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Preparation and characterization of some new complex salts of Cr(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions with tetra propyl ammonium iodide

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Abstract

New series of trivalent and divalent metal complex salts with general formula [R]n[M Cl nIn], where R=Tetra propylammonium iodide, M=Cr^{3+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, n=2 or 3 were prepared and characterized by elemental analysis molar conductance, IR, UV/Visible spectra studies and magnetic measurements. These studies, were revealed on octahedral geometry around Cr^{3+} and Fe^{3+} metal ions and tetrahedral geometry around divalent metal ions.

Keywords: *Ionic complex; complex salts; tetra propyl ammonium halides salts*

1. Introduction

Ionic liquids (ILS) are increasingly attracting the attention of inorganic and materials chemists, because they have attractive properties, such as thermal stability, no flammability, high ionic conductivity and wide electrochemical potential windows [1-3]. In fact (ILS) are expected to be applied in various fields, e.g., synthesis of some organic compounds liquid-liquid extraction, separation of metal ions [4,5]. The interest in ionic liquids has increased significantly in recent years in pharmaceutics' and medicine because of their high biological has been a attracting medical scientists and biochemist. The antibacterial effect of quaternary ammonium salts has been known for about century but the production of new compounds, and usage during COVID-19 pandemic [6].

A series of quaternary ammonium salts with general formula $[R—CH_2—N^+]X^-$ and N, N-dipropyl methyl benzyl ammonium ILS were prepared and expected to enhance the biological action, which kill or inhibit the growth of both gram-positive and gram-negative bacteria, and which are effective over rather-wide pH-range [7-9].

Very recently, the complex ionic salt [DIprim][FeCl4], (DIpr=2,6-diisopropylphenyl) which was obtained as crystal and used as recyclable catalysts for crosser-coupling of aryl Grignard reagents with alkyl halides [10].

In this work, the ionic complex salts of some trivalent and divalent of first transition ions with tetra propylammonium iodide were prepared and characterized. These complex salts may be used and studies as biological materials or used for desulfurization of fuels [11].

2. Experimental section:

Materials and methods:

All materials were obtained commercially and used as recived. The complex salts were analyzed for carbon, hydrogen, nitrogen by using Elementer Vario MicroCube. Molar conductance of organic salts and complexes were done at room temperature for 10^{-3}M solution in DMSO using a Jenway 4070 conductivity meters. Electronic absorption spectra of the complexes were recorded on UV-160 spectrophotometer, while the metal content analysis were made by using an AA24OFS Varian instrument for atomic absorption magnetic moment measurements, were carried out at (25° C) on solid state by Faraday's method using Bruker BM6 instrument. IR spectra were recorded on shimadzu uv - 160 spectrophotometer in the range 400-4000 cm-1 using KBr pellets.

The qualitative elemental determination of halogens were done on the sodium fusion solution of mixed halides complex salts [12].

Synthesis of complex salts

The Synthesis complex salt of the formula $[C_{12}H_{28}N]_3[CrCl_3I_3]$

The complex salt was prepared by adding a solution of $CrCl_3.6H_2O$ (0.267 g, 0.001 mol) in ethanol ($10cm^3$) to a solution of tetra propylammonium iodide (0.313g, 0.003 mol) in ethanol (10 cm^3). After reflex for 3 hours to give a dark green solution, concentrated by evaporation to precipitate a solid, which was filtered off, washed with acetone and dried in vacuum.

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The Synthesis of the complex salt $[C_{12}(H_{28}N]_3[FeCl_3I_3]$

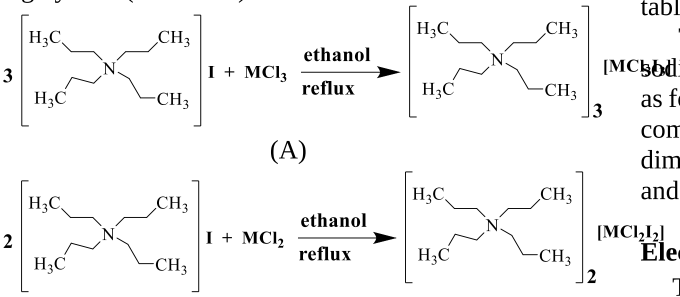
The complex was synthesized as a solid product by employing the above-described procedure using (0.270 g,0.001 mol) of $FeCl_3.6H_2O$.

The Synthesis complex salt $[C_{12}H_{28}N]_2[MCl_2I_2]$ ($M= Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$)

These complex salts were synthesized by mixing 1:2 mole ratio of metal chloride solution (dissolved in a minimum amounted ethanol) and tetra propylammonium iodide in ethanol and followed by the same procedure described above.

Results and discussion:

The reaction of tetra propylammonium iodide with metal chloride salts in ethanol solution were formed in high yields (Scheme 1):



Scheme 1. The synthesiss of the complex salts

(A) Where M = Cr^{3+}or Fe^{+3};**(B)** Where M= Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+},

The complex salts, are stable, non-hydroscopic, coloured solid, the melting points, metal analysis, molar conductance are listed in Table 1.

The values of molar conductance in DMSO for complexes, $[C_{12}H_{28}N]_3[MCl_3I_3]$, $M=Cr^{3+}$ or Fe^{3+} are (120, 108.5) $ohm^{-1}.cm^2\ mole^{-1}$ respectively range suggesting 1:3 electrolytic natures while for complexes of formula $[C_{12}H_{28}N][MCl_2I_2]$ ($M= Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+} , Zn^{2+}) in DMSO solution lies in the range (70.3-97) $ohm^{-1}.cm^2\ mole^{-1}$ are expected for 1:2 electrolyte of these complexes [13].

The metal contents (both theoretically) calculated values and actual values are accordance with the formula $[C_{12}H_{28}N]_3[MCl_3I_3]$ and $[C_{12}H_{28}N][MCl_2I_2]$.

The IR spectra

The positions and values of infrared bands are given in Table (2). The prepared complex salts exhibited two band between (2967-2970 cm^{-1}) and (1462-1469 cm^{-1}) belong to C-H aliphatic group stretching and beading vibrations respectively [14, 15]. ν (N^+–R) shows a band with range (2390-2400 cm^{-1}) [14], these bands of the C-H aliphatic and ν (N^+–R) were shifted in comparison with ligand derived from it. A new band of the prepared complex salts has been observed in the range (343-379 cm^{-1}) indicating (M–Cl) stretching vibration figures (1-4) table (2) [16-17]

The iodide was determinate qualitatively on the sodium fusion solution of mixed halides complex salts as formation of the blue complex with starch [12]. The complex salt of different halogens such as [Bis (1,3-dimethyl) benzotriazole]$_2$ $[CoCl_2I_2]$ has been prepared and structure performed by single crystal X-ray [18]

Electronic spectra and magnetic moment:

The Uv-visible spectra of complexes were recorded as 10^{-3} M solution in DMSO in the range 200-1100 nm and the results are presented in Table 2. The intense band. Between (32051-42372) in the spectrum of ligand is assigned to n→π* transition [19].

The electronic spectra of the Cr^{3+} complex salt in DMSO solution show the main two bands at 15570cm^{-1} and 17720 cm^{-1} assigned to ${}^4A_2(g) \rightarrow {}^4T_2(g)$ and ${}^4A_2(g) \rightarrow {}^4T_1(g)$ respectively indicate an octahedral geometry Fig(5) [20]. Also the value of the magnetic moment (4.41 B.M) is additional evidence for an octahedral structure around Cr^{3+} ion Fig (7A)[21].

Table 1: Physical properties, molar conductance, CHN and metals content of the complex salts

No.	Compound	colour	Melting point ºC	Yield%	Calc. (found) %				ʌ $ohm^{-1}.cm^2$ $mole^{-1}$
					C	H	N	M	
1	$[C_{12}H_{28}N]_3[Cr_3Cl_3I_3]$	Dark green	97 d	70	39.36 (38.92)	7.66 (7.05)	3.82 (3.14)	4.73 (4.04)	120
2	$[C_{12}H_{28}N]_2[MnCl_2I_2]$	Pale yellow	245	98	38.30 (37.78)	7.44 (7.15)	3.72 (3.26)	7.30 (6.97)	91.8
3	$[C_{12}H_{28}N]_3[FeCl_3I_3]$	Brown	98	90	39.22 (38.69)	7.62 (7.18)	3.81 (3.34)	5.07 (4.98)	108.5
4	$[C_{12}H_{28}N]_2[CoCl_2I_2]$	Dark green	260	91	38.09 (37.66)	7.40 (7.32)	3.70 (3.54)	7.79 (7.38)	70.3
5	$[C_{12}H_{28}N]_2[NiCl_2I_2]$	Green	160 d	93	38.11 (38.05)	7.41 (7.22)	3.70 (3.39)	7.76 (7.28)	97
6	$[C_{12}H_{28}N]_2[CuCl_2I_2]$	Brown	242	87	37.86 (36.98)	7.36 (6.92)	3.68 (3.01)	8.35 (8.21)	77.5
7	$[C_{12}H_{28}N]_2[ZnCl_2I_2]$	White	220	95	37.77 (37.16)	7.34 (7.26)	3.67 (3.19)	8.57 (8.28)	76.3

The electronic spectra of Mn(II) complex does not show any transition because it is forbidden due to (Laport rules) [22]. The value of magnetic moment of Mn(II) complex salt was (5.5 B.M), which agrees with tetrahedral geometry [23].

The Fe(III) complex salt show two absorbance bands at 26000 and 28000 cm^{-1} due to $^6A_1(g)\rightarrow{}^4T_2(g)$ (G)(υ2) and $^6A_1(g)\rightarrow{}^4Eg$(υ3) respectively which is in agreement with spin-orbital forbidden transitions of high spin octahedral structure Fig (6) [24,25]. The value of magnetic moment (5.9B.M) also corresponding to high spin octahedral geometry Fig (7A) [25].

The Co (II) complex show d-d transition at 14749cm^{-1} and 16286 cm^{-1} which are assigned to $^4A_2(F)\rightarrow{}^4T_1(F)$(υ2) and $^4A_2(F)\rightarrow{}^4T_2(F)$ respectively [26,27]. The value of magnetic moment (4.2 B.M) is another evidence for a tetrahedral structure of Co(II) ion Fig (7B) [27,28].

Ni(II) complex salt exhibited two bands at 12886cm^{-1} and 27472cm^{-1} and are probably due to the $^3T_1(F)\rightarrow{}^3A_2(F)$ (υ2) and $^3T_1(F)\rightarrow{}^3T_1(P)$ (υ3) transitions of tetrahedral geometry [29]. The magnetic moment value was (3.86 B.M) corresponds for two unpaired electrons and suggests a four coordinate tetrahedral structure [30].

The visible region, the Cu(II) complex exhibits high-intensity band at 22509 cm-1, this result and the value of magnetic moment (1.8 B.M) confirm the tetrahedral geometry around Cu (II), ion [31,32].

he Zn(II) complex salt was found to be diamagnetic as expected and does not give any band in the visible region [33].

Table 2: The magnetic moments, Uv-visible spectroscopy and IR spectra of prepared complex salts

No.	µeff (B.M)	Uv-visible transition λmax(cm^{-1})	Selected IR bands (cm^{-1})		
			υ (N^+–R)	υ (C –H) aliphatic C- str.; (bend)	υ (M–Cl)
Ligand			2500 (w)	2910 (s) ; (1400)(s) 2850 (m)	
1	4.41	15570, 17720, 33783	2499 (w)	2967 (s) ; (1466)(s) 2871 (m)	343
2	5.20	38167	2390 (w)	2968 (s) ; (1467)(s) 2877 (m)	350
3	5.9	26000, 28000, 29585	2397 (w)	2968 (s) ; (1462)(s) 2870 (m)	375
4	4.2	14749, 16286, 39061	2395 (w)	2970 (s) ; (1467)(s) 2877 (m)	360
5	3.86	12886, 27472, 32521	2400 (w)	2968 (s) ; (1469)(s) 2877 (m)	379
6	1.8	22509, 29411	2400 (w)	2969 (s) ; (1465)(s) 2870 (m)	360
7	dia	32971	2395 (w)	2970 (s) ; (1465)(s) 2877 (m)	372

w= weak. m= medium. s= strong

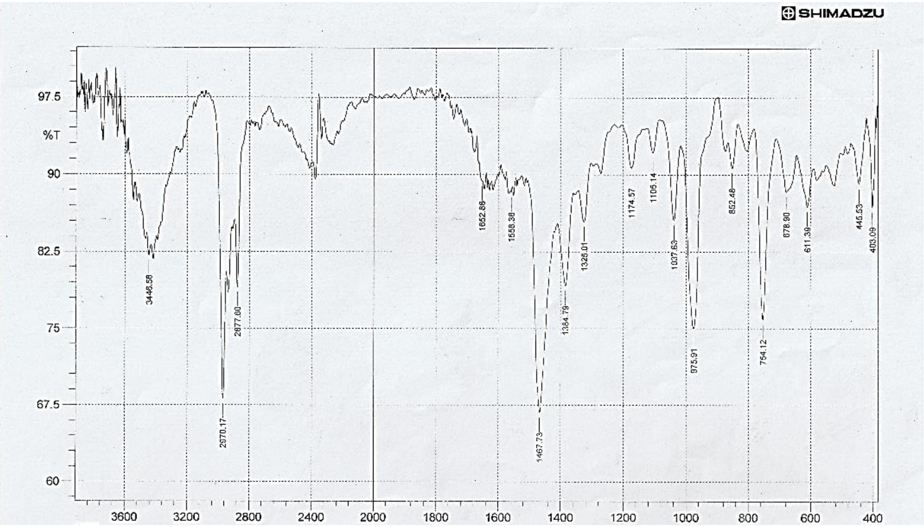


Fig. 1. IR spectra for $[C_{12}H_{28}N]_2[CoCl_2I_2]$ complex salt

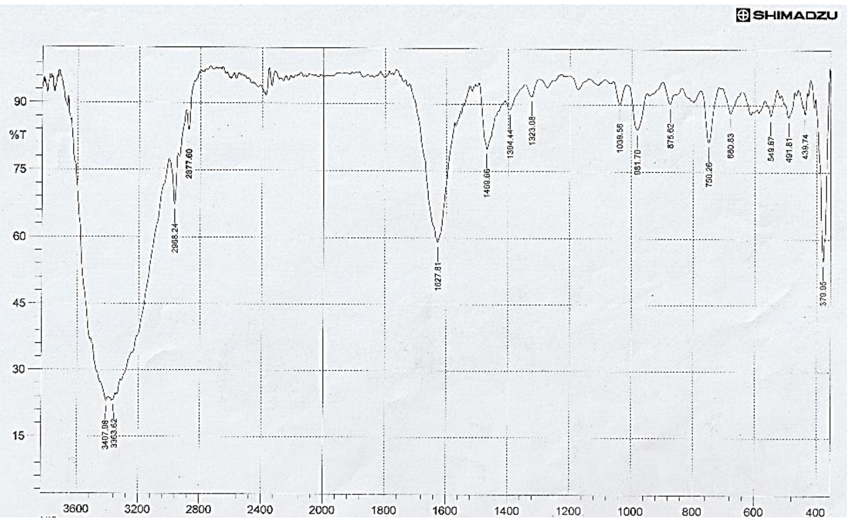


Fig. 2. IR spectra for $[C_{12}H_{28}N]_2[NiCl_2I_2]$ complex

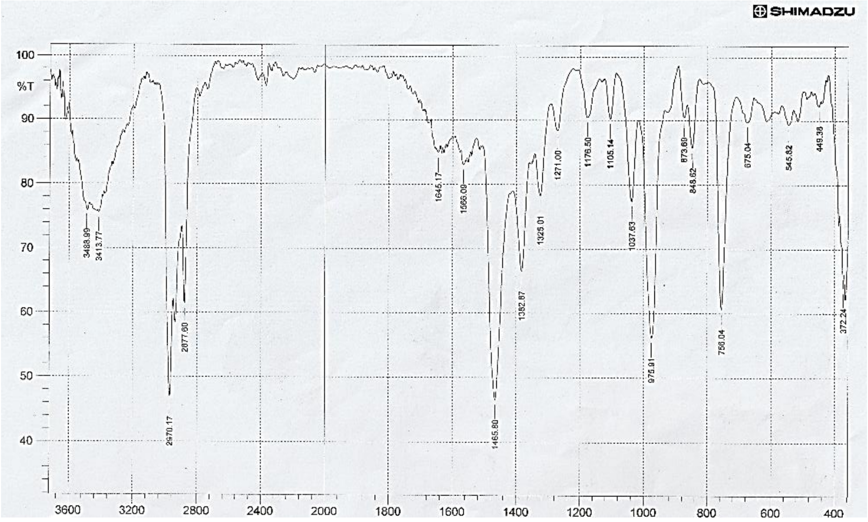


Fig. 3. IR spectra for $[C_{12}H_{28}N]_2[ZnCl_2I_2]$ complex

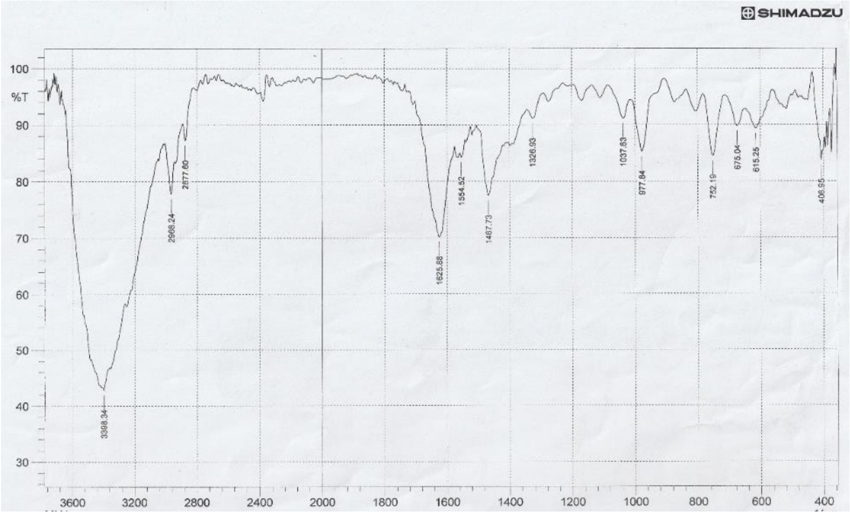


Fig. 4. IR spectra for $[C_{12}H_{28}N]_2[MnCl_2I_2]$ complex

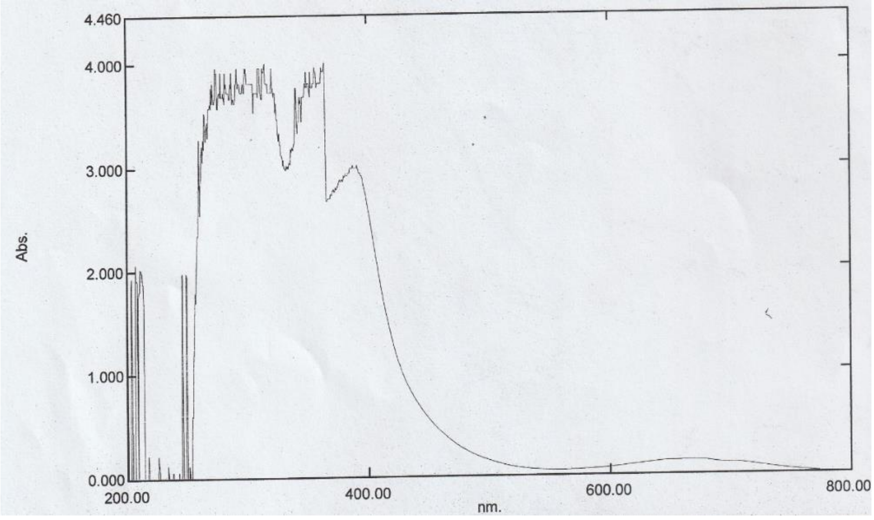


Fig. 5. UV. visible spectra for $[C_{12}H_{28}N]_3[CrCl_3I_3]$ complex salt

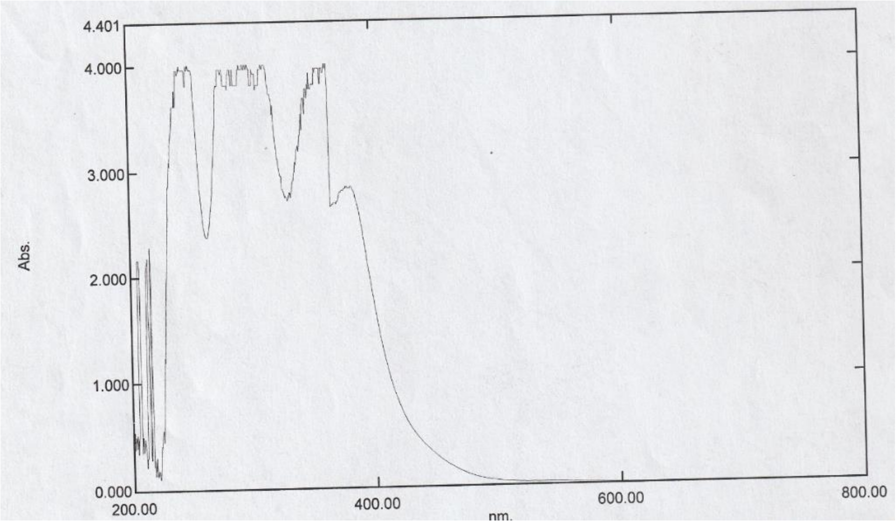
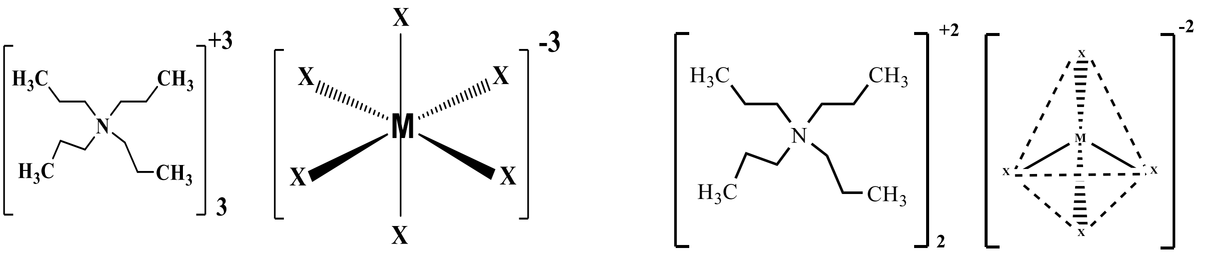


Fig. 6. UV. visible spectra for $[C_{12}H_{28}N]_3[FeCl_3I_3]$ complex salt



(A) suggested geometry for [tetra propyl ammonium]$_3$ $[MCl_3I_3]$ complex
M= Cr^{+3} or Fe^{+3} X= Cl or I

(B) suggested geometry for [tetra propyl ammonium]$_2$ $[MCl_2I_2]$ complex
M= Mn^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} X= Cl or I

Fig. 7. Geometry of octahedral and tetrahedral M^{3+} and M^{2+} metal ions.

Conclusion

In this work, we reported, the preparation, spectral identification, analytical data and magnetic studies of ionic complex of Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} Based on the data of the infrared Uv-vis. Spectroscopy of the prepared complex salts, as well as other technique such as precise analysis of elements (C. H. N), measurement, and the ratio of metal from atomic absorption Spectroscopy and magnetic moment. The structures of the prepared complex salts may be proposed as octahedral geometry around trivalent and tetrahedral around divalent metal ions.

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