

Synthesis and Characterization of Mn^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} Complexes with Pyridinium Salt. Crystal Structure of 1,3, 5- Trimethylpyridinium Iodide

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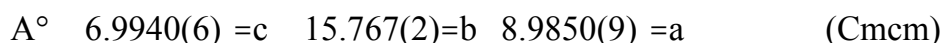
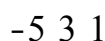
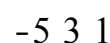
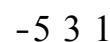
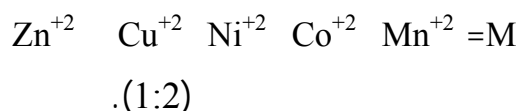
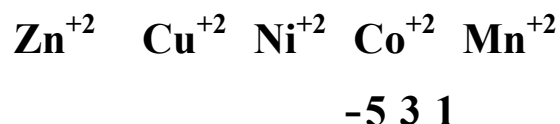
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ABSTRACT

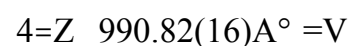
A series of new complex salts of the type $[A]_2[MCl_2I_2]$ where $A=1,3,5$ -trimethylpyridinium cation, $M= Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}$ and Zn^{+2} were prepared by the reaction of the metal chloride and 1,3,5-trimethylpyridinium iodide in (1:2) molar ratio and characterized by elemental analysis, molar conductance, IR, Uv/Vis., spectral studies and magnetic measurements. The crystal structure of 1,3,5-trimethylpyridinium iodide was determined by single crystal x-ray crystallography.

The structure of the anion part and a 1,3,5- trimethylpyridinium cation which crystallizes in the orthorhombic space group (Cmcm) with $a=8.9850(9)$, $b=15.767(2)$, $c=6.9940(6)A^\circ$, $V=990.82 (16)A^\circ$, $Z=4$. Which is on a crystallographic mirror plane perpendicular to C-axis except for methyl hydrogen atoms. The anion and cation are connected through hydrogen bonds between I and the cation by hydrogen bonding, electrostatic interaction and weak π - π interaction are also expected.

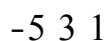
Keywords: Pyridinium Salt, Crystal Structure of 1,3,5-Trimethylpyridinium Iodide.



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$\pi-\pi$



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INTRODUCTION

Considerable interest has also been shown over recently years in the transition metal halide complexes, and a among them tetrahalometalates with various organic counter cations have been subject of theoretical (Navaro *et al.*, 2009), structural (Lozano *et al.*, 2004) magneto-structural (Luque *et al.*, 2002 ; Mazotto *et al.*, 2001) and spectroscopic studies (Luque *et al.*, 1997 ; Hitchman and Cassidy 1979).

The preparation, crystal structure and solid-state properties of four tetrabromocuprate(II) salts using pyridinium and n-methylpyridinium (n=2-,3- and -4-) as counter ions were carried out as a part of studies on hybride organic/ inorganic material based copper (II) halides, in which they show the influence of the organic cation(size, shape and position of the substituent) on the packing interactions that governed the crystal organization (Luque *et al.*, 2001 ; Sertucta and Luque, 1998).

The design and synthesis of copper (II) bromides constitutes to receive much attention owing to their applications in fundamental and applied science, ranging from solid-state physics to bioinorganic chemistry.

A novel pyridinium salt, 2,4-bis[p-(N,N-dimethylamino) styryl]-N-methylpyridinium bromide was synthesized and characterized by TG, ¹HNMR spectroscopy and x-ray crystallography, and the reaction process was studied by using Es-Ms by Hao *et al.*, (2004), they showed that the salt have large two photon absorption.

The nickel and platinum complexes $[MX_2(dppe)]$ ($X=Cl, Br$) ($dppe$ =diphenyl phosphinoethane) react with bi- and tri-valent metal diethylditiocarbamates $[M'(S_2CNET_2)_n]$, ($M'=Pb, Zn, Hg, Ni, n=2, M'=Co, Fe, Mn, n=3$) to afford the salts $[M(S_2(NEt_2)_2dppe)][M'X_4]$ was studied by Exarchos *et al.*, (2001). The salts have been fully characterized by physicochemical properties and x-ray crystallography.

The salts $[MeEtim]_2[MCl_4]$, $[MeEtim]^+$ =1-methyl-3-ethyl imidazolium, $M=Mn, Co$ or Ni) are shown by EXAES to dissolve in basic $[MeEtim]Cl \cdot AlCl_3$ ionic liquid to yield four coordinate $[MCl_4]^{-2}$, and dissolve in acidic $[MeEtim]Cl \cdot AlCl_3$ ionic liquids to yield six coordinate $[M(AlCl_3)_3]^-$ anion (Dent *et al.*, 1990).

Kim *et al.*, (2003) prepared and used the $[RMIM][ZnX_2Y_2]$ ionic liquid system ($R=Me, Et, n-Bu, benzyl, X=Y=Cl$ or Br or $X=Cl, Y=Br$) for the coupling reaction of CO_2 and ethylene or propylene oxide to produce cyclic carbonate. Crystal structure of $[(M)_2IM][ZnBr_2Cl_2]$ $\{(M)=2$ dimethyl $\}$ showed that two imidazolium cations were paired with $[ZnBr_2Cl_2]$.

As a part of an on-going investigation of these metallate salts, we have prepared and studied the properties of 1,3,5-trimethylpyridinium dichlorodiodo metallate (II) salts $(C_8H_{12}N)_2[MI_2Cl_2]$, $M=Mn^{+2}, Co^{+2}, Ni^{+2}$, and Zn^{+2} . Also, the crystal structure of 1,3,5-trimethylpyridinium iodide was determined by x-ray crystallography.

EXPERIMENTAL

All starting materials were obtained commercially and used as received. The solvent were dried by allowing them to stand over $3A^\circ$ molecular sieves overnight. The preparation was carried out under nitrogen atmosphere. Elemental analysis (C,H,N) was performed on a Carlo Erba 1106 analyzer. Metal content analyses were made on Shimadzu AA670 atomic absorption spectrophotometer. IR spectra were recorded on an Infrared spectrophotometer bruker (Tensor 27) in the $200-4000cm^{-1}$ range using CsI discs. Electronic spectra were recorded on a Simadzu UV 160 spectrophotometer using dimethylsulfoxide (DMSO) for 10^{-3} M solution of complexes. Conductivity measurements were made on 10^{-3} M solution of the ionic salt in DMF at room temperature using a conductivity meter model PCM3-Jenway. Magnetic measurements were recorded on a Bruker BM6 instrument at $25^\circ C$ following Faraday method.

SYNTHESIS

1,3,5-trimethylpyridinium iodide

3,5-Dimethylpyridine (2.14 g, 0.02 mol) was dissolved in 10 ml of ethanol, then methyl iodide (4.32 ml, 0.03 mol) was added dropwise into the solution. The mixture was heated to reflux at $80^\circ C$ for one hour to give yellow crystals (m.p $280^\circ C$). Calc. for $C_8H_{12}NI$, C= 38.55, H= 4.85, N= 5.62 ; Found C = 38.53, H= 4.80, N=5.61.

Preparation of $[C_8H_{12}N]_2[MnCl_2I_2]$

A solution of (0.20 g, 1.0 mmol) of $MnCl_2 \cdot 4H_2O$ in ethanol 10 ml was added to a solution of (0.5 g, 2 mmol) of 1,3,5-trimethylpyridinium iodide in ethanol 10 ml. After heating under reflux for 3 hrs., it gives an orange solution, concentration under reduced pressure leads to orange solid, m.p= $85^\circ C$ (Found; C, 30.67 H, 3.82, N, 4.45 Mn, 8.73, Cacl. For $C_{16}H_{24}N_2Cl_2I_2Mn$; C,30.69; H,3.84 N,4.47, Mn, 8.77%, conductivity $162 \Lambda_M ohm^{-1} cm^2 mol^{-1}$.

[C₈H₁₂N]₂[CoCl₂I₂]

This complex was synthesized as a microcrystalline green product employing the above described procedure; m.p= 122°C, (Found C,30.47 H,3.79 N,4.44 Co,9.31, Calc. for C₁₆H₂₄N₂Cl₂Co; C,30.50 H,3.81 N,4.44 Co,9.35, conductivity 169 $\Lambda_M \text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

[C₈H₁₂N]₂[NiCl₂I₂]

This complex was synthesized as dark brown product employing the above described method m.p=150°C (Found C, 30.58, H,3.87, N,4.43, Ni,9.34 Calc. for C₁₆H₂₄N₂Cl₂I₂Ni C,30.60, H,3.89, N,4.46, Ni,9.36. conductivity 164 $\Lambda_M \text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

[C₈H₁₂N]₂[CuCl₂I₂]

The preparation was essentially the same as above and obtained as brown solid, m.p=142°C(Found C,30.10 H,3.75, N,4.37, Cu,9.94 Calc. for C₁₆H₂₄N₂Cl₂I₂Cu C,30.13, H,3.76, N,4.39,Cu,9.96, conductivity 170 $\Lambda_M \text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

[C₈H₁₂N]₂[ZnCl₂I₂]

This complex salt was prepared as orange solid using similar procedure as above, m.p. 119°C; Found C,30.25, H,3.76, N,4.40, Zn,10.29, Calc. for C₁₆H₂₄N₂Cl₂I₂Zn C,30.28, H,3.78, N,4.41, Zn,10.31, conductivity 168 $\Lambda_M \text{ohm}^{-1} \text{cm}^{-1}$.

Crystallography

A yellow block specimen crystal (0.24x0.2x0.17 mm³) was mounted on the RIGAKU R-Axis PAPIDIP camera. The diffraction data was measured at 169(2)K using Moka X-ray ($\lambda=0.71073\text{\AA}$). The crystal structure was solved by direct methods (SHELEX-97 (Sheldrick, 2008) and refined by full-matrix least-squares (SHELEX-97 (Sheldrick, 2008) with anisotropic temperature factors. Hydrogen atoms were located by geometrical calculations and included in the calculation using riding atom model. Crystallographic data and geometrical parameter are listed on Table 1 and 2, respectively.

RESULTS AND DISCUSSION

The reaction steps leading to the formation of complex salts are shown in Fig. 1.

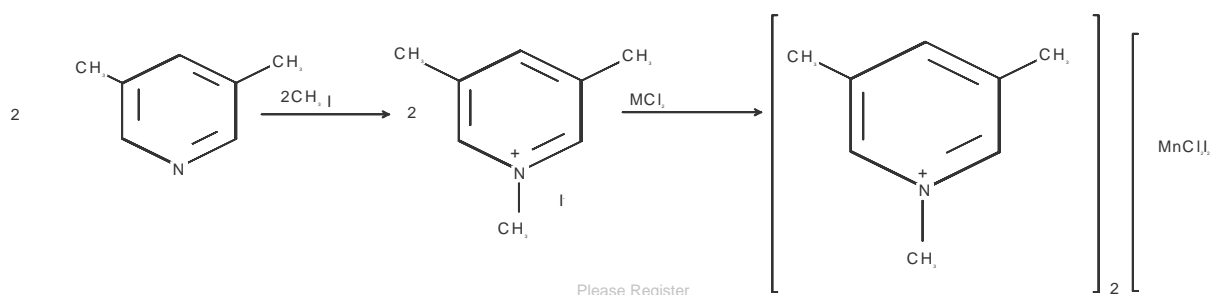


Fig. 1: The steps of reaction to prepare the complex salt.

The complex salts are stable, non hydroscopic and most of them are dark colored solids (Table 7). The conductance data show that the complex salts are 2:1 electrolyte (Geary, 1971). The conductivity of the complex salts are significantly higher than those observed for 1-n-butyl-3-methyl imidazolium tetrachloroaluminate (Fannin *et al.*, 1984). This indicates that the interaction between the anion and cation is essentially electrostatic.

Infrared spectra

The assignment of the IR spectra of the organic salt shows band at 2565 cm^{-1} which is assigned to $\nu(\text{N-CH}_3)^+$ (Nakanishi, 1962). The spectra of the complex salts also reveal the presence of the above band at similar position as well as the presence of new band observed at 310 cm^{-1} and 243 cm^{-1} which was assigned to $\nu(\text{M-Cl})$ and $\nu(\text{M-I})$ (Clark and Williams, 1965), respectively as shown in Table 8.

Magnetic measurements

The results of the magnetic measurements are reported. The magnetic moment of Mn complex salts was found to be 5.30 B.M. corresponding to high spin tetrahedral Mn(II) complex salt (Harriman, 1979). The Co(II) complex salt has magnetic moment value of 4.00 B.M corresponding to high spin tetrahedral Co(II) complex salt (Kavara *et al.*, 2008). The magnetic moment of Ni(II) was found to be 3.32 B.M suggest the presence of two unpaired electrons, which correspond to tetrahedral geometry. The magnetic moment of Cu(II) complex salts has been found to be 2.00 B.M which is in agreement with distorted tetrahedral Cu(II) geometry.

Electronic spectra

The UV/Vis (Table 8) spectra of the complex salts are quite similar showing strong band at 276 nm which correspond to $\pi \rightarrow \pi^*$ transition at the pyridinium cation. The manganese (II) complex salt show band 350 nm associated with ligand to metal charge transfer transition.

The Co(II) complex shows a band observed in the visible region 675 nm, generally considered to correspond to a transition ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$. The position of this band suggests a tetrahedral geometry. The nickel complex shows a band at 710 nm due to the transition for ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ in tetrahedral geometry. The copper complex shows the presence of a band at 790 nm which correspond to the transition ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ which is consistent with distorted tetrahedral geometry.

Crystal structure

The molecular structure of the 1,3,5-trimethylpyridinium iodide is shown in Fig. 2. together with atom numbering scheme. Fractional coordinate for atomic positions with e.s.d.s are given in (Table 2). Hydrogen atoms have the same number as the carbon to which they are attached (Table 5). Details of the geometry of the molecular symmetry are listed in (Table 3). Torsion angles are given in (Table 6). Thermal parameters are listed in Table 4. Only one crystal structure report for 1,3,5-trimethylpyridinium cation without disorder is known in the Cambridge structural Data base (Allen, 2002). The geometry of the pyridinium cation is in a good agreement with the known structure at 150k (Modoc *et al.*, 2005) in which the N-Me length of $1.483(3)\text{ \AA}$ which are comparable well with our

structure 1.493(6)Å°, indicating there is no orientational disorder of pyridinium cation (Sato *et al.*,1998).

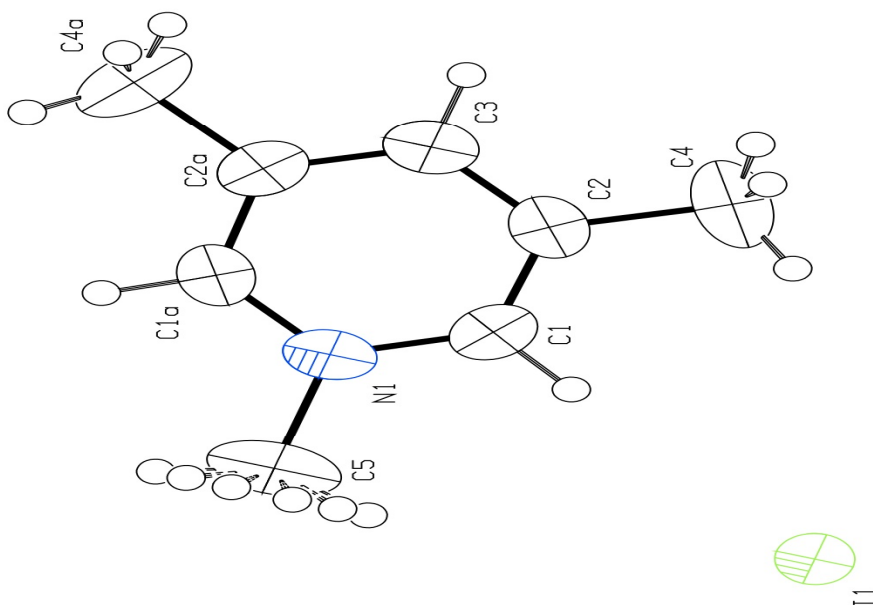


Fig. 2: The crystal structure of 1,3,5-trimethyl pyridinium iodide, thermal ellipsoid, 50% of the molecule methyl hydrogen atoms are disorder due to the c_2v molecular symmetry. Atoms with label (a) are generated by $1-x, y, 3/2$ symmetry.

1,3,5-trimethylpyridinium cation is on a crystallographic mirror plane perpendicular to c -axis except for methyl hydrogen atoms. Also, C3, N1, and C5 are on another crystallographic mirror plane (perpendicular to a -axis), which is perpendicular to the molecular plane and bisects the molecule. Thus, the pyridinium cations have c_2v symmetry and a quarter of the molecule is unique. All methyl hydrogens consequently show disorder structure by mirror planes. The counter iodide anion is also on a section line of those two mirror planes (Wyckoff letter C, Symmetry $m2m$).

The crystal structure of the molecule is shown in Fig. 3. In the crystal structure, iodide anions are on the same mirror plane on which the pyridinium cations locate. Also, one iodine is surrounded by three pyridinium cations and almost equal distance from them (C1...I 3.832(4)Å and C3...I(1/2+x, -1/2+y, z) 3.932(5)Å). Also, the iodine contacts to the Me(N) groups of adjacent parallel mirror planes (C5...I(1/2-x, 1/2-y, 1/2+z) 4.022(5)Å). These distances indicates C-H...I interactions would play important role to stabilize the crystal structure. The pyridinium cations are stacked along c -axis and the inter-planar

distance is 3.497 Å which is a half of c-axis length. As the nearest inter-atomic distance is 3.5268(7)Å (C1...C2(x,-y,-1/2+z)), weak pi...pi interactions are also expected.

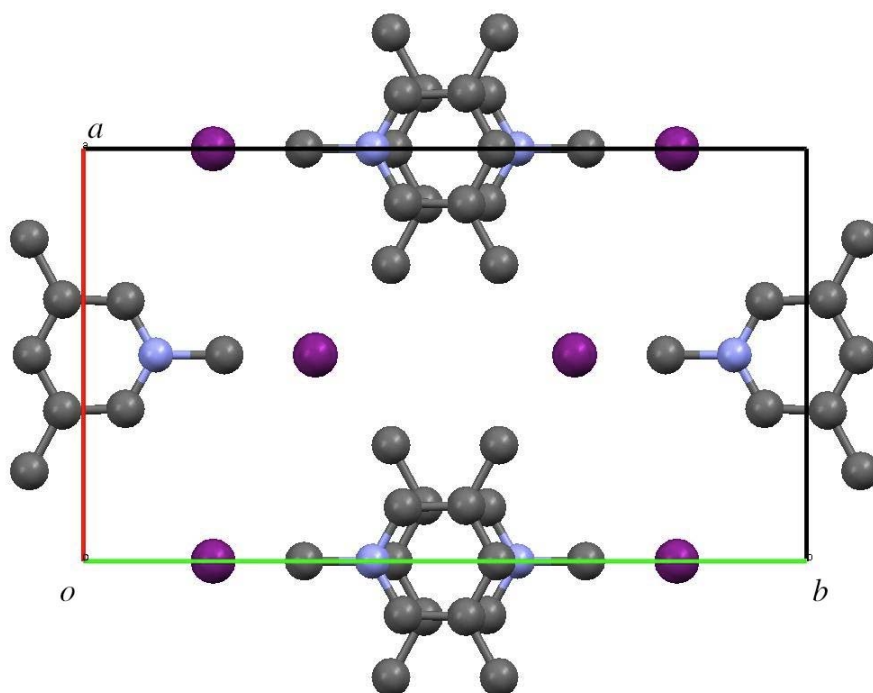


Fig. 3: Crystal structure of the molecule viewed along c-axis. Hydrogen atoms are omitted for clarity.

Table 1. Crystal data and structure refinement for 1,3,5-trimethyl pyridinium iodide.

Identification code	(CCDC 808570)
Empirical formula	C ₈ H ₁₂ I N
Formula weight	249.09
Temperature	169(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>C m c m</i>
Unit cell dimensions	<i>a</i> = 8.9850(9) Å <i>b</i> = 15.767(2) Å <i>c</i> = 6.9940(6) Å
Volume	990.82(16) Å ³
<i>Z</i>	4
Density (calculated)	1.670 Mg/m ³
Absorption coefficient	3.169 mm ⁻¹
F(000)	480
Crystal size	0.24 x 0.20 x 0.17 mm ³
Theta range for data collection	3.89 to 27.37°
Index ranges	-11 ≤ <i>h</i> ≤ 11, -20 ≤ <i>k</i> ≤ 20, -9 ≤ <i>l</i> ≤ 8
Reflections collected	4646
Independent reflections	644 [R(int) = 0.0405]
Completeness to theta = 27.37°	99.4 %

Absorption correction	Multi scan
Max. and min. transmission	1.0000 and 0.4766
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	644 / 0 / 37
Goodness-of-fit on F ²	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0215, wR2 = 0.0522
R indices (all data)	R1 = 0.0224, wR2 = 0.0527
Largest diff. peak and hole	0.399 and -0.480 e.Å ⁻³

Table 2: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 1,3,5-trimethylpyridinium iodide. $U(\text{eq})$ is defined as one third of the trace of the orthogonaized U^{ij} tensor.

	X	Y	Z	U(eq)
I(1)	0	1793(1)	7500	50(1)
C(3)	50000	-713(3)	7500	49(1)
N(1)	5000	1001(2)	7500	47(1)
C(2)	3655(4)	-292(2)	7500	48(1)
C(1)	3696(4)	581(2)	7500	48(1)
C(4)	2186(5)	-747(3)	7500	82(1)
(5)	5000	1947(3)	7500	81(2)

Table 3: Bond lengths [Å] and angles $^\circ$ for 1,3,5- trimethyl pyridinium iodide

C(3)-C(2) #1	1.379(4)
C(3)-C(2)	1.379(4)
C(3)-H(3)	0.9500
N(1)-C(1) #1	1.346(4)
N(1)-C(5)	1.493(6)
C(1)-C(2)	1.376(4)
C(2)-C(4)	1.502(5)
C(1)-H(1)	0.9500
C(4)-H(4B)	0.9899
C(4)-H(4C)	0.9800
C(5)-H(5C)	0.9800
C(2)#1-C(3)-C(2)	122.4(4)
C(2)#1-C(3)-H(3)	118.8
C(2)-C(3)-H(3)	118.8
3C(1)#1-N(1)-C(1)	121.0(4)
C(1)#-N(1)-C(5)	119.48(18)
C(1)-N(1)-C(5)	119.48(18)
C(1)-C(2)-C(3)	117.1(3)
C(1)-C(2)-C(4)	120.1(3)
C(3)-C(2)-C(4)	122.7(3)
N(1)-C(1)-C(2)	121.0(3)
N(1)-C(1)-H(1)	119.5

C(2)-C(1)-H(1)	119.5
C(2)-C(4)-H(4B)	109.5
H(4A)-C(4)H(4B)	109.5
C(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)H(4C)	109.5
N(1)-C(5)-H(5A)	109.5
N(1)-C(5)-H(5B)	109.5
H(5A)-C(5)H(5B)	109.5
N(1)-C(5)-H(5B)	109.5
H(5A)-C(5)H(5C)	109.5
H(5B)-C(5)H(5B)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,z

Table 4: anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 1,3,5 trimethylpyridinium iodid .
The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^2U^{11} + \dots + 2hka*b*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	44(1)	42(1)	65(1)	0	0	0
C(3)	65(3)	45(2)	37(2)	0	0	0
N(1)	63(2)	38(2)	39(2)	0	0	0
C(2)	51(2)	56(2)	37(1)	0	0	-11(1)
4-C(1)	47(2)	56(2)	41(1)	0	0	10(1)
C(4)	66(2)	105(4)	75(3)	0	0	-39(3)
C(5)	132(7)	42(3)	70(4)	0	0	0

Table 5: Hydrogen coordinate($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$).

	X	Y	Z	U(eq)
H(3)	5000	-1315	7500	59
H(1)	2790	891	7500	58
H(4A)	2233	-1231	8378	123
H(4B)	1966	-950	6200	123
H(4C)	1400	-357	7916	123
H(5A)	4288	2145	8453	122
H(5B)	4714	2154	6231	122
H(5C)	5999	2154	7816	122

Table 6: Torsion angles [$^{\circ}$] for 1,3,5 trimethyl pyridinium iodide.

C(2)#1-C(3)-C(2)-C(1)	0.0
C(2)#1-C(3)-C(2)-C(4)	180.0
C(1)#1-N(1)-C(1)-C(2)	0.0
C(5)-N(1)-C(1)-C(2)	180.0
C(3)-C(2)-C(1)-N(1)	0.0
C(4)-C(2)-C(1)-N(1)	180.0

Symmetry transformations used to generate equivalent atoms:

#1-x=1,y,z

Table 7: physical properties of the prepared salts.

No	Complex	Color	Mp $^{\circ}\text{C}$	M% Found, (calc.)	$\Omega \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$	μ_{eff} BM
-	A	Reddish	280	-----	70	-----
1	$[\text{A}]_2[\text{MnCl}_2\text{I}_2]$	Orange	85	8.76(8.79)	162	5.95
2	$[\text{A}]_2[\text{CoCl}_2\text{I}_2]$	Green	122	-----	149	4.47
3	$[\text{A}]_2[\text{NiCl}_2\text{I}_2]$	Reddish brown	150	9.82(9.53)	164	3.91
4	$[\text{A}]_2[\text{CuCl}_2\text{I}_2]$	Brown	142	-----	170	2.14
5	$[\text{A}]_2[\text{ZnCl}_2\text{I}_2]$	Yellowish brown	119	10.18(10.30)	168	-----

A=1,3,5-trimethyl pyridinium iodide.

Table 8: IR absorption cm^{-1} and electronic spectra bands for ionic salts.

No	IR bands cm^{-1}				Uv./visible band maximum(nm)
	$\nu(\text{NCH}_3)^+$	$\nu(\text{C-H})$	$\nu(\text{M-Cl})$	$\nu(\text{M-I})$	
A	2341(w)	2998(w)	-----	-----	276,1350
1	2360(m)	2925(w)	317(w)	243(s)	280
2	2361(m)	2980(w)	302(w)	272(s)	675
3	2336(w)	2975(w)	289(s)	223(m)	710
4	2361(m)	2970(m)	282(w)	237(s)	790
5	2360(m)	2990(m)	280(s)	222(s)	270

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