^{-1}$ on a Perkin Elmer 597/1650 spectrophotometer using KBr pellets.

The simultaneous TG-DTA experiments were carried out using a STA 1500 thermal analyser. The heating rate employed was $10^{\circ}C\ min^{-1}$ in air using platinum crucible to hold 10-15 mg of well powdered solid samples. The X-ray powder diffraction pattern of the complexes and mixed metal oxides were recorded on a Philips X-ray diffractometer model PW 1050/70 employing $CuK\alpha$ radiation ($d=1.5406\text{\AA}$) between $2\theta=10$ to 70° at a scan rate of $2^{\circ}\ min^{-1}$ with scintillation counter as detector. The SEM photographs of the oxides were recorded using a Cambridge Stereoscan model S-150 scanning electron microscope.

RESULTS AND DISCUSSION

The ligand $(N_2H_5)_2H_2EDTA$ was prepared by the neutralization of H_4EDTA with hydrazine hydrate in 1:2 ratio. The mixed metal complex were prepared by the addition of ligand, $(N_2H_5)_2H_2EDTA$ to the aqueous solution containing a mixture of respective metal ions in appropriate ratio. The complexes obtained were found to be stable in air, soluble in water and insoluble in organic solvents such as alcohol and ether.

The CHN and chemical analysis of the complex are in well accordance with the theoretical values expected for the assigned composition, $N_2H_5(M_{1/3}Co_{2/3}EDTA).H_2O$. The ratio of Co^{2+} to M^{2+} is 1.98 – 2.01 for the present set of complexes. The analytical data of the complexes are summarized in Table 1.

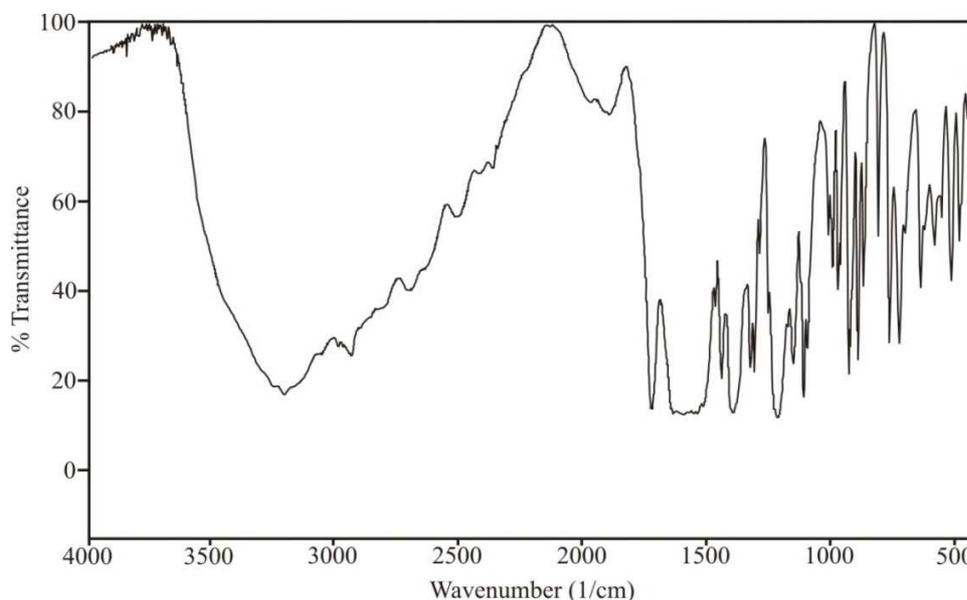
Table 1 Analytical data of $[N_2H_5M_{1/3}Co_{2/3}(HEDTA)] \cdot H_2O$

M	Colour	Yield %	Elemental analysis				Conductance $mho\ cm^2\ mol^{-1}$
			N_2H_4 %	M^{2+} %	Co^{2+} %	Co^{2+}/M^{2+}	
			Observed (Calculated)	Observed (Calculated)	Observed (Calculated)		
Ni 399.14	Dark Greenish pink	70	8.06 (8.04)	4.93 (4.90)	9.80 (9.81)	1.98	20
Cu 410.76	Bluish pink	60	7.92 (8.00)	5.18 (5.29)	9.79 (9.80)	2.01	28
Mg 391.47	Pale pink	70	8.31 (8.27)	2.13 (2.09)	10.17 (10.13)	1.99	26

The molar conductances of the complexes in water are in the range 20 to 30 $mho\ cm^2\ mol^{-1}$ which is in accordance with their non electrolytic nature. Hence, it is expected that the water molecules present outside the coordination sphere and hydrazinium cation coordinates to the metal ion in a monodentate fashion.

The infra-red spectra of the complexes show broad band with splitting in the region 3200 to 3300 cm^{-1} which are assigned to N-H and O-H stretching's of $N_2H_5^+$ and H_2O respectively. A sharp band at 1700 cm^{-1} was observed in all the cases is attributed to the carbonyl stretching of -COOH group. The ν_{asy} and ν_{sym} stretching vibrations of carboxylate ions are observed at 1630 and 1410 cm^{-1} with $\Delta\nu=220\ cm^{-1}$ suggesting their monodentate coordination behavior. Many sharp bands are observed in the finger print regions which are the characteristics of the EDTA complexes [16]. The N-N stretching frequencies of hydrazine molecule in their salts and complexes reveal interesting information about the nature of hydrazinium moiety [17]. In the present case, through a sharp band at 990 cm^{-1} was observed in all cases, presence of several bands close to each other and also bands at 980 cm^{-1} and 960 cm^{-1} makes difficult to conclude the coordination or ionic nature of $N_2H_5^+$ ion.

However, the infrared spectra of the mixed metal complexes with copper and nickel complexes were compared and found to be super imposable and hence the present set of complexes are expected to have similar structure. The crystal structure of nickel [12] and copper [13] complex have been reported and the structure shows that the hydrazinium ion is coordinated to metal ions. In the present case also based on conductivity and infrared spectral studies similar structure has been proposed. The infrared spectra of $[N_2H_5Ni_{1/3}Co_{2/3}(HEDTA)] \cdot H_2O$ is shown in Fig.1 as a representative example.

Fig.1. IR-Spectra of $[N_2H_5Ni_{1/3}Co_{2/3}(HEDTA)](H_2O)$

The thermal data of mixed metal complex show similar trend of degradation. The complexes undergo dehydration at 130-150°C followed by the loss of N_2H_4 molecule around 250°C. The respective mixed metal-EDTA intermediate

further undergo ligand pyrolysis in two stages up to 600°C to yield the respective metal cobaltites as the final residue. The first stage is endothermic while the other stages are exothermic. The final weight loss is in good agreement with the formation of respective metal cobaltite (Table2).

Table 2 Thermal degradation data of $[N_2H_5M_{1/3}Co_{2/3}(HEDTA)].H_2O$

M	TG Temperature range (°C)	DTA Temperature range (°C)	Weight loss found %	Weight loss calculated %
Ni	130-150	140(endo)	4.80	4.5
	220-250	230(exo)	9.00	9.036
	250-520	300,480(exo)	80.00	79.91
Cu	110-130	120(endo)	4.00	4.38
	200-240	220(exo)	8.50	8.78
	240-500	420,480(exo)	8.00	80.09
Mg	120-140	130(endo)	4.00	4.6
	210-230	220(exo)	9.00	9.21
	220-520	400,420(exo)	83.00	82.45

The higher dehydration temperature is attributed to the hydrogen bonding interaction of the water molecule in the structure which is the stabilizing factor. The TG-DTG of $[N_2H_5Ni_{1/3}Co_{2/3}(HEDTA)].H_2O$ is given in Fig. 2.

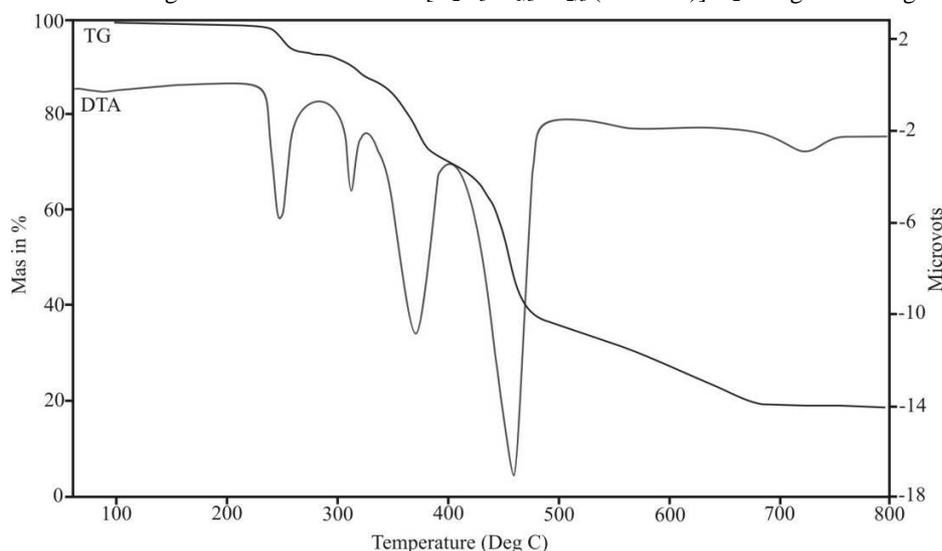


Fig. 2. Simultaneous TG- DTG of $[N_2H_5Ni_{1/3}Co_{2/3}(HEDTA)].(H_2O)$

The X-ray powder diffraction patterns of the complexes are super imposable among themselves and also with the simple nickel and copper complexes indicating their structural similarity. The X-ray powder diffraction patterns of nickel and nickel-cobalt mixed metal complexes are shown in Fig.3a and 3b respectively.

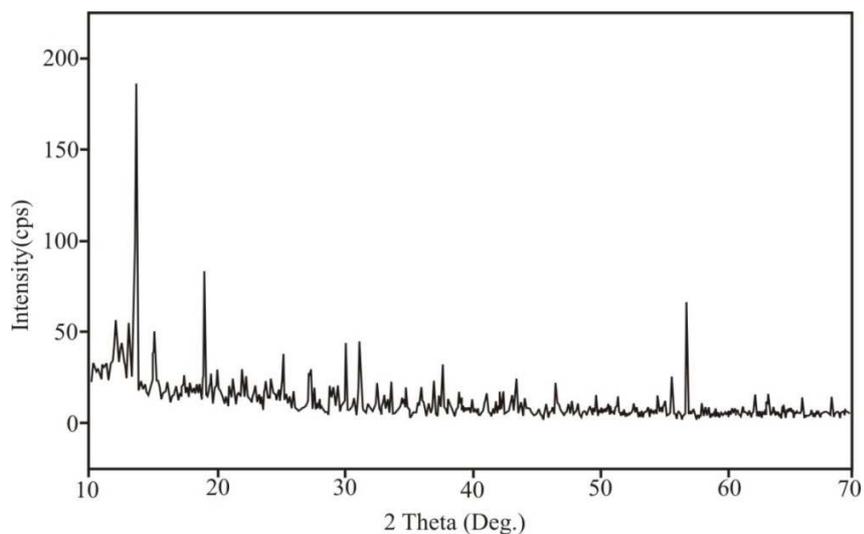


Fig. 3a.X-Ray powder pattern of $[N_2H_5Ni(EDTA)].(H_2O)$

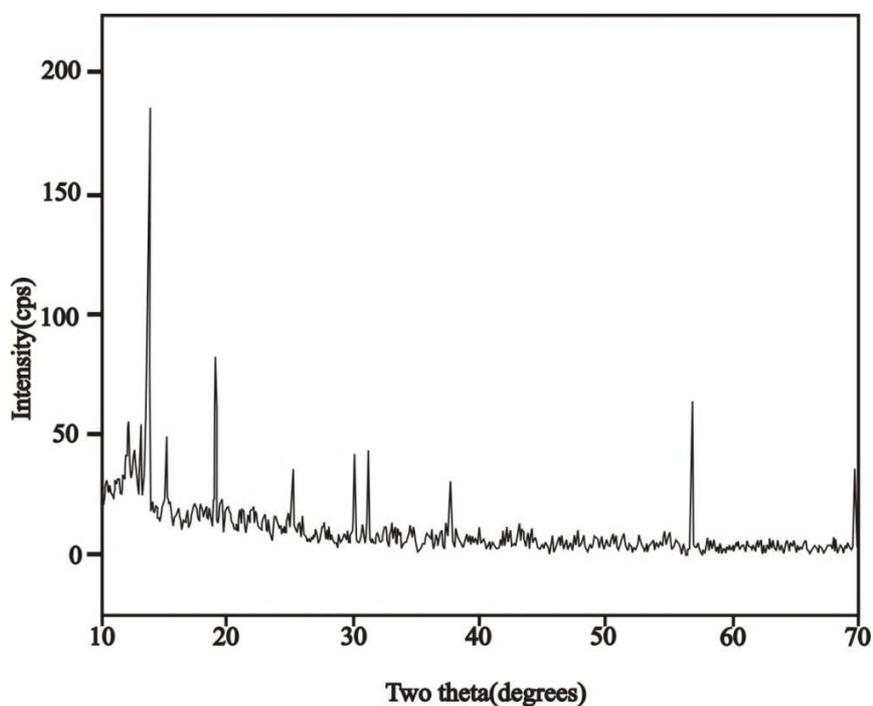


Fig. 3b.X-Ray powder pattern of $[N_2H_5Co_{2/3}Ni_{1/3}(EDTA)].(H_2O)$

Metal Cobaltites

The mixed metal complexes when heated at 600°C in a silica crucible for about five minutes yielded respective metal cobaltites, MCo_2O_4 . The residues were analyzed for their metal contents and it was observed that the cobalt to metal ratio is 1.99-2.01. The formation of metal cobaltites was confirmed by the infrared spectra and X-ray powder diffraction patterns of the residues. The infrared spectrum and XRD pattern of $NiCo_2O_4$ are shown in the Figs.4 and 5 respectively. The SEM photographs of the cobaltites show lots of cracks and voids indicating that large quantity of gases are evolved during decomposition. The SEM photograph of $NiCo_2O_4$ is shown in Fig. 6.

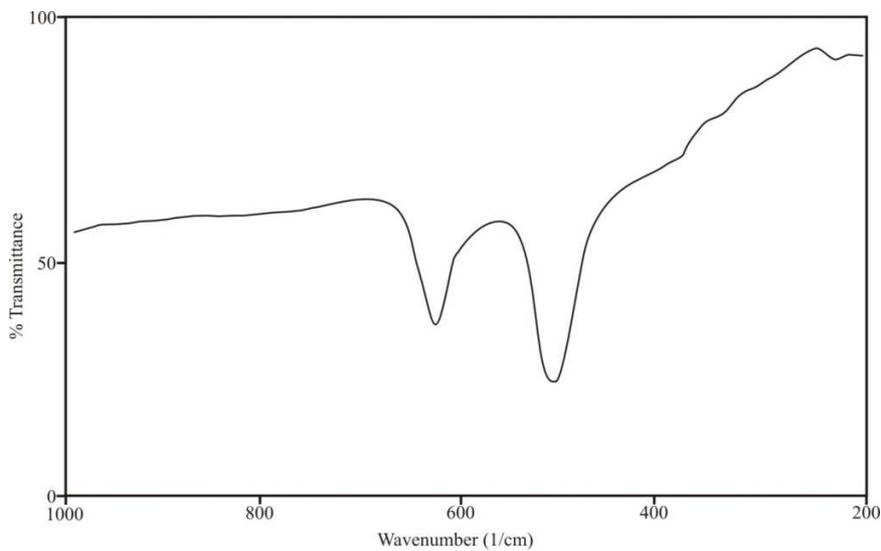


Fig.4. IR-Spectra of NiCo₂O₄

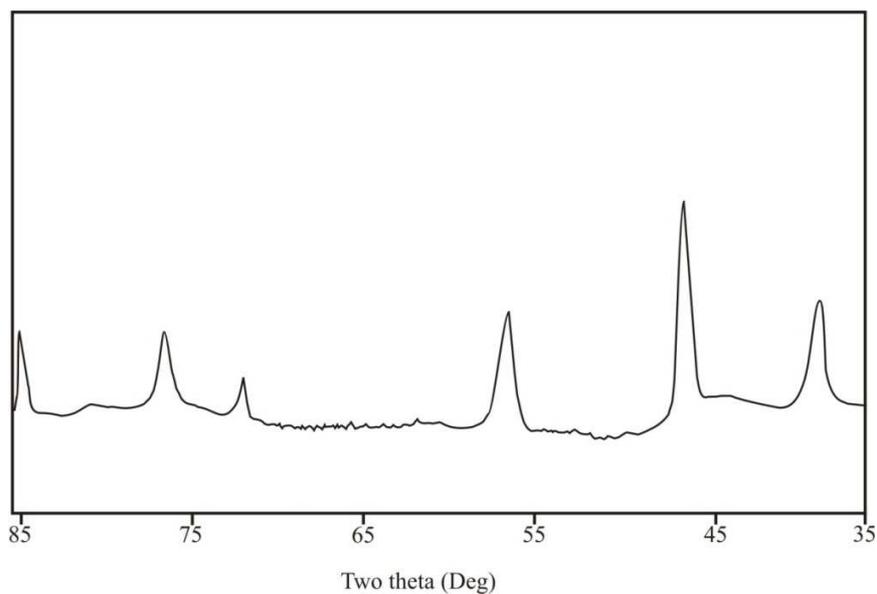


Fig. 5. X-Ray Powder diffraction pattern of NiCo₂O₄

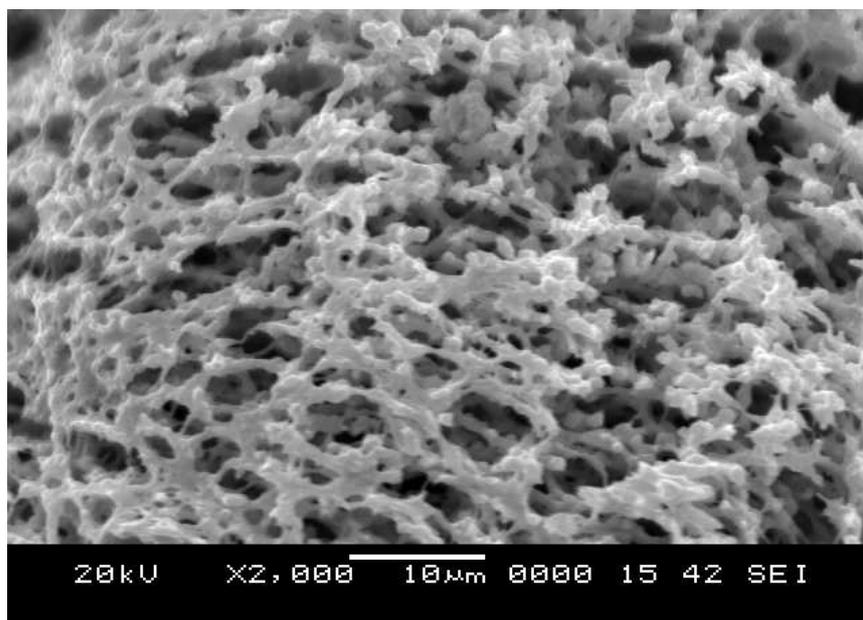


Fig.6.The SEM photograph of NiCo₂O₄

REFERENCES

- [1] PRavindranathan; GV Mahesh;KCPatil.*J.Solid State Chem.*, **1987**, 66, 70.
- [2] PRavindranathan; KC Patil.*Am. Ceram. Soc. Bull.*,**1987**,66,688.
- [3] JS Budkuley; KCPatil.*Synth.ReactInorg. Met.-Org.Chem.*,**1989**,19, 909.
- [4] BN Sivasankar;S.Govidarajan.*Indian J.Chem.***1994**,33A, 329.
- [5] BN Sivasankar; SGovidarajan.*Synth. React. Inorg.Met.-Org.Chem.*,**1995**, 25, 127.
- [6] D Gajapathy; KC Patil; VR Paiverneker.*Met. Res. Bull.***1982**, 17, 29.
- [7] 7.BN Sivasankar; SGovidarajan; Z Naturforsch,**1944**, 49b, 950.
- [8] BNSivasankar.*Indian J.Chem.*,**2005**, 44A, 1806.
- [9] LVikram; BNSivasankar, *Thermochem.Acta*,**2007**, 452, 20.
- [10] BN.Sivasankar; SGovidarajan.*Material Research Bulletin***1996**, 31(1), 47-54.
- [11] LVikram; BNSivasanka. *Indian J.Chem.*,**2007**, 46A, 568-575.
- [12] RRaghul; BNSivasankar.*J.Chem. crys.*,**2012**, 42(6), 533-542.
- [13] LRagunath; BNSivasankar.*J.Chem. crys.*,**2010**,40(12), 1170-1174.
- [14] AIVogel. A Text Book of Quantitative Inorganic Analysis, 3rdedn., Longman, London, **1962**.
- [15] LErdey; IBuzars (Eds.).Gravimetric Analysis, PartII, Pergamon, London,**1965**.
- [16] KNakamoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds,Wiley, Newyork**1978**.
- [17] ABraibanti;FPallavalle; MAPellinghelli; ELeporati.*Inorg Chem.*, **1968**,1430.