Thermochromism and switchable paramagnetism of cobalt(ii) in thiocyanate ionic liquids


Published in:
Dalton Transactions

Document Version:
Publisher's PDF, also known as Version of record

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

Publisher rights
This journal is © The Royal Society of Chemistry 2015. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence (https://creativecommons.org/licenses/by/3.0/), which permits unrestricted use, distribution and reproduction in any medium, provided the author and source are cited.

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen’s institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person’s rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.
Thermochromism and switchable paramagnetism of cobalt(II) in thiocyanate ionic liquids†

Stephen J. Osborne,a‡ Sil Wellens,b Chris Ward,c Solveig Felton,a† Robert M. Bowman,c Koen Binnemans,b Małgorzata Swadżba-Kwaśny,a H. Q. Nimal Gunaratnea and Peter Nockemann*a

Temperature-dependent switching of paramagnetism of a cobalt(II) complex is observed in an ionic liquid solution. Paramagnetic and thermochromic switching occur simultaneously due to a reversible change in coordination. This reversible switching is possible in the ionic liquid solution, which enables mobility of thiocyanate anions by remaining mobile at low temperatures and acts as an anion reservoir.

Magnetic ionic liquids (MILs) have intrinsic paramagnetic properties that can originate from the cation, the anion or both.1–4 These properties derive from MILs containing high effective concentrations of metal centres, which can be transition metals or lanthanides.5,6 1-Methyl-3-butylimidazolium tetrachloroferrate(III), [C4mim][FeCl4], was the first MIL containing magneto-active metal complex anions with antiferromagnetic ordering.7,8 Other MIL systems have since been widely investigated.1,9–12 While ionic liquid systems with thermochromism related to changes in coordination of the metal centre have previously been reported, this has either been in the presence of additives or molecular solvents, or the magnetic properties were not investigated.13–17

Here, we report on solutions of cobalt(II) isothiocyanate in thiocyanate ILs that show reversible switching of the cobalt(II) speciation from tetrahedral [Co(NCS)4]2− at room temperature to octahedral [Co(NCS)6]4− at temperatures around 233 K. These temperature-dependent changes in the coordination environment are accompanied by reversible changes in colour (blue to red) and by significant changes of the effective magnetic moment of these fluids. The IL acts as a reservoir for the thiocyanate anions, enabling a reversible equilibrium, which in turn results in a reversible temperature-dependent switching of the coordination environment; hence a reversible switching of the magnetic moment. The main difference to previous studies is that we present a fully self-contained simple ionic liquid thermochromic and magnetically switchable system.

Peppel et al. have reported on stoichiometric compounds of [Co(NCS)4]2− ion with either [C2mim]− (1-ethyl-3-methylimidazolium) or [C4mim]+ (1-butyl-3-methylimidazolium) cations, which form bright blue metal-containing ILs with very low glass transition temperatures (around 206 K), a relatively low viscosity and an expected paramagnetic behaviour.18 However, the solutions of cobalt(II) isothiocyanate in the thiocyanate IL, we report here, contain additional mobile thiocyanate anions surrounding the metal complexes; there is thus a large excess of thiocyanate ions with respect to cobalt(II) ions present.

The tetrahedral [Co(NCS)4]2− complex that is found in the IL solutions at room temperature and down to 233 K, has a characteristic bright blue colour. UV-Vis absorption spectra of a thin film of the liquid solutions of 1 equivalent of cobalt(II) thiocyanate in 10 equivalents of [C2mim][SCN] (1) and a solution of cobalt(II) thiocyanate in [C4mim][SCN] (2), have been recorded at temperatures ranging from 293 K to 203 K (see Fig. 2 for (2); (1) is shown in Fig. 1-ESI†). A high dilution was chosen due to the high absorbance of cobalt(II), even in thin films. The same colour changes can also be observed for more concentrated systems with 1 : 4 mixtures (equivalents cobalt : equivalents IL), but not for 1 : 2 mixtures, nor in other solvents with thiocyanate excess (more information in ESI†).

The UV-Vis absorption spectra of the solutions (1) and (2) at room temperature exhibit a strong absorption band at 630 nm (15 870 cm−1), with a shoulder with weaker absorptions at 618 nm (16 181 cm−1) and 592 nm (16 890 cm−1). These bands correspond to the characteristic transitions of tetrahedral...
cobalt(II) from the $^4A_2$ ground state to the excited states $^4T_2$, $^4T_1(F)$, and $^4T_1(P)$, in order of increasing energy.

Upon cooling of the IL solution, the coordination of cobalt(II) changes from a tetrahedral to an octahedral environment at 233 K, and the coordinative transition is accompanied by a colour change from bright blue to bright red (see Fig. 1). There is a sole example in the literature that reports on the structural characterisation of an octahedral, bright red [Co(NCS)$_6$]$^{4-}$ complex. Upon cooling, shoulders at 2123 and 2090 cm$^{-1}$ appear, which can be assigned to the C–N stretching frequencies of six-coordinate octahedral cobalt(II), in accordance with reported analogue nickel(II) hexaisothiocyanate complexes. Changes in the S–C stretching vibration region upon cooling are less distinct with a disappearing band at 880 cm$^{-1}$ (w) and a shift from 747 (w) to 753 cm$^{-1}$ (w).

The effective magnetic moment that Peppel et al. reported for the [Co(NCS)$_4$]$^{2-}$ ion in the [C$_4$mim]$^+$ ILs is $\mu_{\text{eff}} = 4.40 \mu_B$ in the range 2–333 K, which is typical for a high-spin cobalt(II) system ($S = 3/2$; spin-only value $\mu_{\text{eff}} = 3.87 \mu_B$). No change in effective magnetic moment as a function of temperature was reported. In our study, the temperature-dependent magnetisation of solutions of cobalt(II) isothiocyanate in thiocyanate ILs was measured in the range 180 K to 330 K by SQUID magnetometry (Fig. 3 and 4-ESI†).

The ionic liquid acts as a reservoir of thiocyanate anions enabling the reversible coordinative change from tetrahedral to octahedral isothiocyanate environment of cobalt(II). Upon cooling, a change in effective moment is observed from the high-temperature values of 3.4(2)$\mu_B$ and 3.2(2)$\mu_B$ to low temperature values of $\mu_{\text{eff}} = 4.5(2)\mu_B$ and 4.0(2)$\mu_B$ for samples (1) and (2), respectively.
Conclusions

Solutions of cobalt(II) isothiocyanate in 1-alkyl-3-methyl-imidazolium thiocyanate ILs show reversible switching of the coordination of cobalt(II) from a tetrahedral [Co(SCN)4]2− environment at ambient temperature to an octahedral [Co(SCN)6]4− coordination at temperatures below 230 K. This temperature-dependent change in coordination is correlated with a reversible change in colour (blue to red), showing typical UV-Vis spectral transitions for tetrahedral and octahedral coordination. The most prominent consequence is reversible switching of the effective magnetic moment in such ionic liquid solutions. The observed equilibrium between the two coordination modes can be interpreted in terms of an entropic effect. This effect is also cation-dependent and has only been observed for imidazolium cations, whereas larger phosphonium cations such as [P666(14)]+ do not feature this behaviour, and even small changes such as an ethyl/butyl chain on the cation results in major differences in behaviour. The ILs provide a reservoir for the anions, that enables mobility of the thiocyanate anions in the liquid state over a wide temperature range. The system studied here are fully self-contained simple ionic liquid systems, where paramagnetic and thermochromic switching occur simultaneously due to a reversible change in coordination of the Co(II) centre. This observation could pave the way towards novel stimuli-responsive self-contained, non-volatile liquid materials.

Acknowledgements

P.N. and S.F. thank the Royal Society for a Research Grant (RG130739). This research was supported by the Flemish Institute for the Promotion of Innovation by Science and Technology (IWT Vlaanderen) via a Baekeland PhD fellowship to Sil Wellens (IWT 090272) and by Umicore Group Research. The authors also acknowledge financial support by the FWO-Flanders (Research Community “Ionic Liquids”). We thank Seagate Technology (Ireland) for their financial support to establish ANSIN (http://www.ansin.eu).

Notes and references


