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Synthesis and Characterization of some complex salts of Ti(III) and VO(V) chlorides with pyrrolium , imidazolium , indolium and their benzyl derivative

N.H.Buttrus[1*] , T.J.Mohamad[2] and I.A.Saeed[3]
1 - Chem. Dept. College of Science, Mosul University
2 - Chem. Dept .College of Science, Dohouk University
3 – College of Nursing, Mosul University

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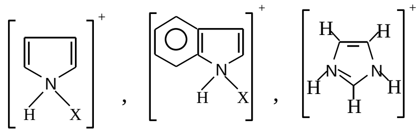
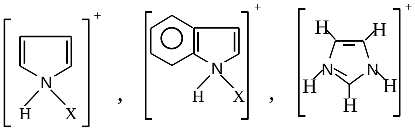
الملخص

يتضمن البحث تحضير أملاح معقدة جديدة والتي تحمل الصيغ العامة $A_2[VOCl_5]$ و $A_3[TiCl_6]$ عندما A =  و X = H أو CH_2Ph ، وذلك من خلال مفاعلة الأملاح العضوية مع كلوريد الفلزات بنسب مولية (3:1) أو (2:1) . تم تشخيص الأملاح المعقدة بالتحليل الدقيق للعناصر، قياسات التوصلية ، قياسات أطياف الأشعة تحت الحمراء وفوق البنفسجية وكذلك القياسات المغناطيسية ومن الدراسات أعلاه بينت الأملاح المعقدة موصلة بنسبة (1:2) وامتلكت الايونات الفلزية VO (V) وTi(III) في الايونات السالبة للأملاح المعقدة هيئة سداسية التناسق.

Abstract

New complexes salts of $A_2[VOCl_5]$ and $A_3[TiCl_6]$,where A =  , X = H or CH_2Ph, were prepared by treatment of above organic salts with metal chloride in (3:1) or (2:1) molar ratio. The new complex salts were characterized by microelemental analysis, conductivity measurements, spectroscopic data (IR and U.V/Visible) as well as the magnetic measurements. These studies confirm that the complex salts are 2:1 electrolytes and the VO (V) or Ti(III) in the anionic moiety of the complex salts achieve octahedral environment.

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[*] Correspondance auother

Introduction:

Certain molten salt mixtures of aluminum chloride and alkyl pyridinium halides are liquid at ambient temperatures, the broad compositional range, thereby providing unusual ionic solvents for studies of acid-base chemistry, ion complication, electrochemically generated organic compounds[1-4].

The reaction of 1-n-butyl-3-methylimidazolium chloride (BMI.Cl) with sodium tetrafluoroborate or sodium hexafluoroborate affords the molten salts BMI.X (1)X=BF_4 and (2)X=PF_6. Compounds 1 and 2 are viscous liquids within a wide range of temperature (192K). IR,^{1}H NMR, density ,viscosity and conductivity measurements suggest that compound (2) behaves quasi-molecular . Compound (1) is quasi-molecular below 279K, but at higher temperature is probably composed imidazolium and BF_4 ions in an extended by hydrogen bonded network [5].

New ionic bimetallic complexes of the type $[Cu(en)_2][MCl_4]$, where M=Cu^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2}, were prepared by reacting bis (ethylene diamine) copper(II) dichloride with copper ,zinc, cadmium and mercury dichloride in absolute alcohol. Physical, spectroscopic data (IR,U.V-vis and EPR) conductivity and magnetic measurements confirm that the compounds are 2:2 electrolytes in MeOH and the metal ions in the anionic moiety of the complexes achieve their usual tetrahedral environment[6].

A new class of compounds were prepared from mixtures of metal halide and organoamine such as $[Ni(en)_3][CdBr_4]$, $[Ni(bpy)_3][CdCl_4]$ and $[Ni(bpy)_2(H_2O)_2][CdBr_4]$, were en=ethylendiamine , bpy=2,2´-bipyrridyl, the above complex salts where characterized physicochemically and their structures were determined by using x-ray crystallographically were reported by Chestnut et al.[7].

A novel mixed valence complex salts of the type $[Ni(phen)_3]_2$, $[Ni(mnt)_2]_3$.2DMF, where phen=1,10-phenanthroline ,mnt= 1,2-dicyno-vinylene-1,2-ditholate, DMF=N,N´-dimethylformamide were prepared and its structure was determined by x-ray diffraction by single crystals. Its crystal structure consist of two different types of $[Ni(mnt)_2]$ units ; $[Ni(mnt)_2]^-$ and $[Ni(mnt)_2]^{-2}$ [8].

The synthesis of new bimetallic complex salts by halide/sulfur chelate cross transfer was reported by Exarchas et al.[9].The structures of the prepared complex salts $[Ni(S_2CNEt_2)(dppe)]_2[HgBr_4]$, $[Pt(S_2CNEt_2)(dppe)]_2[CdCl_4]$, $[Pt(S_2CNEt_2)(dppe)]_2[VOCl_4]$ and $[Pd(S_2CNBu^n{}_2)(bipy)]$ $[CdCl_4]$ were carried out using x-ray diffraction by single crystals.

In view of these interesting results and as a continuation of our comprehensive studies on transition and non transition complex salts[10-12] we have prepared new complex salts of VO^{+3} and Ti^{+3} metal ions with pyrrolium indolium and imidazolium salts and their derivatives with benzyl chloride.

Experimental:

General: All reagent used were of chemically pure or analytical grade .All preparative work were carried out under nitrogen using standard Schlenk tube technique. IR spectra were recorded on a Perkin Elmer 580B IR spectrophotometer in the 4000-200 cm^{-1} range using CsI discs. Elemental analysis were carried out on a CHN analyzer model type 1106 (Carlo Erba). The metal content were determined spectrophotometrically using Shimdza spectrophotometer AA670. Conductivity measurements were made on 10^{-3}M solutions of the complex salts in DMSO at room temperature using conductivity meter model PCM3-Jenway. Electronic spectra were recorded an a Shimadzu UV-Vis. Spectrophotometer UV-160 for 10^{-3}M solutions of the complex salt in DMSO at room temperature (25ºC) using (1 cm) quartz cell. Magnetic measurements were carried out at 25ºC by the Faraday’s method the solid complex salts in a Pyrex tube using Burker BM6 instrument.

Preparation of organic salts:

2-Benzyl pyrrolium chloride:(2-bpyc).

To a solution of benzyl chloride (1.26g,0.01 mol) in ethanol (10 cm^3) was added a solution of (0.67g,0.01 mol) pyrrole in ethanol (10 cm^3) with stirring, the addition was continued for 30 min., and the reaction mixture was refluxed for 2h. The mixture was left 24h., at room temperature to give brown precipitate, which was filtered off, washed twice with ethanol (10 cm^3) ,then dried under vacuum for 3h.

The 2-benzyl indolium chloride was prepared using similar method

Preparation of the complex salts:

They were prepared by using the following methods.

1- Direct method

Preparation of $[Py]_3[TiCl_6]$

A solution of $TiCl_3$ (0.15g,0.001 mol) in ethanol (10 cm^3) was added to a stirred of pyrrole (0.18g,0.001 mol) in ethanol (10 cm^3). To this mixture concentrated HCl was added drop wise with stirring until the pH of the solution became (2.5-3.0) the mixture was left with stirring for 2h. Then left for 3 days. The solid thus formed, was filtered off, washed with ethanol ,diethylether and dried under vacuum for 3h.

The rest of the complex salts were prepared using the above procedure

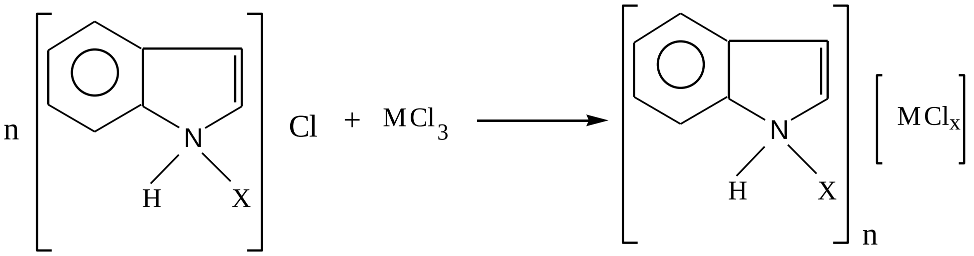
2- Preparation of $(2\text{-bpyc})_3[TiCl_6]$

The salt $TiCl_3$ (0.15g,0.001 mol) was dissolve in ethanol (10 cm^3) , the resulting solution was added slowly with stirring to a solution of the salt 2-benzylpyrrolium chloride (0.53g,0.03 mol) in methyl chloride (10 cm^3). The mixture was refluxed for 2h. then the solution was allowed to cool to room temperature. The solid thus formed, was filtered off, washed with ethanol (10 cm^3) diethylether (10 cm^3) and dried under vacuum for 3h.

The rest of the complex salts of the general formula $[2\text{-bic}]_3[TiCl_6]$,$(2\text{-bpyc})_2[VOCl_5]$,$(bic)_2[VOCl_5]$ were prepared using similar procedure, were bpyc = 2-benzylpyrrolium chloride, bic= 2-benzyl indolium chloride.

Results and discussion:

The reaction of pyrrolium, imidazolium, indolium chloride , 2-benzyl pyrrolium chloride or 2-benzyl indolium chloride with $TiCl_3$ or $VOCl_3$ in 1:2 or 1:3 molar ratio in ethanol afforded after 3 days the complex salts in high yield as in the following equation



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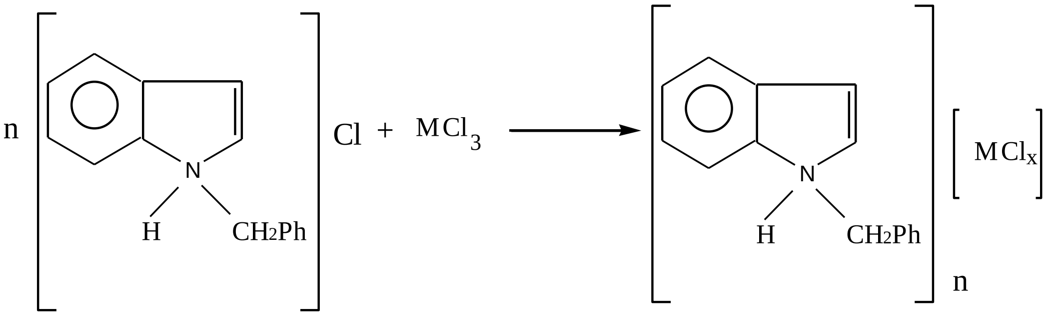

........(2)

n= 3 , X= 6 M=Ti
n= 2 , X= 5 M=VO

The complex salts are microcrystalline solids, quit stable in solid and solution state. They are insoluble in most of the organic solvent except for dimethylsulfoxide (DMSO). The physical properties of the complex salts are tabulated in Table 1.

It is interesting to note that the conductivities of the molten salts are significantly lower than those observed for the 1-n-butyl-3-methyl imidazolium tetrachloroaluminate[13]. This indicates that the interaction between the anion and cation in organoaluminate molten salt is essentially electrostatic, contrarily, a strong interaction between anions and cations the organic salts.

The conductance data (Table 1) show that the complex salts are 2:1 electrolytes. The conductivities of the complex salts are also significantly higher than those observed for pyridinium trans-bis(pyridine) tetrarchloro ruthenate (III)[14]. This indicates that the interaction between the cantions and the anions is essentially electrostatic with small contribution of hydrogen bonds[13].

The frequencies (cm^{-1}) of the most relevant absorption bands in the IR spectra of organic and the complex salts and their tentative assignments are presented in Table 2. The spectra of organic salts show a bands at 2560-2600 and 1625-1630 cm^{-1} due to $\upsilon(NH^+)$[15] and $\upsilon(C=N)$[16] respectively.

The spectra of the complex salts also reveals the presence of the above bands at same positions as well as the presence of a new bands at 300-350 cm^{-1}, which was assigned to $\upsilon(M–Cl)$.

The IR spectra of vanadyl complex salts showed a strong absorption band in the range 975-990 cm^{-1} which assigned to $\upsilon(V–O)$ stretching frequency[17].

The electronic spectra of the studied complex salts are complicated, exhibiting a number of overlapping intense bands in the ultraviolet and visible region. The tentative assignments of the absorption bands from electronic spectra of the complex salts are reported in Table 2. The broad band observed in the range 30100-32000 cm^{-1} have been due to $n - \pi^*$ or $\pi - \pi^*$ transitions of the organic salts, while the new additional bands were observed at the 28000-29000 cm^{-1} which may correspond ligand to metal charge transfer , suggested hexacoordinate structure for vanadyl complexes salts[18]. Titanium (III) belongs to d^1 and has one electron in the outer orbital. Ti^{+3} complex salts show magnetic moments of 1.83-1.87 B.M at room temperature. Further, the electronic spectra of these complex salts positively affirm the presence of octahedral geometry[19]. One d–d spin allowed transition are expected corresponding to the transitions from lower lying d-levels to the empty dx^2-y^2 orbitals . The ground state is $^2T_2(g)$ and the excited state $^2E_2(g)$. The electronic spectral bands (Table 2) appearing at 14000-20000 cm^{-1} in the present complex salts. Other electronic spectral bands appearing at ~ 30000 cm^{-1} are due to charge transfer.

Table 1: Analytical and conductance data for the organic and complex salts

No.	Complex	Colour	m.p (ºc)	Analysis** % found (calc.)			Λ ohm^{1}.cm^{2}. mol^{-1}	M_{eff} (B.M)
				C	H	N		
	(2bpyc)	dark brown	180*	46.78 (47.13)	4.41 (4.28)	4.67 (4.99)	68.1	---
1	$(2bpyc)_2[VOCl_5]$	brown	200	68.20 (68.21)	6.18 (6.20)	7.20 (7.24)	38	---
2	$(2bpyc)_3[TiCl_6]$	black	240	53.81 (53.87)	4.82 (4.89)	5.70 (5.71)	95	1.83
	(2binc)		115	73.90 (73.92)	5.72 (5.75)	5.73 (5.75)	45	---
3	$(2binc)_2[VOCl_5]$	black	89	54.33 (54.54)	4.09 (4.24)	4.09 (4.24)	79.3	---
4	$(2binc)_3[TiCl_6]$	black	140	61.00 (61.02)	4.71 (4.74)	4.72 (4.74)	110	1.86
5	$(Py)_2[VOCl_5]$	black	220*	23.95 (24.20)	3.04 (3.15)	7.09 (7.36)	80	---
6	$(Py)_3[TiCl_6]$	dark violet	260*	30.89 (30.96)	3.85 (3.87)	9.01 (9.03)	120	1.85
7	$(Im)_2[VOCl_5]$	black	170	18.65 (18.84)	2.59 (2.61)	14.29 (14.65)	87	---
8	$(Im)_3[TiCl_6]$	black	200	23.00 (23.08)	3.15 (3.20)	17.88 (17.94)	115	1.83
9	$(In)_2[VOCl_5]$	brown	115*	39.66 (39.98)	3.38 (3.33)	5.67 (5.83)	76	---
10	$(In)_3[TiCl_6]$	dark violet	150*	46.72 (46.83)	3.85 (3.90)	6.79 (6.83)	112	1.87

Py = Pyrrelium , Im= Imidazolium , In = Indolium

** CHN were carried out using Carlo Erba (C.E 1100) in Germany by Prof.Dr.T.K.AL-Allaf.

* de composition temperature

Table 2: IR absorption (cm^{-1}) and electronic and infrared spectral bands of the complexes and adducts

No.	Complex	IR bands (cm^{-1})				U.V/Visible band maxima in (cm^{-1})
		$\upsilon(NH)^+$	υ(C = N)	υ(M–Cl)	υ(VO)	
	(2bpyc)	$2560_{(S)}$	$1630_{(S)}$	---	---	32080
1	$(2bpyc)_2[VOCl_5]$	$2550_{(S)}$	$1625_{(S)}$	$300_{(m)}$	990	28100,28500
2	$(2bpyc)_3[TiCl_6]$	$2560_{(S)}$	$1630_{(S)}$	$320_{(m)}$	---	14060,29300
	(2binc)	$2600_{(S)}$	$1625_{(S)}$	---	---	30100
3	$(2binc)_2[VOCl_5]$	$2590_{(S)}$	$1620_{(S)}$	300,386	980	29000
4	(2bi ethanol nc)$_3[TiCl_6]$	$2595_{(S)}$	$1624_{(S)}$	$300_{(m)}$,$340_{(m)}$	---	14900,20000,28000
5	$(Py)_2[VOCl_5]$	$2555_{(S)}$	$1628_{(S)}$	310,330	975	28700,31000
6	$(Py)_3[TiCl_6]$	$2560_{(S)}$	$1625_{(S)}$	310,340	---	14000,28100
7	$(Im)_2[VOCl_5]$	$2600_{(S)}$	$1620_{(S)}$	300,330	990	28800,30500
8	$(Im)_3[TiCl_6]$	$2600_{(S)}$	$1625_{(S)}$	320	---	14900,19000,29000
9	$(In)_2[VOCl_5]$	$2550_{(S)}$	$1620_{(S)}$	320,350	983	28000,30666
10	$(In)_3[TiCl_6]$	$2580_{(S)}$	$1625_{(S)}$	300,350	---	14000,2000,31000

s= strong, m = medium

References

1- J.Robinson and R.A.Osteryoung, J.Am.Chem.Soc.,101,323(1979).

2- R.J.Gale, B.Gilbert and R.A.Osteryoung ,Inorg.Chem., 18, 2725, (1979).

3- T.M.Laher and C.L.Hussey,Inorg.Chem.21,4079,(1982).

4- P.Koronaios and R.A.Osteryoung,J.Electro.Soc.147,(9),3414,(2000).

5- P.A.Z.Suarez,S.Einloft,J.EL.Dullius,R.F.de Souza and J.Dupont.J. Chim. Phys., 95,1626,(1998).

6- F.M.A.Aqra, S.A.Shah, S.Tabassum and R.M.A.Jamhour,Trans.Met. Chem.,20,123,(1995).

7- D.J.Chesnut, R.C.Haushalter and J.Zubieta.Inorg.Chim.Acta, 292,41, (1991).

8- C.Wang,Z.Peng,W.Guo,Z.Yunhong and G.Cheng,J.Molecul. Structu., 702,1,(2004).

9- G.Exarchos,S.D.Robinson and J.W.Steed, Polyhedron,20 (24),2951, (2001).

10- N.H.Buttrus,I.A.Saeed and T.J.Mohamed,J.Edu.Sci.,15(1),11,(2003).

11- N. H. Buttrus, I. A. Saeed and S. A. AL-Joboi , Jordan J.Appl.Sci. Accepted, (2006).

12- N.H.Buttrus,I.A.Saeed ,J.Edu.Sci.,17(1),1,(2005).

13- A.A.Fannin, D.A.Floreani, L.A.King, J.S.Landers, B.J.Piersm, R.L. Vanghn, J.S.Wikes and J.L.Williams,J.Phys.Chem.,88,2614,(1984).

14- A.A.Batista,S.A.Onofre,S.L.Queiroz,G.Oliva,M.R.M.Fontes and O. R. Nascimento,J.Braz,Chem.Soc.,8(6),641,(1997).

15- K.Nakanishi "Infrared Absorption Spectroscopy", 1st Ed., Japan, (1962).

16- H.A.Bayoumi, E.M.Shouky and M.M.Mostafa, Synth.React.Inorg. Met-Org. Chem.,31, 579,(2001).

17- N.H.Buttrus, F.H.Awad,Raf.Jour.Sci.,15(2),133,(2004).

18- N.S.Biradar and T.R.Goudav,J.Inorg.Nucl.Chem.,39,358,(1977).

19- R.Ameis,S.Kremor and D.Reinen,Inorg.Chem.,24,2751,(1985).