Salicylaldoxime and salen containing imidazolium ionic liquids for biphasic catalysis and metal extractions†

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Imidazolium salts containing salicylaldoxime or salen ligands readily form ionic metal complexes with copper and manganese; hence offering applications in metal extractions and biphasic catalysis.

Ionic liquids are now well entrenched in the chemical literature as potential alternative solvents.[1] They have also garnered interest in a rather wide array of potential different applications other than as solvents in chemical reactions. Among these more specialized applications is the use of ionic liquids in a variety of electrochemical scenarios such as electrolytes in batteries and fuel cells.[2] They have also seen potential application as lubricants,[3] in biomass processing[4] and even embalming.[5] Ionic liquids have been recognized for a number of their useful physical properties from both a green chemistry point of view and a purely chemical point of view. Such properties include polar, non-coordinating nature, generally low flammability due primarily to low volatility, and their ability to dissolve a range of organic and inorganic compounds.[6] Exploitation of these properties has resulted in an increased use of ionic liquids in both separations and in catalysis. In particular, ionic liquids have proven to have great potential in the extraction of metal ions from aqueous waste streams.[7] Additionally, catalysts have been successfully immobilized and recycled when used in conjunction with ionic liquids and this is well documented in a number of popular papers and review articles on the topic.[8]

A recent area of ionic liquids research receiving a considerable amount of attention is that of task specific ionic liquids (TSILs).[9] We first showed our interest in the design and preparation of so called TSILs capable of performing a specific function when we published a preliminary communication on our work in which an ethylamine diacetic acid moiety was built into an imidazolium salt.[10] These salts readily formed neutral complexes with metals such as copper(II) and therefore offered promise for the removal of metals such as copper from effluents from industrial sites.

However, in order for industry to adopt such a chelating agent it would first have to demonstrate selectivity and low cost. With these goals in mind we strived to develop a chelating ionic liquid from comparatively less expensive and readily available starting materials. Furthermore, if the chelating ligand incorporated into the ionic liquid framework was a novel modification of similar chelating agents already used in industry then we would have access to an abundance of comparative data should these new chelating ionic liquids prove successful in chelating metals of interest.

Furthermore, if the precursor to the chelating ionic liquid was versatile enough, then a range of chelating groups could be designed into the chelating ionic liquid hence demonstrating a potential range of applications such as in catalysis. Such a strategy adopted herein represents an evolution of that which we reported in our earlier paper describing the preparation of imidazolium salts containing an ethylamine diacetic acid moiety.[10] Hence, we report herein the design of chelating ionic liquids[11] which show great promise in separations and catalytic applications. Starting with the same imidazolium hexafluorophosphate salt containing a salicylaldehyde moiety we were able to prepare imidazolium salts containing either a salicylaldoxime moiety or a salen moiety. Both chelating ionic liquids are capable of forming metals complexes for which we report the single crystal X-ray structures for the copper(II) complexes.

The key starting material, **1**, was obtained through the reaction of salicylaldehyde with formaldehyde in the presence of HCl at room temperature over 1 d.[12] Compound **1** allowed the preparation of the common precursor, **2**, to both chelating ionic liquids reported herein through the quarternization reaction of methylimidazole with **1** to afford the imidazolium chloride salt (Scheme 1). This salt was then readily metathesized into the hexafluorophosphate salt, **2**, *via* reaction with aqueous hexafluorophosphoric acid, HPF_6(aq).

Preparation of the chelating salt, **3**, containing a salicylaldoxime ligand involved the formation of an oxime through the reaction of compound **2** with hydroxylamine hydrochloride in the presence of sodium hydroxide. The salicylaldoxime ligand is well established as a selective chelator for copper(II).[13] Hence we sought to demonstrate the ability of chelating salt, **3**, to form a complex with copper(II). This was accomplished by reacting a solution of **3** with copper(II) acetate monohydrate in methanol. Recrystallization of the resulting precipitate in a methanol–water mixture afforded a dark brown crystalline solid, **4**, in 70% yield.

The X-ray crystal structure of compound **4** is shown in Fig. 1.‡ The IL-bis(oxime)-Cu^{II} complex, **4**, has a square planar geometry about the copper centre with two bidentate salicylaldoxime imidazolium ligands for every copper atom. The two chelating phenolic oxygen atoms are *trans* to each other as are the chelating nitrogen atoms of the oxime moieties. The complex carries a +2 charge due to the two imidazolium cationic moieties and hence requires the presence of two hexafluorophosphate ions to aquire overall neutrality.

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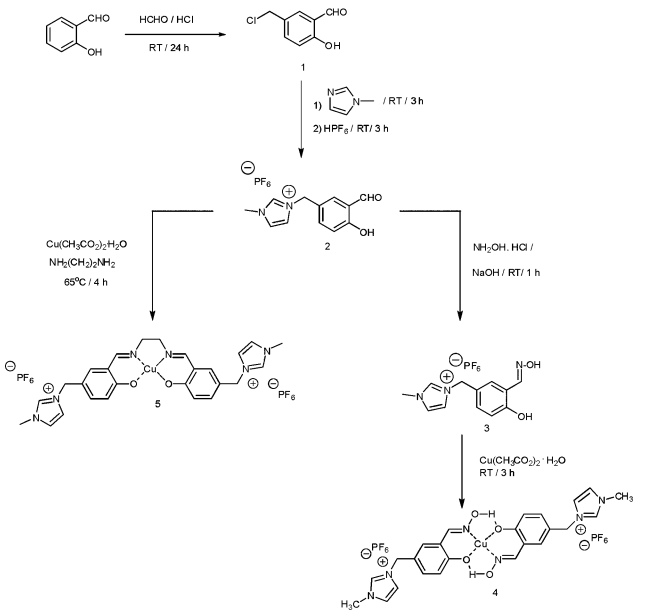


Scheme 1 Synthesis of IL-bis(oxime)-Cu^{II}, **4**, and IL-salen-Cu^{II} chelate, **5**, complexes.

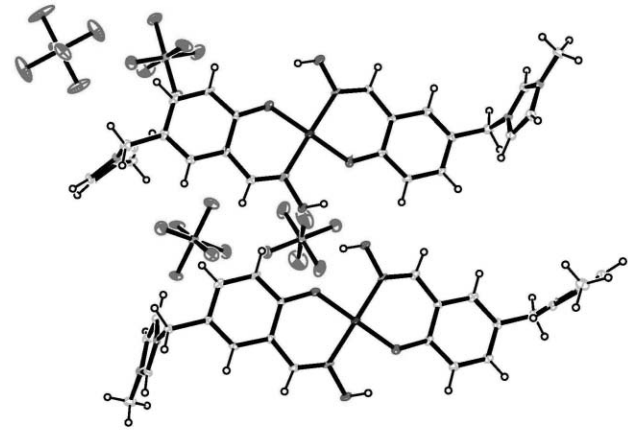


Fig. 1 ORTEP perspective of IL-bis(oxime)-Cu^{II} chelate complex, **4**. Thermal ellipsoids are drawn at 30% probability.

Preparation of the chelate complex, **5**, containing a salen ligand was accomplished directly through the reaction of the common precursor, **2**, in the presence of ethylenediamine and copper(II) acetate monohydrate in refluxing methanol (Scheme 1). This reaction afforded a 78% yield that produced crystals appropriate for X-ray diffraction upon recrystallization in a methanol–water mixture.

The X-ray crystal structure of compound **5** is shown in Fig. 2.§ The structure displays essentially a square planar geometry around the copper(II) centre. In contrast with the IL-bis(oxime)-Cu^{II} complex **4**, the chelating phenolic oxygen atoms in **5** are in a *cis* arrangement as are the two chelating nitrogen atoms. The two imidazolium cationic centres are directed away from the centre of the complex. This feature bodes well for the potential application of this type of complex in catalysis in other ionic liquids as it enhances the solubility of the complex in ionic liquids. The IL-salen-Cu^{II} complex **5** is readily soluble in a number of ionic liquids including those commonly used to immobilize catalysts (*i.e.* [bmim][BF$_4$], [bmim][PF$_6$], and [bmim]Cl where bmim = 1-butyl-3-methylimidazolium). Complex **5** is +2 overall and there are hence two hexafluorophosphate counterions.

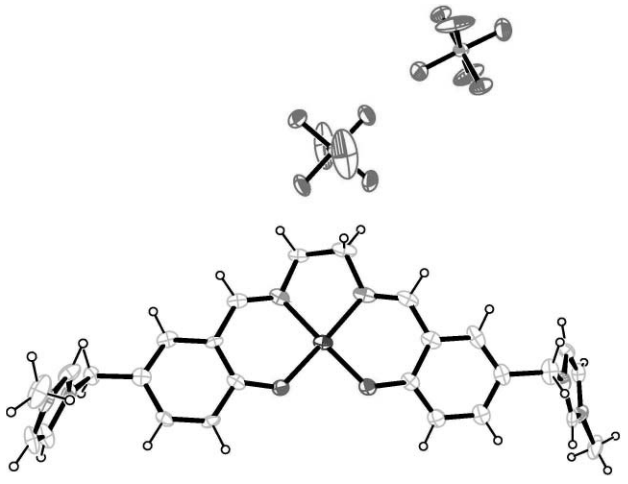
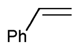
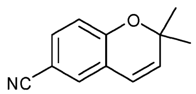
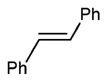
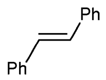
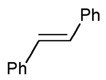


Fig. 2 ORTEP perspective of IL-salen-Cu^{II} chelate complex, **5**. Thermal ellipsoids are drawn at 30% probability.

To demonstrate the ability to use such IL-salen complexes in biphasic catalysis we have been able to prepare the Mn(III) chloride complex IL-salen-Mn^{III}-Cl, **6**, analogous to IL-salen-Cu^{II} complex, **5**. This complex was easily immobilized in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF$_6$], and used to catalyze the epoxidation of alkenes.[14] In all cases epoxidations using 10 mol% of IL-salen-Mn^{III}-Cl, **6**, as a catalyst and iodosobenzene as the oxidant provided a high yield of oxirane products (Table 1). Styrene was quantitatively epoxidized in 1 h using a 5 mol excess of iodosobenzene relative to alkene (Table 1, entry 1) while 6-cyano-2,2-dimethylchromene took 3 h to react completely (Table 1, entry 2). *trans*-Stilbene underwent a 74% conversion to the epoxide after 3 h, 90% after 6 h, and was only completely reacted after 24 h (Table 1, entries 3, 4, and 5).

Table 1 Epoxidations using IL-salen-Mn^{III}-Cl, **6**, in [bmim][PF$_6$]

Entry	Substrate	Time/h	Yield[a] (%)
1		1	100
2		3	100
3		3	74
4		6	90
5		24	100

[a] Yield determined by GC analysis.

In conclusion we have demonstrated that two different classes of ionic liquid chelate complexes can be prepared from a common precursor, **2**, that is derived from comparatively less expensive starting materials than other chelating ionic liquids that have appeared in the literature. Whereas the IL-bis(oxime)-Cu^{II} chelate complex, **4**, is related to oxime complexes used in the hydrometallurgical refinement of copper it has great promise in such an application. Given the excellent solubility of the IL-salen-Cu^{II} complex, **5**, and IL-salen-Mn^{III}-Cl, **6**, in various ionic liquids commonly used in catalytic applications it is likely that complexes containing the IL-salen ligand will have great potential for use in such instances. It is antipicated that a number of other metals can be incorporated into IL-salen-metal complexes of this class and that these could be immobilized in ionic liquid solvents to a greater extent than traditional catalysts.

We are actively pursuing the ability of the IL-bis(oxime)-metal complexes to extract metals from aqueous systems and are applying the use of the IL-salen-metal complexes in catalytic applications. Details of these studies will be a topic of forthcoming full accounts.

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Notes and references

‡ Crystal data and structure refinement for IL-bis(oxime)-Cu^{II} chelate complex, **4**. Empirical formula $C_{24}H_{26}CuF_{12}N_6O_4P_2$; formula weight 815.99; temperature 100(2) K; wavelength 0.71073 Å; crystal system: triclinic; space group $P\bar{1}$; unit cell dimensions a = 10.115(4) Å, α = 70.115(8)°, b = 18.066(7) Å, β = 85.613(8)°; c = 18.153(6) Å, γ = 74.682(7)°; volume 3008.5(19) Å^3; $Z = 4$; density (calculated) 1.802 Mg m^{-3}; absorption coefficient 0.952 mm^{-1}; $F(000)$ 1644; crystal size 0.20 × 0.15 × 0.10 mm; theta range for data collection 1.19 to 28.31°; index ranges $-13 \le h \le 13$, $-23 \le k \le 20$, $-20 \le l \le 23$; reflections collected = 17 825; independent reflections = 13 69 [R(int) = 0.0544]; completeness to theta = 26.00°, 97.1%; refinement method = full-matrix least-squares on F^2; data/restraints/parameters 13069/0/891; goodness-of-fit on F^2 = 0.965; final R indices [$I > 2\sigma(I)$] $R1 = 0.0802$, $wR2 = 0.1615$; R indices (all data): $R1 = 0.1574$, $wR2 = 0.2037$; largest diff. peak and hole = 0.906 and −0.735 e Å^{-3}.

§ Crystal data and structure refinement for IL-salen-Cu^{II} chelate complex, **5**. Empirical formula $C_{26}H_{28}CuF_{12}N_6O_4P_2$; formula weight 842.02; temperature 100(2) K; wavelength 0.71073 Å; crystal system: monoclinic; space group $P2(1)/c$; unit cell dimensions: a = 8.492(4) Å, b = 10.988(5) Å, β = 91.442(12)°, c = 35.208(17) Å; volume = 3284(3) Å^3; $Z = 4$; density (calculated) = 1.703 Mg m^{-3}; absorption coefficient = 0.875 mm^{-1}; $F(000)$ 1700; crystal size 0.35 × 0.20 × 0.10 mm; theta range for data collection 1.16 to 25.23°; index ranges $-7 \le h \le 10$, $-10 \le k \le 12$, $-42 \le l \le 36$; reflections collected = 12988; independent reflections = 5754 [R(int) = 0.1029]; completeness to theta = 25.23°, 96.9%; absorption correction semi-empirical from equivalents; max. and min. transmission 1.000 and 0.480; refinement method = full-matrix least-squares on F^2; data/restraints/parameters 5754/0/462; goodness-of-fit on F^2 = 1.106; final R indices [$I > 2\sigma(I)$], $R1 = 0.1151$, $wR2 = 0.2477$; R indices (all data) $R1 = 0.2015$, $wR2 = 0.2935$; largest diff. peak and hole 0.896 and −0.555 e Å^{-3}.

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