Coordination chemistry of the bis(trifluoromethylsulfonyl)imide anion: molecular interactions in room temperature ionic liquids

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Room temperature ionic liquids composed of bis(trifluoromethylsulfonyl)imide anions and 1,3-ethylmethylimidazolium (EMI) cations are shown to stabilize monomeric ligand deficient transition metal complexes *via* four distinct binding modes: monodentate nitrogen or oxygen coordination and/or bidentate oxygen–oxygen′ or nitrogen–oxygen coordination (η^1–N, η^1–O, η^2–O,O′ and η^2–N,O).

Room temperature ionic liquids (RTILs) are being actively investigated as alternative solvent media in synthesis,[1] catalysis,[2] separations,[3] and electrochemistry.[4] A primary motivation of these studies is the desire to develop clean chemical processes that take advantage of the unique properties of RTILs such as their non-volatility and electrical conductivity. These solvent systems also offer a novel chemical environment that may uniquely influence the course of chemical reactions compared to traditional solvents.[5] In applications involving dissolved metal species, interaction of either the ionic liquid cation[6] or anion[7] with the metal complex may in fact control or strongly influence its chemical behaviour. However, the coordination chemistry of ligand deficient metal complexes dissolved in ionic liquid solvents remains almost completely unknown.

Recently, organic salts of the bis(trifluoromethylsulfonyl)imide anion ($^-$N(SO$_2$CF$_3$)$_2$; abbreviated as $^-$NTf$_2$) have emerged as perhaps the most generally useful RTILs because of their relatively low viscosity, excellent thermal and chemical stability, and their ease of synthesis.[8] Although $^-$NTf$_2$ typically behaves as a weakly or non-coordinating anion,[9,10] in the absence of more competent ligands, discreet complexes may be formed. This work describes the preparation of four new transition metal complexes of the $^-$NTf$_2$ anion. These complexes were specifically chosen for presentation in order to illustrate the range of $^-$NTf$_2$–metal binding modes identified to date and to address the more general question of how ionic liquid solvents might influence the chemical and electrochemical behaviour of ligand deficient metal species.

Ligand deficient metal complexes may be accessed in ionic liquid solvents either by treatment of metal alkyl or hydride complexes with HNTf$_2$ (liberating alkane or hydrogen) or by metathesis of metal halide complexes with AgNTf$_2$.[11] For example treatment of a bright yellow solution of (C$_5$H$_5$)Fe(CO)$_2$Me in [EMI]NTf$_2$ with HNTf$_2$ rapidly yields a deep red solution from which bubbles of methane are liberated. The same species is identified by ionic liquid phase IR spectroscopy upon reaction of (C$_5$H$_5$)Fe(CO)$_2$I with AgNTf$_2$. The new complex, assigned as (C$_5$H$_5$)Fe(CO)$_2$(NTf$_2$) (**1**)

displays ν(CO) bands in the solution phase IR spectrum shifted to significantly higher energy compared to the parent chloride complex, consistent with the weak donor ability of the $^-$NTf$_2$ anion.[12,13]

Reactions carried out in weakly coordinating molecular solvents such as dichloromethane or benzene have allowed the isolation of single crystals suitable for structural determination. We note that analysis of these solutions by IR spectroscopy gives identical ν(CO) bands as compared to the ionic liquid reactions. A thermal ellipsoid plot of **1** is shown in Fig. 1(a). The (C$_5$H$_5$)(CO)$_2$Fe fragment, characterized by typical bond lengths and angles, is directly coordinated to the nitrogen atom of the $^-$NTf$_2$ anion with an Fe–N bond length of 2.084(4) Å. Comparison of the structural parameters for simple $^-$NTf$_2$ salts[14] and the $^-$NTf$_2$ ligand in **1** reveals that the N–S bond lengths become significantly longer upon nitrogen coordination (N(1)–S(1) and N(1)–S(2) are 1.630(4) and 1.643(4) Å, respectively *versus* 1.56–1.57 in the free anion). Further, the S–N–S angle becomes more acute in the complex (117° *vs.* 125°), although the S–O bond lengths remain short at *ca.* 1.42 Å. Similar changes in metrical parameters are seen in the comparison of HNTf$_2$ and the uncomplexed anion.[14] Using analogous procedures, complexes (C$_5$H$_5$)$_2$Ti(NTf$_2$)$_2$ (**2**), [(Me$_2$Si(η-C$_5$Me$_4$)(N-t-Bu)]Ti(NTf$_2$)$_2$ (**3**) and (cymene)–Ru(NTf$_2$)$_2$ (**4**) were each prepared and structurally characterized.‡

Fig. 1(b) depicts a thermal ellipsoid plot of **2**, illustrating a typical titanocene fragment coordinated to two $^-$NTf$_2$ ligands through a monodentate metal–oxygen binding mode. The titanium–oxygen bond lengths of 2.050(3) and 2.067(3) Å are within the limits of normal Ti–O σ-bonds. Significant structural changes are observed in the $^-$NTf$_2$ ligands compared to the free anion, though these changes are of a different nature compared to **1** (*e.g.* **A** below). The S–O bond lengths of the titanium bound oxygen atoms, O(1) and O(5), are lengthened to 1.467(4) and 1.468(3) Å compared to the remaining S–O bond lengths, which remain short (*ca.* 1.42 Å). The N–S bond lengths in **2** reveal significant distortion indicated by a pair of short (N(1)–S(1) = 1.523(5) and N(2)–S(3) = 1.542(4) Å) and a pair of long (N(1)–S(2) = 1.613(5) and N(2)–S(4) = 1.605(4) Å) distances that are represented by structure **B** below.[15]

A   **B**
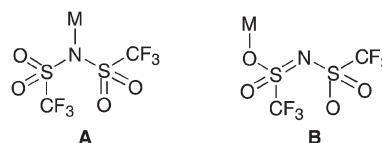
Thermal ellipsoid plots of **3** and **4** are shown in Figs. 1(c) and (d). The "constrained geometry" ligand in **3** serves to reduce steric
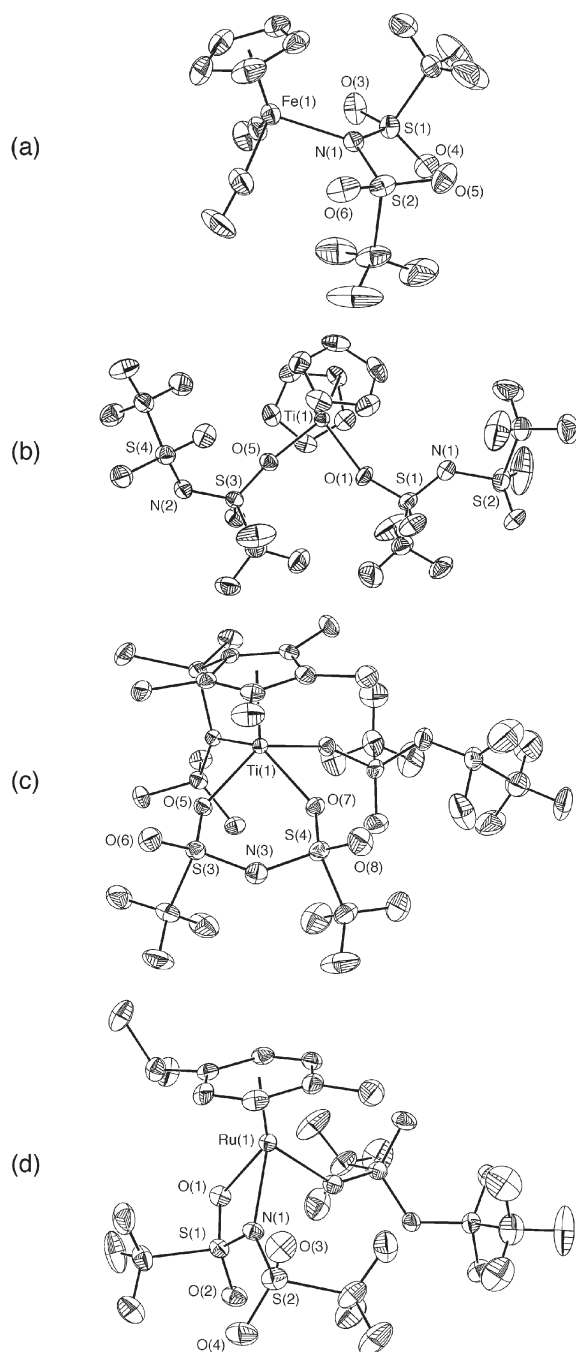
Fig. 1 Thermal ellipsoid plots of (a) $(C_5H_5)Fe(CO)_2NTf_2$ (**1**), (b) $(C_5H_5)_2Ti(NTf_2)_2$ (**2**), (c) $[Me_2Si(\eta-C_5Me_4)(N\text{-}t\text{-}Bu)]Ti(NTf_2)_2$ (**3**), (d) (cymene)Ru(NTf_2)_2 (**4**). Hydrogen atoms have been omitted for clarity. Only one contribution of the disordered components of a $^-NTf_2$ ligand in complexes **2** and **3** is shown.

saturation around the titanium metal center compared to **2** resulting in both monodentate and bidentate oxygen coordinated $^-NTf_2$ anions. Similarly for complex **4**, a sterically saturated (cymene)Ru fragment should also support three binding sites. In this case a monodentate oxygen bound anion is obtained in addition to a chelating η^2–N,O coordinated anion. For both **3** and **4**, metrical parameters for the η^1–O–NTf_2 anion are quite similar to those already described for complex **2**. The

bidentate η^2–O,O′–NTf_2 ligand is locked in a cisoid configuration in which the two trifluoromethyl groups eclipse one another.[16] Delocalization of negative charge across the O–S–N–S–O chelate is indicated by the observed bond lengths and their comparison to complexes **1** and **2** (**3**: S(3)–O(5) = 1.4497(32), S(4)–O(7) = 1.4435(34), N(3)–S(3) = 1.5512(45), N(3) = S(4) = 1.5722(42) Å). Delocalized charge is further indicated by weaker coulombic interactions compared to the monodentate anion as reflected in the respective Ti–O bond lengths (Ti(1)–O(1), –O(5), –O(7) = 2.0795(32), 2.1372(31), and 2.1500(34) Å).

Complex **4** is supported by an η^2–N,O coordinated anion. As observed for $(C_5H_5)(CO)_2Fe(NTf_2)$ and $(CO)_2Cu(NTf_2)$,[17] soft metal centers including the (cymene)Ru fragment are expected to prefer nitrogen coordination over oxygen. Complications of steric demand apparently prevent two nitrogen bound anions from being accommodated in **4**. For the η^2–N,O–NTf_2 anion, a stronger ruthenium–nitrogen interaction is indicated by the comparison: Ru(1)–N(1) = 2.166(5) *vs.* Ru(1)–O(1) = 2.252(5) Å. Key bond lengths in **4** include: S(1)–O(1) = 1.449(5), S(1)–N(1) = 1.604(6), N(1)–S(2) = 1.625(6), S–O_avg (uncoordinated) = 1.414(5) Å.

This work demonstrates that ligand deficient metal complexes can be stabilized in ionic liquid solvents by coordination to the $^-NTf_2$ anion through a range of nitrogen and/or oxygen binding modes depending on the electronic and steric demands of the metal center. Recognition of the coordinating properties of RTIL solvents is important for a proper understanding of the behaviour of metallic species in catalytic applications, as well as in separations and electrochemistry. For example metal complexes stabilized by the $^-NTf_2$ anion are rendered significantly more electrophilic compared to analogous halide species with resulting profound effects on the reduction potential of metal ions and complexes dissolved in this medium. Comparison of the Ti(IV)/Ti(III) couple for ionic liquid solutions of $(C_5H_5)_2TiCl_2$ and **2** reveals a remarkable shift in $E_{1/2}$ from −1.031 to −0.103 V *versus* the ferrocene/ferrocenium couple upon substitution of chloride for $^-NTf_2$. The anion substitution causes a stabilization of the metal-based LUMO by 0.93 V and produces a significantly more electrophilic metal species.

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Notes and references

‡ *Crystal data* for **1**, $C_9H_5F_6FeNO_6S_2$: $M = 457.11$, $T = 203(2)$ K, trigonal, space group $P3_221$, $a = 9.1524(14)$, $c = 31.283(7)$ Å, $V = 2269.4(7)$ Å^3, $Z = 6$, μ(Mo–Kα) = 1.371 mm^{-1}, 12 400 reflections, 2177 unique ($R_{int} = 0.0523$), $R1 = 0.0362$ [$I > 2\sigma(I)$], GOF = 1.689, CCDC 255447. *Crystal data* for **2**, $C_{14}H_{10}F_{12}N_2O_8S_4Ti$: $M = 738.38$, $T = 203(2)$ K, triclinic, space group $P\bar{1}$, $a = 9.862(3)$, $b = 10.505(3)$, $c = 12.736(4)$ Å, $\alpha = 94.226(5)$, $\beta = 109.178(4)$, $\gamma = 92.533(5)°$, $V = 1239.5(6)$ Å^3, $Z = 2$, μ(Mo–Kα) = 0.818 mm^{-1}, 6429 reflections, 3305 unique ($R_{int} = 0.0227$), $R1 = 0.0517$ [$I > 2\sigma(I)$], GOF = 1.407, CCDC 255448. *Crystal data* for **3**, $C_{22}H_{34}F_{12}N_3O_8S_4SiTi$: $M = 900.75$, $T = 203(2)$ K, triclinic, space group $P\bar{1}$, $a = 10.244(3)$, $b = 12.187(3)$, $c = 15.560(4)$ Å, $\alpha = 92.299(5)$, $\beta = 102.362(4)$, $\gamma = 114.124(4)°$,

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16 A similar coordination mode has been identified for homoleptic Zn(NTf$_2$)$_2$ in ref 7. The solid state structure consists of bidentate O,O′–NTf$_2$ anions that also link adjacent metal centers through a third oxygen atom to form chains of six-coordinate Zn(II) ions.

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