

## Synthesis, Characterization of Cr<sup>3+</sup>, Fe<sup>3+</sup>, Y<sup>3+</sup>, La<sup>3+</sup> and Ce<sup>3+</sup> complex salts with 2,3,5-(triphenyl)tetrazolium chloride and tetraethylammonium iodide

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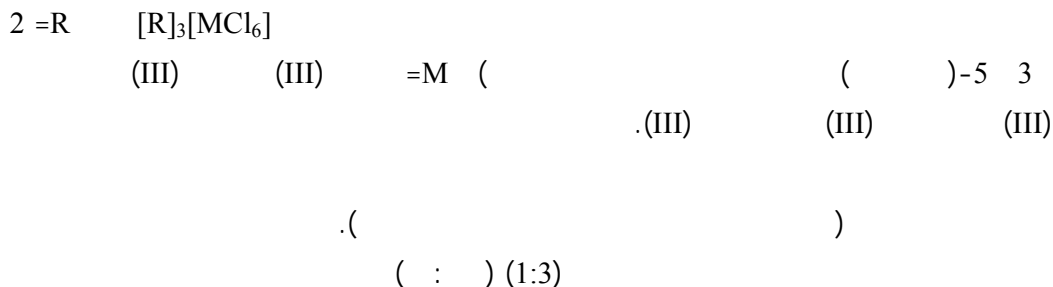
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### Abstract

New series of trivalent metal complex salts with the general formula [R]<sub>3</sub>[MCl<sub>6</sub>] where R=2,3,5-(triphenyl)tetrazolium or tetraethylammonium, M= Cr<sup>3+</sup>, Fe<sup>3+</sup>, Y<sup>3+</sup>, La<sup>3+</sup> and Ce<sup>3+</sup> were prepared and characterized by metal analysis, molar conductance measurements, magnetic susceptibilities and spectroscopic data (IR and UV/Vis). Molar conductance studies indicate 1:3 electrolytic behaviors for the complex salts. The UV-Visible spectra and magnetic measurements of complex salts suggests an octahedral geometry around metal.



### Introduction

Ionic liquids are a new class of solvents for use in environmentally benign industrial processes and are seen as alternative to toxic volatile organic compounds<sup>(1-3)</sup>. The ionic nature of ionic liquids has important consequences for the liquid on monosonic level<sup>(4,5)</sup>. spectroscopic evidence is suggesting the presence and important of the formation of

intermolecular cation/anion hydrogen bonds<sup>(6,7)</sup>.

Application of ionic liquids include today as solvents for a clean green chemical synthesis<sup>(8,9)</sup>, crystal X-ray structure of metal-containing ionic liquid complexes<sup>(10)</sup> and in wood related industries<sup>(11)</sup>.

The preparation, crystal structure and solid slate properties of tetrabromocuparate (II) and

hexachlorouranate (IV) with  $[\text{Py}]^+$ ,  $[\text{NMe}_4]^+$  and  $[\text{NEt}_4]^+$  as counter ions were carried out, which show the ionic interaction between anion (metal halide) and the cation (organic ion)<sup>(12,13)</sup>.

Synthesis and crystal structure of anionic lanthanide halides(III) chlorides and iodide complexes in imidazolium ionic liquid were studied. The single crystal x-ray structure show that the lanthanum atom in a perfect geometry<sup>(14-16)</sup>.

There has been huge research on preparation and properties of trivalent lanthanide metal ions coordination complexes with many different organic ligands such as anthranilic acid<sup>(17)</sup>, benzimidazol-2-acetic acid<sup>(18)</sup>, 1,2,4-triazol<sup>(19)</sup> and pruric acid<sup>(20)</sup>, but a little work has been done concerning the preparation of lanthanide(III) complex salts, so as part of an on-going investigation of these metallate and their role in ionic liquid system, we have prepared and studied the properties of complex salt, of 2,3,5-triphenyltetrazolium chloride and tetraethyl ammonium iodide with  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  metal halides.

## Experimental

### General

All materials were obtained commercially and used as received. Molar conductance were carried out for  $10^{-3}$  M solution in dimethyl sulfoxide (DMSO) using an electronic conductivity measuring device model LF-42 at 25 °C. Magnetic susceptibility measurements were performed on a Brukel BM6 instrument. The electronic spectra of the complex salts in DMSO solution were recorded on Shimadzu UV-160 spectrophotometer at 25 °C using a 1 cm quartz cell. IR spectra were recorded on solid state in nujol mull in the range 200-4000  $\text{cm}^{-1}$ . Metal analysis were carried out by using an AA240FS Varian instrument for

atomic absorption, EDTA-titration and gravimetric methods according to the standard procedures<sup>(22-24)</sup>. The qualitative element determination of halogens were done on the sodium fusion solution of mixed halides complex salts<sup>(21)</sup>.

### Syntheses of complex salts

#### $[(\text{C}_6\text{H}_5)_3\text{CN}_4]_3[\text{CrCl}_6]$

Microcrystalline sample of this salt was prepared as follows: A solution of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (0.267 g; 0.001 mol) in ethanol (10 ml) was added to a solution of 2,3,5-(triphenyl)tetrazolium chloride (1.012 g; 0.003 mol) in ethanol (10 ml). After refluxing for 3 hours, and concentration by evaporation a pale green solid, was obtained which was filtered off, washed with acetone and dried in vacuum.

#### $[(\text{C}_6\text{H}_5)_3\text{CN}_4]_3[\text{MCl}_6]$ , (M = $\text{Fe}^{3+}$ , $\text{Ce}^{3+}$ )

These complex salts were synthesized as a solid product by employing the above-described procedure using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{CeCl}_3$  as salts.

#### $[(\text{C}_6\text{H}_5)_3\text{CN}_4]_3[\text{La}(\text{NO}_3)_3\text{Cl}_3]$

Complex salt was synthesized as pale yellow product by employing the above procedure using  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ .

#### $[\text{C}_8\text{H}_{20}\text{N}]_3[\text{MCl}_3\text{I}_3]$ (M = $\text{Cr}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Y}^{3+}$ and $\text{Ce}^{3+}$ )

These complex salts were prepared by mixing 1:3 mole ratio of metal chloride solution (dissolved in minimum amount of ethanol) and tetraethylammonium iodide (in ethanol). The mixture was refluxed for about three hours. The resulting solution was cooled in ice to give a solid product, filtered off, washed with acetone and dried in vacuum.

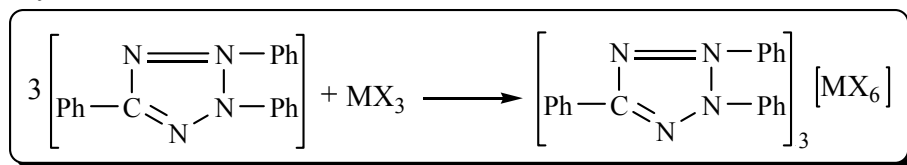
#### $[\text{C}_8\text{H}_2\text{N}]_3[\text{La}(\text{NO}_3)_3\text{I}_3]$

The salt was prepared by employing the above-described procedure using  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ .

## Results and Discussion

The reaction of 2,3,5-(triphenyl) tetrazolium chloride (scheme 1) or tetraethylammonium

iodide with metal salts in ethanol afforded the complex salts in high yields.



(Scheme 1)

(M= Cr<sup>3+</sup>, Fe<sup>3+</sup>, Y<sup>3+</sup>, La<sup>3+</sup> and Ce<sup>3+</sup>; X=Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>)

The complex salts are stable, non hygroscopic, solid. The melting points, colour, metal analyses and conductance measurements are listed in Table 1.

All complex salts are soluble in DMSO, the values of electronic conductances in DMSO (Table 1) were

between (130-230) cm<sup>2</sup>. ohm<sup>-1</sup> indicating 1:3 electrolyte nature as expected<sup>(25,26)</sup>. Infrared spectra of some mixed halides complex salts show bands between (250-310 cm<sup>-1</sup>) due to ν(M-Cl) bands, the assignment of these bands frequencies agreed quite well with those of meta-chloride<sup>(27,28)</sup>.

## Magnetic measurements

The results of the magnetic moment are presented in Table 2. The magnetic moment for Cr (III) complex salt was found to be in range 4.2-4.4 B.M corresponding to high spin octahedral<sup>(29)</sup>. The Fe (III) complex salts have magnetic values of 5.7-5.9 B.M corresponding to high spin octahedral geometry<sup>(30)</sup>. Diamagnetic behaviors of Y (III) and La (III) complex salts was found as expected from their closed-shell electronic configuration and concomitant of unpaired electronic<sup>(30,31)</sup>. The magnetic moment for Ce (III) complex salts was found to be in range 2.4-2.8 B.M due to the presence of unpaired electrons<sup>(31)</sup>.

## Electronic spectra

The electronic absorption spectra of these salts and complex salts

are summarized in Table 2. All complex salts of the present series exhibit a strong spectral absorption band between 30987 and 38971 cm<sup>-1</sup>, which have been attributed to a charge transfer M → L<sup>(33)</sup> and intraligand transition of the type π → π\*<sup>(34,35)</sup>.

The electronic of Cr (III) complex salts show two bands between 15670 cm<sup>-1</sup> and 17720 cm<sup>-1</sup> which assigned to <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub>, and <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub> respectively indicate an octahedral geometry<sup>(36)</sup>. The Fe (III) complex salts show two absorbance bands at 26000 and 28000 cm<sup>-1</sup> due to <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub> (G) (ν<sub>2</sub>) and <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>E<sub>g</sub> (G) (ν<sub>3</sub>) respectively which is agreement with reported octahedral geometry<sup>(30,37)</sup>.

The yttrium (III) and lanthanum (III) complex salts do not show any

significant absorption bands in visible region due to the absences of d-d or f-f transition for these metal ions as expected from their closed-shell electronic configuration<sup>(38,39)</sup>.

The electronic spectra of Ce (III) complex salts show band 18000

and 28000  $\text{cm}^{-1}$  (Table 2). These bands attributed to electron transfer from ground state  $^2F_{5/2}(4f^1)$  or  $^2D_{3/2}$ ,  $5/2(5d^1)$  to the lowest ligands-field components<sup>(40-42)</sup>.

**Table (1): Analytical and characterization data for complex salts**

Compound	M. P °C	colour	Yield %	$\Lambda$ ohm <sup>-1</sup> . cm <sup>2</sup> . mol <sup>-1</sup>	M% Calculated (found)
[CN <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ]Cl	250	White	-	-	-
[C <sub>8</sub> H <sub>20</sub> N]I	230 d	White	-	-	-
[CN <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub> [CrCl <sub>6</sub> ]	100 d	Pale green	82	135	4.4 (4.1) <sup>a</sup>
[CN <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub> [FeCl <sub>6</sub> ]	200	Yellow	94	130	4.7 (4.3) <sup>b</sup>
[CN <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub> [La(NO <sub>3</sub> ) <sub>3</sub> Cl <sub>3</sub> ]	190	Pale yellow	95	145	10.4 (10.1) <sup>b</sup>
[CN <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub> [CeCl <sub>6</sub> ]	140	White	88	210	4.13 (3.8) <sup>c</sup>
[C <sub>8</sub> H <sub>20</sub> N] <sub>3</sub> [CrCl <sub>3</sub> I <sub>3</sub> ]	120	Dark green	80	140	5.6 (5.2) <sup>a</sup>
[C <sub>8</sub> H <sub>20</sub> N] <sub>3</sub> [FeCl <sub>3</sub> I <sub>3</sub> ]	245	Brown	92	150	5.98 (5.62) <sup>b</sup>
[C <sub>8</sub> H <sub>20</sub> N] <sub>3</sub> [YCl <sub>3</sub> I <sub>3</sub> ]	200	Pale orange	97	175	8.93 (8.5) <sup>c</sup>
[C <sub>8</sub> H <sub>20</sub> N] <sub>3</sub> [La(NO <sub>3</sub> ) <sub>3</sub> I <sub>3</sub> ]	275	Pale yellow	93	150	12.9 (12.6) <sup>b</sup>
[C <sub>8</sub> H <sub>20</sub> N] <sub>3</sub> [CeCl <sub>3</sub> I <sub>3</sub> ]	200 d	White	80	230	8.93 (8.5) <sup>b</sup>

a= atomic absorption method

b= EDTA-titration method

c= precipitation method

**Table (2): Selected infrared bands, magnetic measurements and electronic spectral data of the complex salts**

Compound	$\mu_{\text{eff}}$ (B. M)	$\lambda_{\text{max}}$ (cm <sup>-1</sup> )	$\nu(\text{M-Cl})$ cm <sup>-1</sup>
[CN <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ]Cl	-	30169, 32895	
[C <sub>8</sub> H <sub>20</sub> N]I	-	34722, 37879	
[CN <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub> [CrCl <sub>6</sub> ]	4.4	15723, 17720, 30087, 32051	
[CN <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub> [FeCl <sub>6</sub> ]	5.7	26782, 28409, 33557, 35216	
[CN <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub> [La(NO <sub>3</sub> ) <sub>3</sub> Cl <sub>3</sub> ]	Dia	30325, 32532	
[CN <sub>4</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub> [CeCl <sub>6</sub> ]	2.8	18720, 28458, 32752, 34521	
[C <sub>8</sub> H <sub>20</sub> N] <sub>3</sub> [CrCl <sub>3</sub> I <sub>3</sub> ]	4.2	15670, 17201, 31746, 3584	
[C <sub>8</sub> H <sub>20</sub> N] <sub>3</sub> [FeCl <sub>3</sub> I <sub>3</sub> ]	5.9	26812, 28302, 33675, 38972	310
[C <sub>8</sub> H <sub>20</sub> N] <sub>3</sub> [YCl <sub>3</sub> I <sub>3</sub> ]	Dia	34446, 37846	283
[C <sub>8</sub> H <sub>20</sub> N] <sub>3</sub> [La(NO <sub>3</sub> ) <sub>3</sub> I <sub>3</sub> ]	Dia	32154, 38024	
[C <sub>8</sub> H <sub>20</sub> N] <sub>3</sub> [CeCl <sub>3</sub> I <sub>3</sub> ]	2.4	18007, 2325, 31645, 37593	262

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