



Studies on coordination environment of transition metal chloride anionic speciation of N, N-disulfodiisopropylammonium ionic salts and assessment of their Brønsted-Lewis acidic properties

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Four ionic salts of N, N-disulfodiisopropylammonium cation with complex anionic speciation of metal chlorides such as $[\text{FeCl}_4]^-$, $[\text{NiCl}_4]^{2-}$, $[\text{Zn}_2\text{Cl}_6]^{2-}/[\text{Zn}_4\text{Cl}_{10}]^{2-}$, $[\text{CoCl}_4]^{2-}/[\text{CoCl}_3]^-$ have been synthesized and characterized with FTIR, NMR, TGA, Raman and electronic spectra. Comparative Brønsted and Lewis acidic strength of the salts have been assessed for catalytic uses in organic reactions *via* UV-visible Hammett plot and FTIR spectra using pyridine as probe molecule. Band gap values obtained from Tauc plot present their semiconductor behavior to design ionic liquid-based photo catalysts in future.

Keywords: Brønsted-Lewis acidic, Chlorometallates, Anionic speciation, Transition metal cation, Ammonium cation

Ionic liquids of chlorometallates are considered as important class of acidic/basic/neutral material with varied metal halide anionic species which can be tuned by adjusting molar ratio of metal chloride with respect to molar ratio of organic chloride salt.¹ The composition of anionic speciation is the dominating factor for change of any physicochemical properties of chlorometallate ionic liquids such as viscosity, density, ionic conductivity, thermal stability, sensitivity towards moisture, acidity etc. For designing of efficient Lewis acidic chlorometallates, one must consider the electron deficient state of metal cation and also availability of its lowest unoccupied molecular orbitals (LUMO). For example, chlorozincate(II) ionic systems are weaker in acidic properties as compared to the chloroaluminate(III) ionic systems.² The speciation of neutral chlorozincate (II) anion is $[\text{ZnCl}_4]^-$ at $\chi_{\text{ZnCl}_2}=0.33$ in contrast to neutral chloroaluminate (III) anion $[\text{AlCl}_4]^-$ or $[\text{Al}_2\text{Cl}_7]^-$ at mole fraction $\chi_{\text{AlCl}_3}=0.5$.² All compositions of the chlorozincate (II) with mole fraction $\chi_{\text{ZnCl}_2} > 0.33$ are Lewis acidic and contain oligomeric $[\text{Zn}_x\text{Cl}_{(2x+2)}]^{2-}$ species. The mild Lewis acidity of In(III) centre is also responsible for moderate Lewis acidity of chloroindate(III) ionic liquids with neutral anionic speciation $[\text{InCl}_6]^{3-}$ at mole fraction = 0.25.

The water tolerant capacity of chloroferrate (III) ionic liquids gives lots of scope for development of strong Lewis acidic ionic systems for efficient application as industrial catalysts in spite of limited capacity to form the most acidic dimeric $[\text{Fe}_2\text{Cl}_7]^-$ anion in homogeneous composition.^{3,4} The catalytic uses of various types of chlorometallates salts were observed for number of acid catalyzed organic reactions.^{2,5-9} They were also applied in electroplating and polishing treatment, metal oxide dissolution,¹⁰ controlled separation/extraction processes,¹¹ development of newer inorganic semiconductor materials,¹² etc.

Functionalization of imidazolium or ammonium cation with one or two $-\text{SO}_3\text{H}$ groups through nitrogen atom of the chlorometallates change their complex co-ordination chemistry brought in by the anionic part helps to develop more efficient potent functional materials suitable for different purposes.¹³ These developments forge a path towards systematic correlation of the anion speciation and physicochemical properties across the series of different metals, and hence bring out opportunities to gain much control over properties such as Lewis acidity, stability, reactivity etc. Therefore, a wide array of innovative applications in chemistry and material science can be developed by taking advantage of the specific properties and complex co-

ordination environment present in the chlorometallate ionic liquids. Herein, we were interested to develop four ionic salts of N, N-disulfo-diisopropylammonium chlorometallate ($[\text{DSDIP}]_x[\text{A}]$ where $[\text{A}] = [\text{FeCl}_4]^-$, $[\text{NiCl}_4]^{2-}$, $[\text{Zn}_2\text{Cl}_6]^{2-}/[\text{Zn}_4\text{Cl}_{10}]^{2-}$, $[\text{CoCl}_4]^{2-}/[\text{CoCl}_3]^-$ from an equimolar mixture of N,N-disulfo-diisopropylammonium chloride ($[\text{DSDIP}]\text{Cl}$) with metal chlorides, namely FeCl_3 , NiCl_2 , ZnCl_2 , and CoCl_2 respectively (Scheme 1) as Brønsted-Lewis acidic material.

Materials and Methods

General information

All chemicals were purchased from Merck and Aldrich chemical suppliers in pure state. The electronic spectra were recorded on a UV 2450 Shimadzu spectrophotometer. IR spectra of the ionic salts and their qualitative assessment of Lewis acidity were done on a Perkin Elmer Frontier MIR-FIR FTIR spectrophotometer using dry pyridine as the molecular probe. The quantitative Brønsted acidity of the ionic salts was determined using UV 2550 spectrophotometer. Raman analyses were performed on Horiba LabRAM HR spectrophotometer equipped with a He-Ne laser of excitation wavelength of 514.5 nm. Shimadzu TGA-50 was used to conduct thermogravimetric analysis. The ^1H and ^{13}C NMR spectra of parent chloride ionic were recorded on JEOL 400 MHz spectrophotometer (δ in ppm) in DMSO-d_6 .

General procedure for synthesis of $[\text{DSDIPA}]_x[\text{MCl}_x]$ ionic salts

The four chlorometallate ionic salts were prepared by a two-step reaction (Scheme 1). The first step involved through dropwise addition of chlorosulfonic acid (20 mmol) to a stirred solution of diisopropylamine (10 mmol) in dry CH_2Cl_2 (30 mL) at 0°C within a period of 5 min under nitrogen atmosphere in a 100 mL round bottom flask. Then the mixture was stirred for one hour to complete the synthesis of disulfo-diisopropylammonium chloride

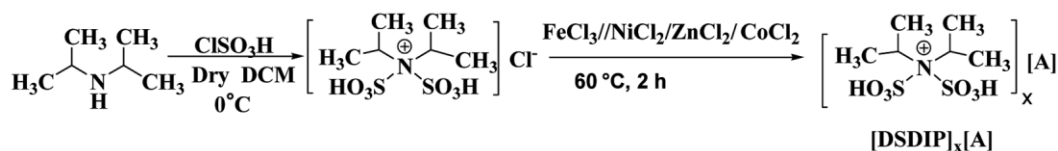
$[\text{DSDIPA}][\text{Cl}]$. The viscous ionic liquid layer was washed three times with fresh CH_2Cl_2 (3×10 mL) by decantation of dichloromethane solution. The residue was dried under vacuum which produced 98% pale yellow viscous oil of $[\text{DSDIPA}][\text{Cl}]$. The 2nd step was performed by mixing equimolar amount of respective metal chlorides (FeCl_3 , NiCl_2 , ZnCl_2 , and CoCl_2) with the $[\text{DSDIPA}][\text{Cl}]$ at 60°C for 2 h with continuous stirring. The crude molten product was cooled to room temperature and washed with dry dichloromethane to eliminate any residual parent IL. The ionic salts were dried in vacuum to get desired chlorometallates of the $\text{Fe}(+3)$, $\text{Ni}(+2)$, $\text{Zn}(+2)$ and $\text{Co}(+2)$ cations as brown solid (**IL I** = 87% yield), yellowish green solid (**IL II** = 85% yield), light brown semi-solid (**IL III** = 90% yield) and bluish grey solid (**IL IV** = 84% yield) acidic material respectively.

Results and Discussion

The preparation of four $-\text{SO}_3\text{H}$ functionalized N, N-disulfo-diisopropylammonium chlorometallates was carried out in two step method in inert atmosphere (Scheme 1). Their structural compositions were determined using various analytical techniques.

FTIR spectra of these acidic materials displayed medium to strong absorptions peaks (Fig. 1) at $1130\text{--}1203\text{ cm}^{-1}$ for S-O symmetric and 1049 cm^{-1} for S-O antisymmetric stretching vibrations of the sulfonic groups in addition to S-O bending around $613\text{--}575\text{ cm}^{-1}$. The anchoring of $-\text{SO}_3\text{H}$ group to the diisopropylamine moiety was confirmed from N-S stretching peak at $886\text{--}874\text{ cm}^{-1}$. The C-N stretching band of the ammonium moiety overlapped with the S-O symmetric stretching frequency. The C-H bending of $-\text{CH}_3$ and $-\text{CH}_2-$ groups observed in the same region at $1479\text{--}1433\text{ cm}^{-1}$, while C-H bending related to gem-dimethyl group of the diisopropyl group was observed at $1397\text{--}1377\text{ cm}^{-1}$.

The ^1H NMR spectrum of N, N-disulfo-diisopropylammonium chloride $[\text{DSDIPA}][\text{Cl}]$



IL I: $[\text{DSDIPA}][\text{FeCl}_4]$

IL II: $[\text{DSDIPA}]_2[\text{NiCl}_4]$

IL III: $[\text{DSDIPA}]_2[\text{Zn}_2\text{Cl}_6]/[\text{Zn}_4\text{Cl}_{10}]$

IL IV: $[\text{DSDIPA}]_2[\text{CoCl}_4]/[\text{DSDIPA}][\text{CoCl}_3]$

where $[\text{A}] = [\text{FeCl}_4]^-$, $[\text{NiCl}_4]^{2-}$,

$[\text{Zn}_2\text{Cl}_6]^{2-}/[\text{Zn}_4\text{Cl}_{10}]^{2-}$, $[\text{CoCl}_4]^{2-}/[\text{CoCl}_3]^-$

and $x = 1, 2$

Scheme 1 — Preparation of N,N-disulfo-diisopropylammonium chlorometallates.

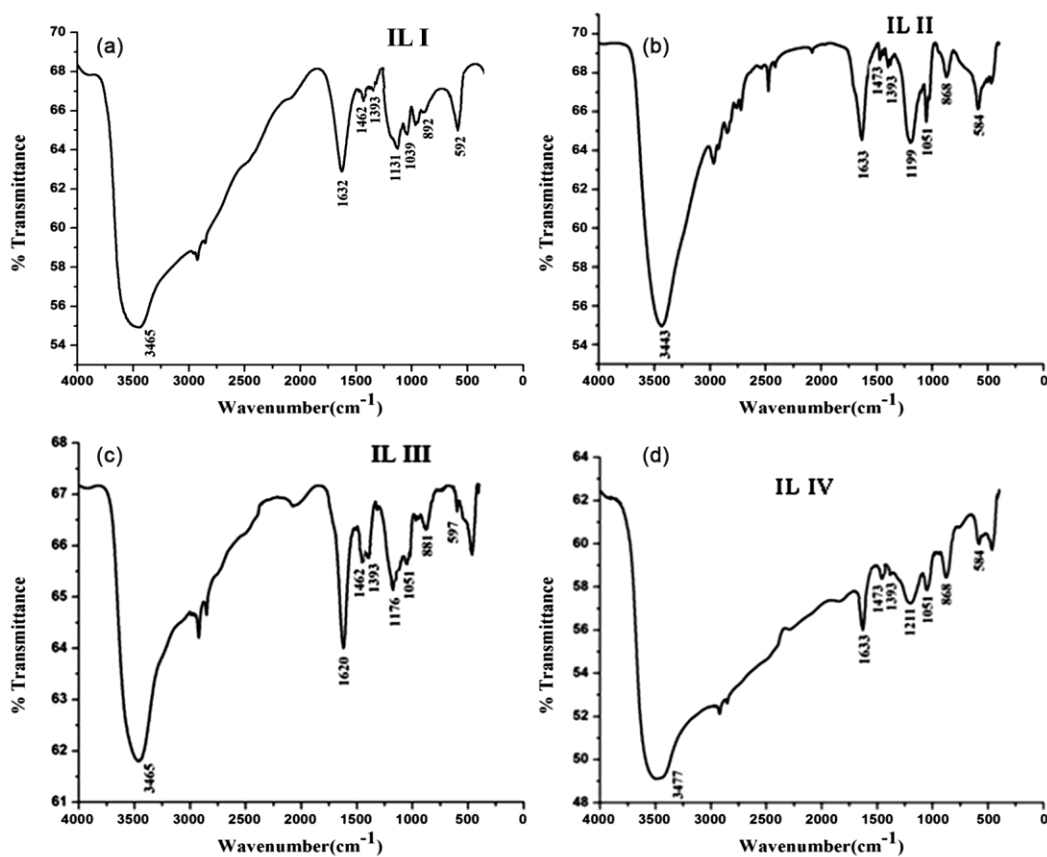


Fig. 1 — FTIR spectra of disulfodiisopropylammonium chlorometallates.

ionic liquid in Fig. 2a identified two acidic protons of the $-\text{SO}_3\text{H}$ group as singlet at 9.95 ppm. The two equivalent $-\text{CH}$ protons of disulfodiisopropylammonium cation appeared as multiplet in the range of 1.94-1.88 ppm. For the 12 equivalent methyl protons of isopropyl groups, a doublet at 1.13 ppm with coupling constant value $J = 4.0$ Hz was obtained. Similarly, in ^{13}C NMR spectrum, two peaks at 46.0 and 19.0 ppm appeared characteristic of the $-\text{CH}$ and $-\text{CH}_3$ carbons (Fig. 2b). The lower solubility of chlorometallates salts in $\text{DMSO}-d_6$ limited their NMR studies for the four ionic salts.

The electronic spectra of three ionic salts of Fe (+2), Ni(+2) and Co(+2) cations (**IL I**, **IL II** and **IL IV**) are shown in Fig. 3 excluding the semi-solid ionic salt of Zn(+2) cation (**IL III**). The sample of Fe (+2) (**IL I**) exhibited one broad absorption band near 314 nm originate from ligand to metal charge transfer transition along with d-d transition at 576 nm.¹⁴⁻¹⁶ For Ni (+2) anionic complex (**IL II**), we observed ligand charge transfer transition band at 262 nm NiCl_4^{2-} .¹⁷ It also displayed two characteristic peaks for tetrahedral NiCl_4^{2-} anionic species with comparable intensities

around 700 nm and 773 nm.¹⁸ The peak at 416 nm can be accounted for an equilibrium mixture of little amount of mono and dichloro nickel species with the NiCl_4^{2-} complex.¹⁷ The analysis of electronic spectra supports the existence of anionic species as tetrahedral complex of $[\text{NiCl}_4]^{2-}$. The electronic spectra of Co(+2) anionic complex (**IL IV**) represents one triplet peak in the range of 600-700 nm with absorption maximum at 628 nm, 664 nm and 696 nm respectively. These peaks can be accounted for the ${}^4\text{T}_1(\text{P}) \rightarrow {}^4\text{A}_2(\text{F})$ transition imparting a strong gray-blue color to the ionic salt and it confirms the formation of tetrahedral $[\text{CoCl}_4]^{2-}$ complex.¹⁸ The formation of this species can be speculated according to Eqn 1.



The formation of minor amount of other cobalt-chloro complex clusters can also be expected depending on the mole fraction of CoCl_2 employed. It is supported by a literature report from Heish *et al* on influence of anion speciation over electrodeposition of Co from Lewis-acidic cobalt chloride based

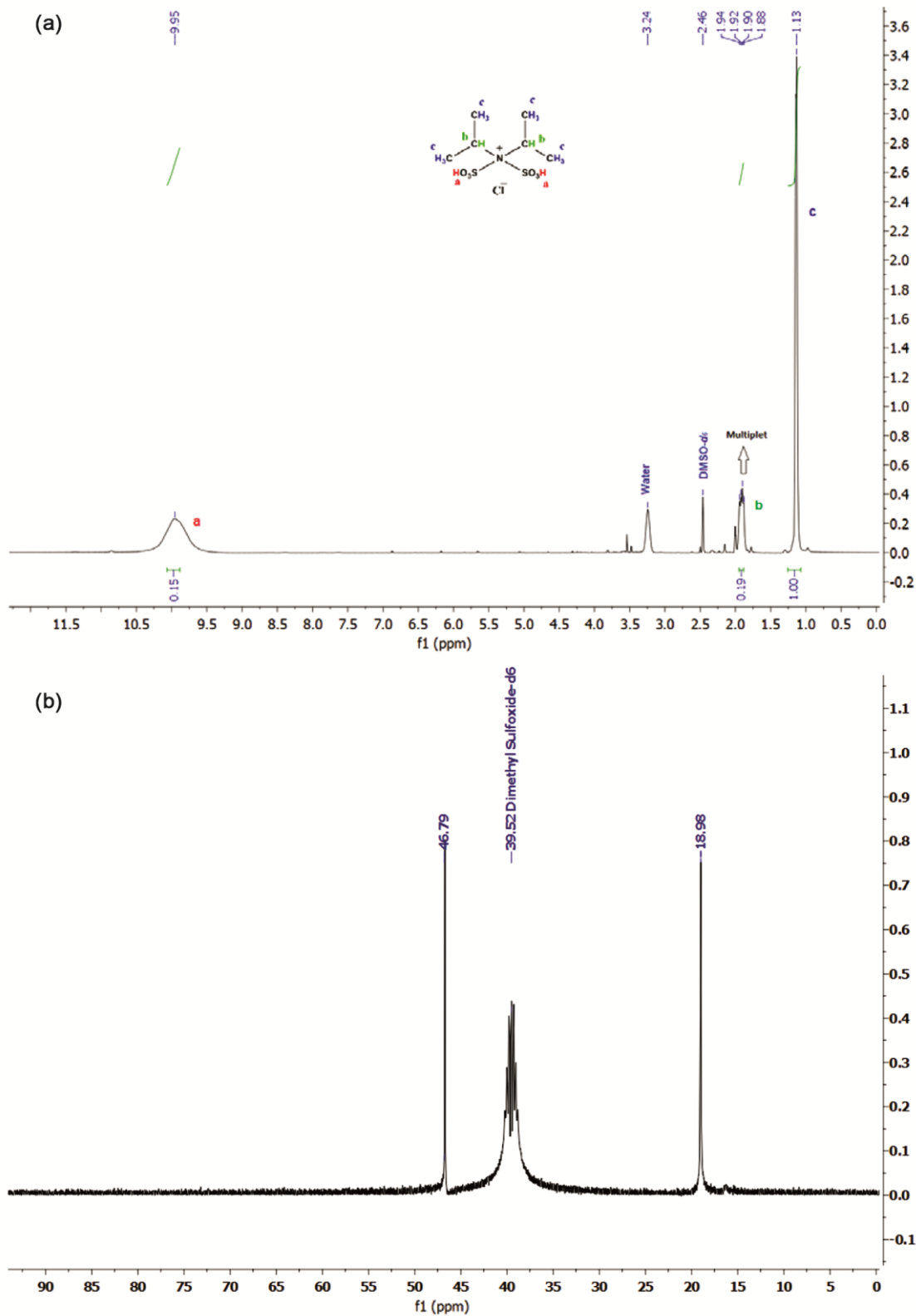


Fig. 2 — (a) 400 MHz ¹H NMR and (b) 100 MHz ¹³C NMR spectra of [DSDPA][Cl] in DMSO-d₆

imidazolium ionic liquids.¹⁹ The formation of other cobalt chloride anionic speciation like CoCl_3^- , Co_2Cl_5^- and Co_3Cl_7^- clusters along with CoCl_4^{2-} might be possible from equilibrium reactions of CoCl_2 with the organic chloride employed during the preparation of this ionic salt system. Due to weak coordination power and lower dielectric constant of tetrahedral $[\text{CoCl}_4]^{2-}$ species than CoCl_2 , it preferably absorbs UV light at a longer wavelength than other coordination-unsaturated cobalt-chloro complex clusters. In such case the characteristic absorption maximum for other complex cobalt-chloride anions like $[\text{CoCl}_3]^-$ may shift to shorter wavelength indicating the presence of minor amount of these species along with the CoCl_4^{2-} complex. Therefore, the appearance of a weak shoulder at 545 nm for **IL IV** can be accounted for little amount of $[\text{CoCl}_3]^-$ along with CoCl_4^{2-} complex.²⁰ The peak around 265 nm can be assigned for ligand to metal charge transfer transition for the tetrahedral complex of $[\text{CoCl}_4]^{2-}$ based on ligand field theory. This ionic liquid was observed as the most Lewis acidic

chlorometallate salt out of the four ionic salts during Lewis acidity study via FTIR spectra using pyridine as probe molecule.

Raman study was carried out for Fe (+2), Ni (+2), and Zn(+2) metal containing chlorometallates ionic salts i.e. **IL I-III** to confirm their possible anion speciation. The Raman spectra of these ionic salts are presented in Fig. 4. The sharp peak at 350 cm^{-1} for $[\text{DSDIPA}][\text{FeCl}_4]$ confirms the anion composition as FeCl_4^- in **IL I**.²¹ The Raman spectrum for **IL II** produced a sharp peak at 264 cm^{-1} which is characteristic of NiCl_4^{2-} complex.²² For the chlorozincate system, weak-strong bands were obtained in the Raman spectrum. The strong band at 310 cm^{-1} can be ascribed to a dimeric $[\text{Zn}_2\text{Cl}_6]^{2-}$ complex with reference to a study carried out for an equimolar mixture of 1-octyl-3-methylimidazolium chloride $[\text{C}_8\text{mim}][\text{Cl}]$ and ZnCl_2 .²³ Presence of a relatively weak shoulder at 282 cm^{-1} can be assigned to the T_d structure of $[\text{ZnCl}_4]^{2-}$ which may be present in lesser amount.²⁴ The chlorozincate system also displayed another strong band at 239 cm^{-1} and one shoulder at 360 cm^{-1} . These two peaks were found to resemble the literature data of nonlinear chlorozincate anion with molecular formulae: $[\text{Zn}_4\text{Cl}_{10}]^{2-}$ at 232 cm^{-1} and 348 cm^{-1} .²⁵ No absorption peaks were found corresponding to linear trinuclear $[\text{Zn}_3\text{Cl}_8]^{2-}$ complex at 288 cm^{-1} and 340 cm^{-1} in the Raman spectra of **IL III**.^{23,25} In literature, the band at 232 cm^{-1} was ascribed to represent the bridging vibrations in $(\text{ZnCl}_4)_2\text{Zn}$ with a central tetrahedral zinc for all acidic composition of the chlorozincate anion.²⁴ The Raman analysis of Co(+2) ionic salt was not included in this study due to its complicated pattern which can be attributed for presence of hygroscopic $\text{CoCl}_4^{2-}/[\text{CoCl}_3]^{2-}$ anionic speciation as evidenced from the electronic spectrum (Fig. 3) and TGA analysis (Fig. 6).

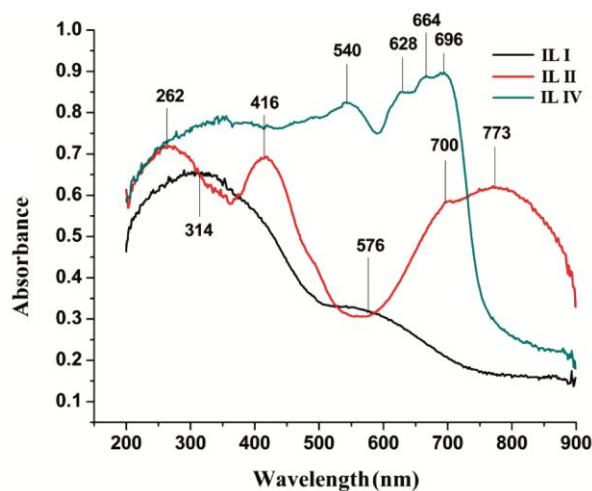


Fig. 3 — Electronic spectra of the ionic salts.

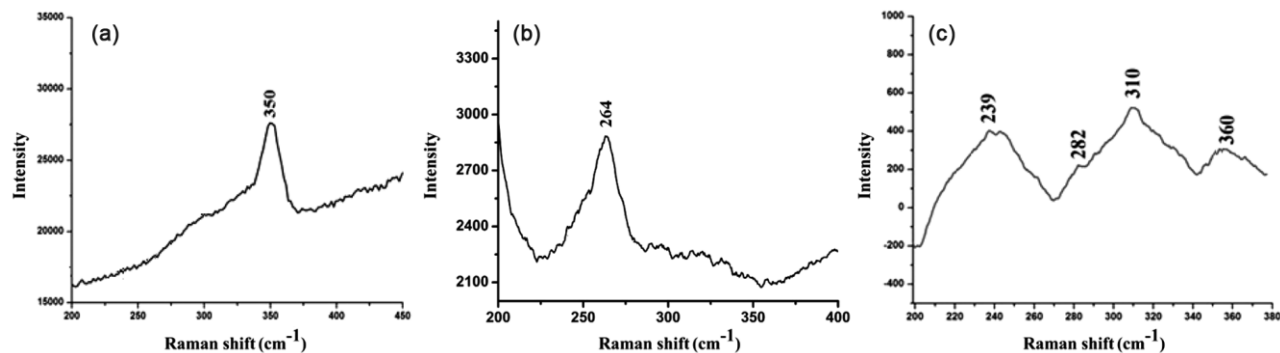


Fig. 4 — Raman spectra of ionic liquids: (a) IL I, (b) IL II and (c) IL III.

From the electronic spectra of three ionic salts (Fig. 4), it would be possible to estimate the semiconductor properties by calculation of optical band gap from Tauc plot (Fig. 5). The Tauc plot was generated from Eqn 2:

$$\alpha h\nu = (h\nu - E_g)^n \quad \dots (2)$$

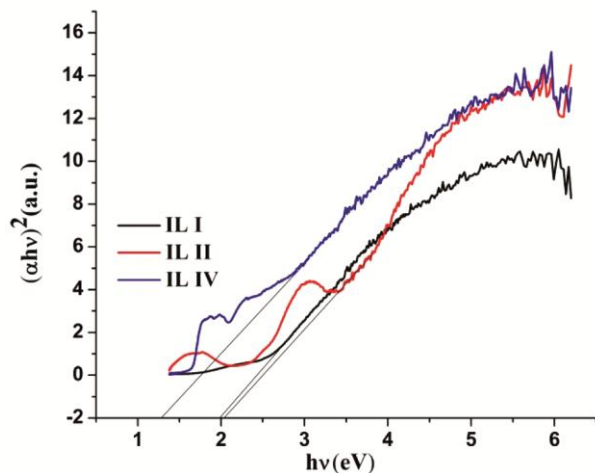


Fig. 5 — Tauc plot for three chlorometallate ionic systems.

where α is the absorption coefficient, $h\nu$ is the photon energy and E_g is the optical band gap for direct or indirect transition ($n = 1/2$ or 2 respectively). Considering the transitions to be direct and allowed type, extrapolation of the linear regime to the abscissa gave the E_g values as 1.99, 2.71 and 1.21 eV for **IL I**, **IL II** and **IL IV**, respectively. These values are close to standard semiconductor material which signifies their importance.

The thermal stability of the chlorometallate ionic salts was assessed *via* thermogravimetric analysis coupled with differential thermal analysis (DTA) and the results are shown in Fig. 6. The TGA profile for the four ionic salts suggests minimum weight loss (around 2-5 %) for adsorbed water below 100 °C. They witnessed variable thermal stabilities within the range of 100-130 °C. The approximate 18-20% weight loss up to 200 °C can be attributed to the loss of two $-\text{SO}_3\text{H}$ groups. It was followed by decomposition of the cationic part at once. The remaining 40-60% volatile matters of the ionic salts were completely removed around 300 °C. Weight loss above 300 °C may be attributed to

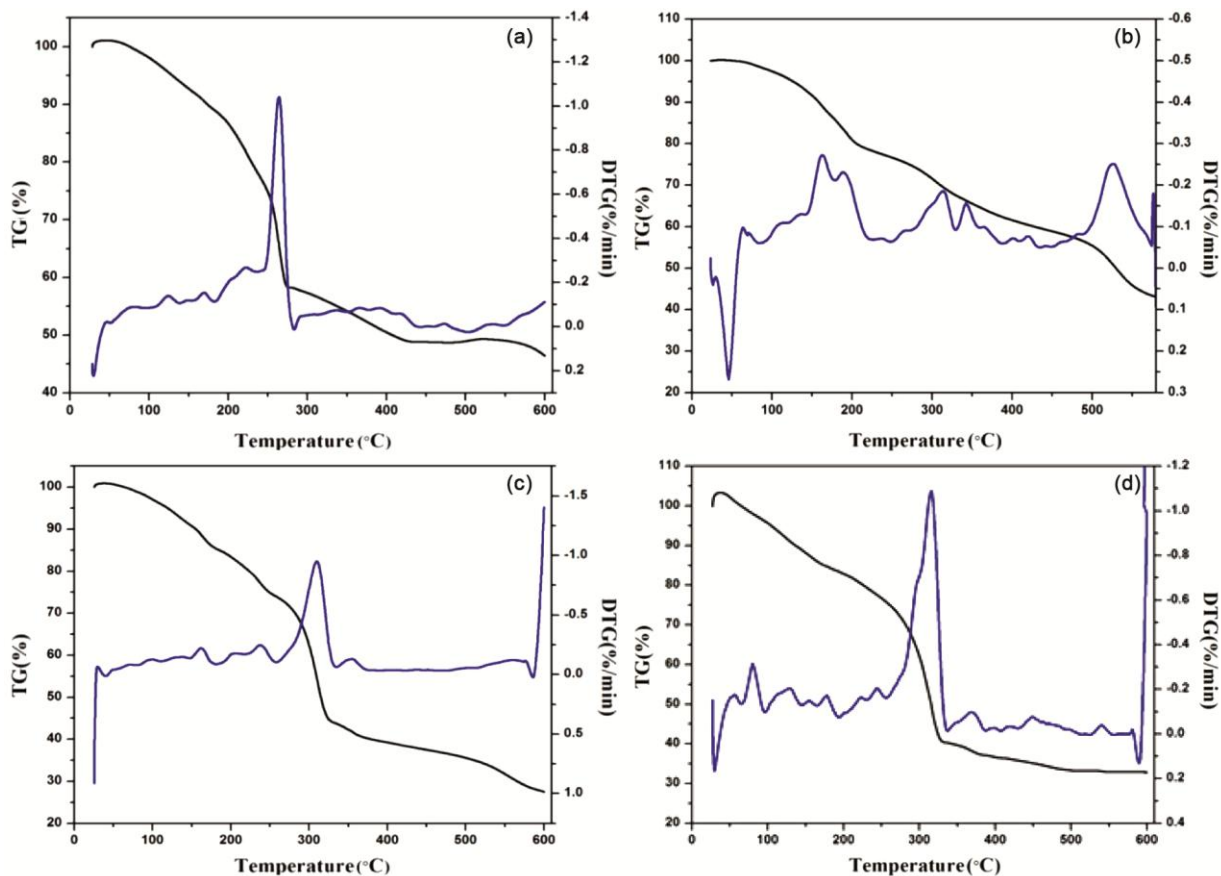


Fig. 6 — TGA profiles for (a) IL I, (b) IL II, (c) IL III and (d) IL IV.

dechlorination of the complex anionic part which was further followed by oxidation of elemental form of metals to respective oxides near around 500 °C.²⁶

By monitoring the ring vibration modes (Fig. 7) in the range 1650-1250 cm⁻¹, pyridine can be used as a probe molecule for distinguishing Lewis/ Brønsted acidic sites as well as for determination of Lewis acidic strength of the ionic salts. Neat pyridine shows a well resolved band at 1438 cm⁻¹ which was unchanged in the parent ionic liquid, [DSDIPA][Cl], as there is no Lewis acidic site present. However, in the four spectra of chlorometallates, this ring vibration band of pyridine shifted towards higher wave number after interaction with the probe pyridine molecule. The characteristic wave number 1438 cm⁻¹ of pyridine ring shifted to higher number such as 1463 cm⁻¹ for **IL I** ([DSDIPA][FeCl₄]), 1466 cm⁻¹ for **IL II** ([DSDIPA]₂[NiCl₄]), 1444 cm⁻¹ for **IL III** ([DSDIPA]₂[Zn₂Cl₆]/[Zn₄Cl₁₀]) and 1474 cm⁻¹ for **IL IV** [CoCl₄]²⁻/[CoCl₃]⁻. The Lewis acidic strength of these chlorometallates can be arranged in following increasing order on the basis of wave number values of pyridine ring: **IL III**<**IL I**<**IL II**<**IL IV** when mole fraction of metal chloride is $\chi = 0.5$. In addition to it, another band at 1533-1535 cm⁻¹ arises indicating the formation of pyridinium ions resulting from the presence of Brønsted acidic sites.

Quantitative assessment of the Brønsted acidity for the ionic salts was performed on UV-visible spectrophotometer using Hammett acidity function (H^0) defined in Eqn 3 in ethanol solution according to literature procedure²⁷ in presence of 4-nitroaniline as basic indicator where $pK(I)_{aq}$ is the pK_a value of the basic indicator in aqueous solution. The plot in Fig. 8

displayed lowering of absorbance intensities of the basic indicator [I] with increasing acidic strength of the ionic salt solutions by protonation of the basic indicator i.e. [HI]⁺. No absorbance was appeared for the protonated form [HI]⁺ because of lower molar absorptivity of this intermediate.

$$H^0 = pK(I)_{aq} + \log [I]/[IH]^+ \quad \dots (3)$$

From the Hammett plot (Fig. 8), we estimated their comparative Hammett functions in Table 1 and thus expressed the acidity order for the ionic liquid systems as: **IL IV**<**IL III**<**IL II**<**IL I**.

The overall acidity order obtained from the two different methods varied depending on the composition of anionic species and their tendency to form secondary co-ordination shell with chloride anions in the ionic salt. The possibility for presence of

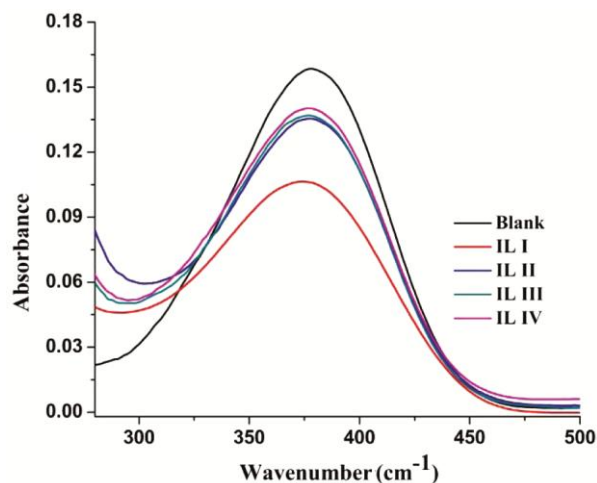


Fig. 8 — Hammett plots of ILs.

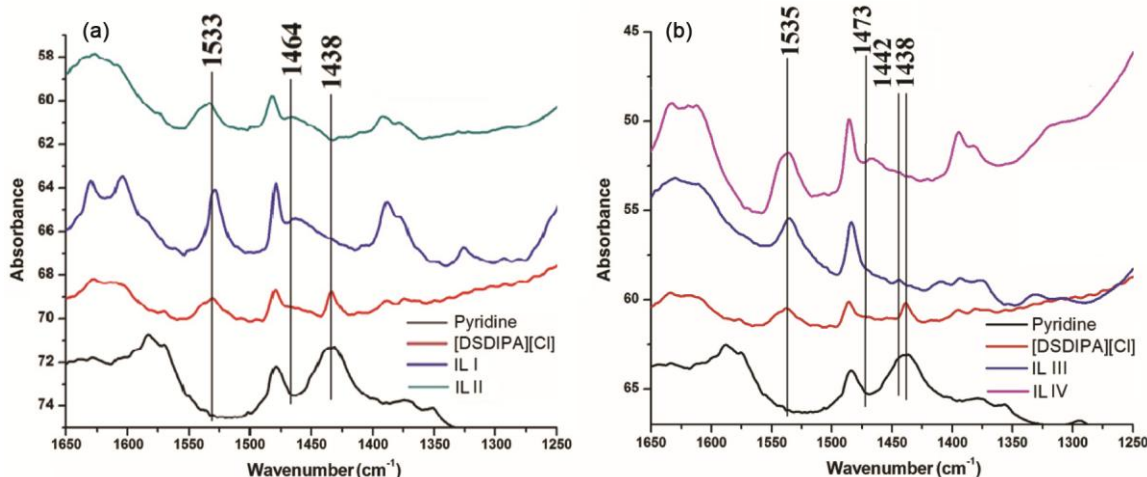


Fig. 7 — FTIR spectra of pyridine-IL complexes.

Table 1 — Brønsted acidity determination from Hammett plot

Entry	Sample name	A _{max}	[I]%	[IH]%	H ⁰
1.	Indicator	0.158	100	0	-
2.	IL I	0.105	66.5	33.5	1.04
3.	IL II	0.135	85.4	14.6	1.12
4.	IL III	0.136	86.1	13.9	1.13
5.	IL IV	0.139	87.9	12.1	1.15

other complex anionic speciation in **IL IV** along with major amount of $[\text{CoCl}_4]^{2-}$ makes more numbers of Lewis acidic sites available in contrast to only one anionic speciation of Fe salt (FeCl_4^-) in **IL I**. The acidity of **IL I** was favorably controlled by the two Brønsted acidic sites of sulfonic group.

Conclusions

In summary, a new series of transition metal chloride salts of disulfodiisopropylammonium cation were successfully synthesized as Brønsted-Lewis acidic material and characterized with various analytical techniques. The anionic speciation of the chlorometallate salts were examined using the combined indicative studies of FTIR, Raman and electronic spectroscopy. In conjunction with literature support, the co-ordination sphere of metal anionic species has been proposed and expressed accordingly based on the analysis data in these chlorometallate salts. These chlorometallate ionic liquids displayed variable thermal stabilities within the range of 100-130 °C with loss of minimum amount of adsorbed water (~2-5%) below 100 °C. The acidity studies displayed highest Brønsted acidic strength for the Fe(+2) salt and Lewis acidic strength for the Co(+2) salt. Depending on their thermal stability and hydrophobic properties, they can be applicable as potential acidic catalyst in organic synthesis, for development of ionic liquid based photocatalyst and in electrochemical studies.

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References

- Estager J, Holbrey J D & Swadźba-Kwaśny M, *Chem Soc Rev*, 43 (2014) 847.
- Gunaratne H N, Lotz T J & Seddon K R, *New J Chem*, 4 (2010) 1821.
- Csuhony S, Mehdi H & Horváth I T, *Green Chem*, 3 (2001) 307.
- Sitze M S, Schreiter E R, Patterson E V & Freeman R G, *Inorg Chem*, 40 (2001) 2298.
- Cai X, Cui S, Qu L, Yuan D, Lu B & Cai Q, *Catal Commun*, 9 (2008) 1173.
- Atkins M P, Seddon K R & Swadźba-Kwaśny M, *Pure App Chem*, 83 (2011) 1391.
- Yang S, Liu Z, Meng X & Xu C, *Energy Fuels*, 23 (2008) 70.
- Gao J, Wang J Q, Song Q W & He L N, *Green Chem*, 13 (2011) 1182.
- Wang G, Yu N, Peng L, Tan R, Zhao H, Yin D, Qiu H, Fu Z & Yin D, *Catal Lett*, 123 (2008) 252.
- Abbott A P, Frisch G & Ryder K S, *Annu Rep Prog Chem Sect A: Inorg Chem*, 104 (2008) 21.
- Zhang J, Huang C, Chen B, Ren P & Lei Z, *Energy Fuels*, 21 (2007) 1724.
- Biswas K, Zhang Q, Chung I, Song J H, Androulakis J, Freeman A J & Kanatzidis M G, *J Am Chem Soc*, 132 (2010) 14760.
- Sarma P, Dutta A K & Borah R, *Catal Survey Asia*, 21 (2017) 70
- Mineralurgii F P, *Physicochemical Problems of Mineral Processing*, 36 (2002) 217.
- Bäcker T, Breunig O, Valldor M, Merz K, Vasylyeva V & Mudring A V, *Cryst Growth Des*, 11 (2011) 2564.
- Kogelnig D, Stojanovic A, Kammer F v d, Terzieff P, Galanski M, Jirsa F, Krachler R, Hofmann T & Keppler B K, *Inorg Chem Commun*, 13 (2010) 1485.
- Khokhryakov A A, Mikhaleva M V & Paivin A S, *J Inorg Chem*, 51 (2006) 1311.
- Kettle S F A, *Physical Inorganic Chemistry: A Coordination Chemistry Approach* (Oxford University Press New York) 1998.
- Hsieh Y T, Lai M C, Huang H L & Sun I W, *Electrochimica Acta*, 117 (2014) 217.
- Rao A P & Dubey S P, *Anal Chem*, 44 (1972) 686.
- Wang L, Lu B, Zhu A, Sun H & Shen Q, *Sci Bull*, 30 (2013) 3624.
- Yan C, Wang L, Gao H, Sun H & Shen Q, *Chinese Sci Bull*, 57 (2012) 1953.
- Estager J, Nockemann P, Seddon K R, Swadźba-Kwaśny M & Tyrrell S, *Inorg Chem*, 50 (2011) 5258.
- Quicksall C O & Spiro T G, *Inorg Chem*, 5 (1966) 2232.
- Yannopoulos S N, Kalamounias A G, Chrissanthopoulos A & Papatheodorou G N, *J Chem Phys* 118 (2003) 3197.
- Haines P, *Methods of Analysis Principles, Applications and Problems, 1st Edition*, (Springer Science and Business Media) 1995.
- Gogoi P, Dutta A K, Sarma P & Borah R, *Appl Cata A*, 492 (2015) 133.