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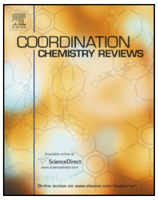

Review

Low-melting complexes with cationic side chains – Phosphonium-, ammonium- and imidazolium-tagged coordination compounds

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ABSTRACT

Citing 120 references, this article gives an overview of low-melting cationically tagged coordination compounds of transition metal ions. In three sections, focussing on Werner-type complexes, carbonyls and ferrocenes, ammonium-, phosphonium- and imidazolium-tagged complexes that have $T_{fus} < 200\,^{\circ}C$ are summarised. Many of these compounds are identified as Ionic Liquids. Influences of the ligand, the metal ion and the anionic counterion on the melting point of the complexes are discussed. Together about 220 coordination compounds of about 100 ligands are described and shown in 11 figures.

Abbreviations: amphos, $Ph_2PCH_2CH_2NMe_3$; BBIm, 1,3-dibutylimidazolium; bipy, 2,2′-bipyridine; BMIm, 1-butyl-3-methylimidazolium; C_nIm, *N*-alkylimidazole; C_nMIm, 1-alkyl-3-methylimidazolium; EMIm, 1-ethyl-3-methylimidazolium; en, ethylene-1,2-diamine; FAP, tris(pentafluoroethyl)-trifluorphosphate; hfip, hexafluoroisopropoxy; IL, Ionic Liquid; MBz, N-methylbenzoimidazolium; MeC_{2CN}-pyr, 1-(2-cyanoethyl)-1-methyl-pyrrolidinium; MeIL, metal containing Ionic Liquid; MeMIm, 2,3-dimethylimidazolium; MePEG, oligomeric polyether; $MePEG_{350}$-, $Me(OCH_2CH_2)_7$; RTMeIL, metal containing room temperature Ionic Liquid; MIm, *N*-methylimidazolium; MIm-CH_2CO_2H, 3-carboxymethyl-1-methylimidazolium; MMIm, 1,3-dimethylimidazolium; M1Tz, 4-methyl-1,2,4-triazolium-1-yl; M4Tz, 2-methyl-1,2,4-triazolium-4-yl; NHC, *N*-heterocyclic carbene; $NH_2CH(Ph)CH(Ph)NHTos$, (1*R*,2*R*)-*N*-tosyl-1,2,-diphenylethylenediamin; $NH_2CH(Ph)CH(Ph)OH$, (1*S*,2*R*)-2-amino-1,2,-diphenylethanol; NTf_2^-, bis(trifluoromethylsulfonyl)imide; Pip, 1,1-dimethylpiperidinium; 1-Py, 1-pyridinium; Py-BMIm, 3-butyl-1-methyl-2-(2-pyridyl)-imidazolium; Py-$(CH_2)_3$CN, 1-(3-cyanopropyl)-pyridinium; Py-$(CH_2)_2CO_2H$, 1-(2-carboxyethyl)-pyridinium; TCNQ, 7,7,8,8-tetracyanoquinodimethane; Tol, toluyl; Tos, tosyl; TSIL, task-specific Ionic Liquid; WCA, weakly coordinating anion.

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1. Introduction

The melting point T_{fus} or temperature of decomposition of inorganic salts and simple coordination compounds generally exceeds a few hundred degrees. Alkali metal and earth alkali metal halides for example melt at 415 °C ($BeCl_2$) to 1477 °C (SrF_2) and coordination compounds like Prussian blue or $[Co(NH_3)_6]Cl_3$ commonly decompose before they melt. However, for quite some time salts have been noticed that melt far below those temperatures or are fused even at RT. For a long time these salts were regarded as chemical curiosities but recently with the discovery that such compounds can be air and water stable [1] chemists became more and more interested in this type of salt. Nowadays such low-melting salts are generally known as Ionic Liquids [2–8]. Convention today recognises a salt that melts below 100 °C, the boiling point of water, as IL. Ionic complexes melting below 200 °C will be classified as "low-melting" hereupon. ILs feature some specific interesting physical properties [6,8,9], like extremely low vapour pressure at RT, high ionic conductivity and electrochemical stability [10]. Especially worth mentioning are the very good solvent properties of ILs that make them popular alternative reaction media for electrochemical investigations [11], electrodeposition of reactive elements [12], organic [5,13] and inorganic synthesis [5,14], separation science [15,16], catalysis [5,13,16–19] and others [9]. In this aspect, ILs are commonly called "green solvents" as solvent evaporation is prevented and high reusability of catalytic systems is often achieved [18–20].

Unusually low melting points will generally be achieved with salts that have unusual high fusion entropies ΔS_{fus}. The fusion entropy is a function of the symmetry factor σ and the number of torsion angles τ: the lower the symmetry and the higher the number of torsion angles, the higher ΔS_{fus} and the lower the melting point T_{fus} [21]. That is why an IL cation is generally composed of an organic ion with low symmetry and side chains with especially high torsion and rotational degrees of freedom.

Common IL cations are tetraalkylammonium, tetraalkylphosphonium, 1,3-dialkylimidazolium or *N*-alkylpyridinium (Fig. 1a) [22]. Lately the variety of organic IL cations has extended and compounds have especially been designed for specific physical and/or chemical properties. These cations can, for example, be particularly polar, or be highly fluorinated, have chiral side chains, have specific functional groups or selected donor atoms for coordination chemistry. ILs with such cations are commonly known as task-specific ILs and in theory they can be optimised for a desired application [8,23]. As the variety of potential TSILs is tremendous, physical and chemical properties of TSILs are yet little explored.

IL-anions are usually monoanionic weakly coordinating anions with high distribution of charge density, to minimise resulting coulomb interactions between them and the IL cation and therefore lower the capability to form ionic pairs [24]. Approved WCAs for IL syntheses are dicyanamide $[N{\equiv}C{-}N{-}C{\equiv}N^-]$, tosylate, *n*-alkylsulfate [25], highly or perfluorinated anions like $[Al(hfip)_4]^-$ [26], bis(trifluoromethylsulfonyl)imide (NTf_2^-), trifluoromethanesulfonate or tris(pentafluoroethyl)-trifluorphosphate (Fig. 1b) [27].

Regarding properties of ILs, promising new materials have been described as metal containing ILs, so-called MeILs that additionally feature the typical characteristics of the metal ion. Although strictly speaking an IL exhibiting a main group metal ion, such as for example $[EMIm][Al(hfip)_4]$ [26] can be regarded as MeIL as well. In this review an IL is meant that contains a transition metal complex of any kind. Rare-earth containing ILs are also known (see Refs. [28–32] for some examples), but are excluded at this point. Obviously the metal centre can be introduced in both parts of the IL, the anion or the cation. MeILs of the first type usually are composed of halido or pseudohalido metallates in combination with imidazolium-based cations, the best-known examples probably being $[C_nMIm][FeCl_4]$ [33,34]. These MeILs have some very interesting additional properties, like paramagnetism, luminescence or enhancement of catalytic reactions and have been subject of specialist reviews [33–37]. Far less common are the latter type of MeILs, that contain the metal centre in their cationic part.

Two types of such MeILs are thinkable. The first has a simple cationic chromophore like e.g. $[M^{II}\mathbf{L}_n]^{2+}$ (M = transition metal) with **L** being a ligand of neutral charge. Here fused ferrocene NTf_2^--complexes [33,34] or $[Ag(en)_2]NTf_2$ and $[Zn(en)_4](NTf_2)_2$-derivatives [38], both with alkyl side chains, complexes like $[M(C_nIm)_m]X_2$ (m = 2–6, X = ClO_4, BF_4, Cl, Br, NO_3, NTf_2) [39–42]

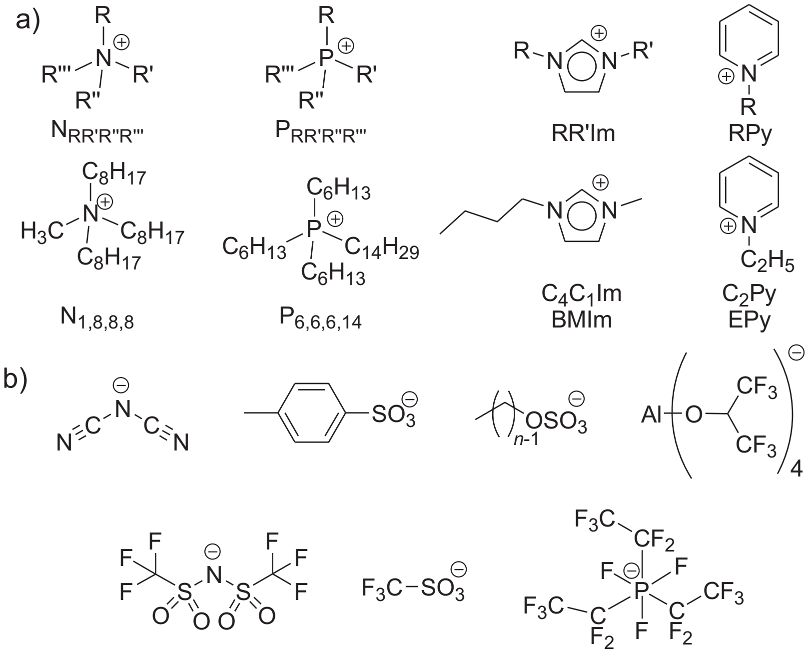

Fig. 1. Examples of (a) organic IL cations and their abbreviations (from left) tetraalkylammonium, tetraalkylphosphonium, 1,3-dialkylimidazolium and *N*-alkylpyridinium. (b) WCAs (from upper left) dicyanamide, tosylate, *n*-alkylsulfate, $[Al(hfip)_4]^-$, NTf_2^-, trifluoromethanesulfonate, FAP^-, commonly used for the preparation of ILs.