Thermochromism and Switchable Paramagnetism of Cobalt(II) in Thiocyanate Ionic Liquids

Stephen Osborne,[a,d] Sil Wellens,[b] Chris Ward,[c] Solveig Felton,[c*] Robert M. Bowman,[c]

Koen Binnemans,[b] Małgorzata Swadźba-Kwaśny,[a] H.Q. Nimal Gunaratne,[a]

Peter Nockemann [a*]

a. The QUILL Research Centre, School of Chemistry and Chemical Engineering, David Keir Building,
    Queen's University Belfast, Stranmillis Road Belfast BT9 5AG, United Kingdom
b. Department of Chemistry, KU Leuven, Celestijnenlaan 200F P.O. Box 2404, B-3001 Leuven, Belgium
c. Centre for Nanostructured Media, School of Mathematics and Physics, Queen's University Belfast,
    Belfast, BT7 1NN, United Kingdom
d. Current address: Atomistic Simulation Centre, School of Mathematics and Physics, Queen's
    University Belfast, Belfast, BT7 1NN, United Kingdom

Experimental

General Procedure for Recording Low Temperature UV/Vis Spectra

An Oxford Instruments Optistat DN2 was placed into a PerkinElmer Lambda 950 UV/Vis spectrometer, modified to accommodate the low temperature cell. The cell was aligned to the spectrometer beam, a blank taken. The sample was then placed into the cuvette holder and the room temperature spectra recorded. The cell was then cooled to 180 K for 1.5 hours. Every time the temperature was increased the sample was allowed to equilibrate for 30 minutes before a spectrum was recorded. Spectra were analysed using eFTIR software for PC.

Preparation of solutions

$Co(NCS)_2 \cdot 4H_2O$ (purchased from Sigma Aldrich) was added in the respective molar ratio 1:4 or 1:10 to the ionic liquids [C_2mim][SCN] or [C_4mim][SCN] (purchased from IoLiTec, Germany), respectively, which were placed in a round bottom flask equipped with a magnetic stirrer bar. The addition caused an almost instant colour change to a

deep blue solution. The mixture was left to stir for 2 hours and any water was removed under reduced pressure at 40°C, followed by high vacuum at 60°C for 6 hours.
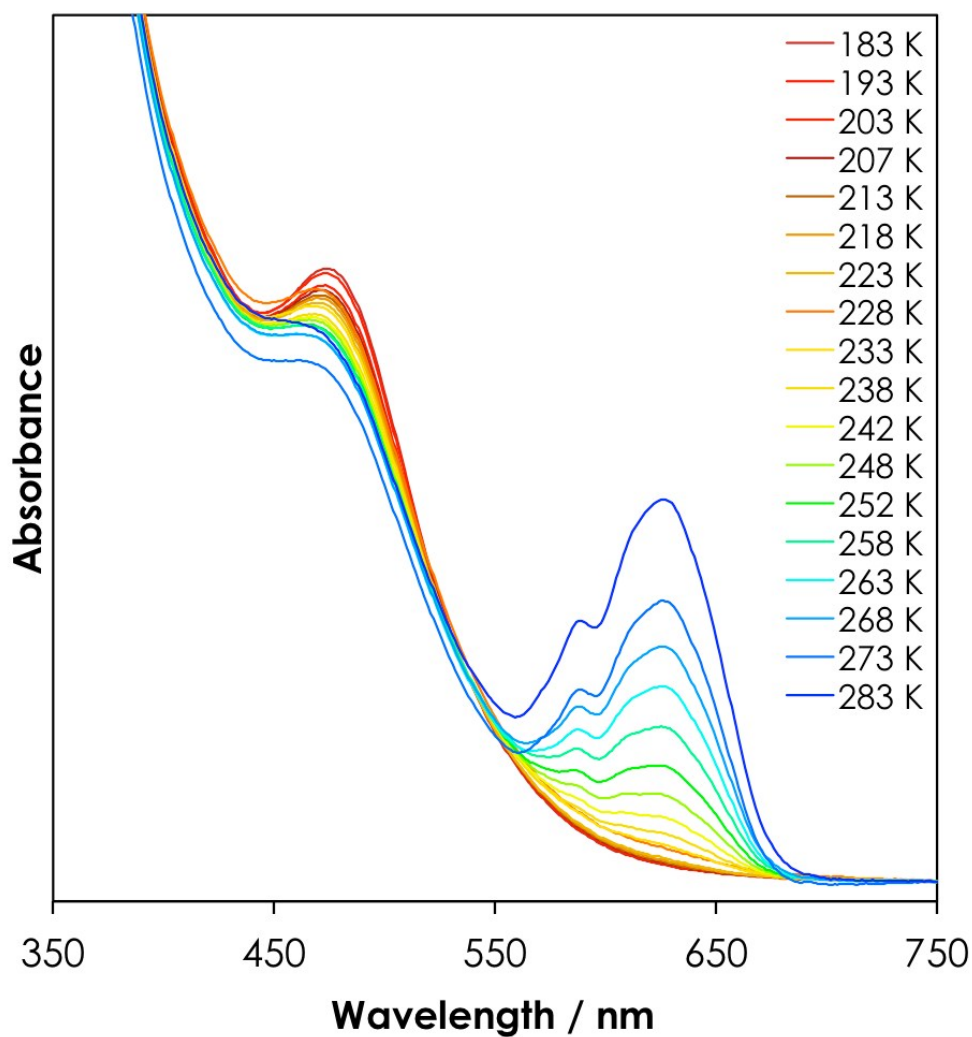

Figure 1-SI: Temperature-dependent UV-Vis absorption spectra of cobalt(II) thiocyanate dissolved in 1-ethyl-3-methylimidazolium thiocyanate, [C$_2$mim][SCN]. The strong absorption band around 630 nm corresponds to the tetrahedral [Co(NCS)$_4$]$^{2-}$, whereas the transition around 472 nm corresponds to [Co(NCS)$_6$]$^{4-}$.
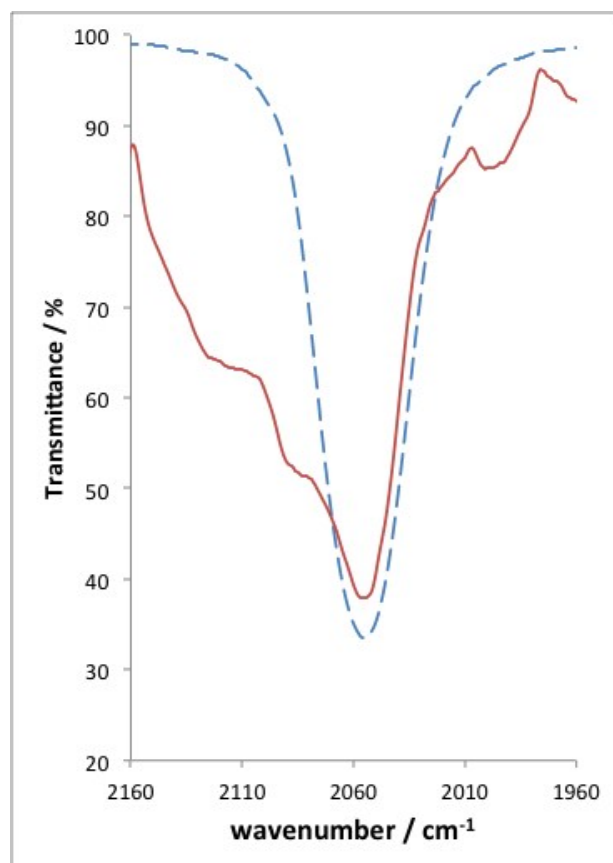
Figure 2-SI: A fragment of the IR spectra of cobalt(II) thiocyanate dissolved in 1-ethyl-3-methylimidazolium thiocyanate, [C₄mim][SCN], recorded at ambient temperature (blue line) and below 233 K (red line). Transmittance is normalised.
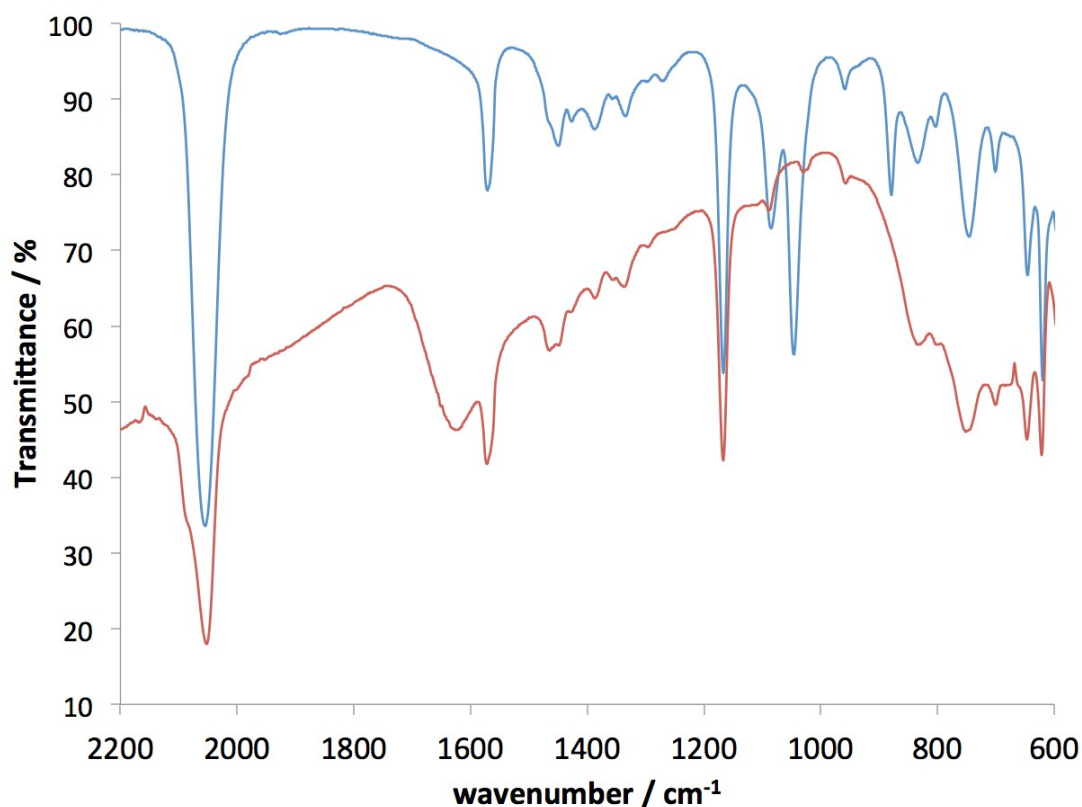
Figure 3-SI: IR spectra of cobalt(II) thiocyanate dissolved in 1-ethyl-3-methylimidazolium thiocyanate, [C$_4$mim][SCN], recorded at ambient temperature (blue line) and below 233 K (red line).

Magnetic measurements were carried out with a MPMS Quantum Design DC SQUID at a fixed field of 500 Oe. Samples were introduced at room temperature and allowed to equilibrate at 330 K before cooling at a rate of 0.5 K min^{-1} down to 180 K and then returning to 330 K at the same rate. Figure 4-SI shows the typical cooling and heating rates.
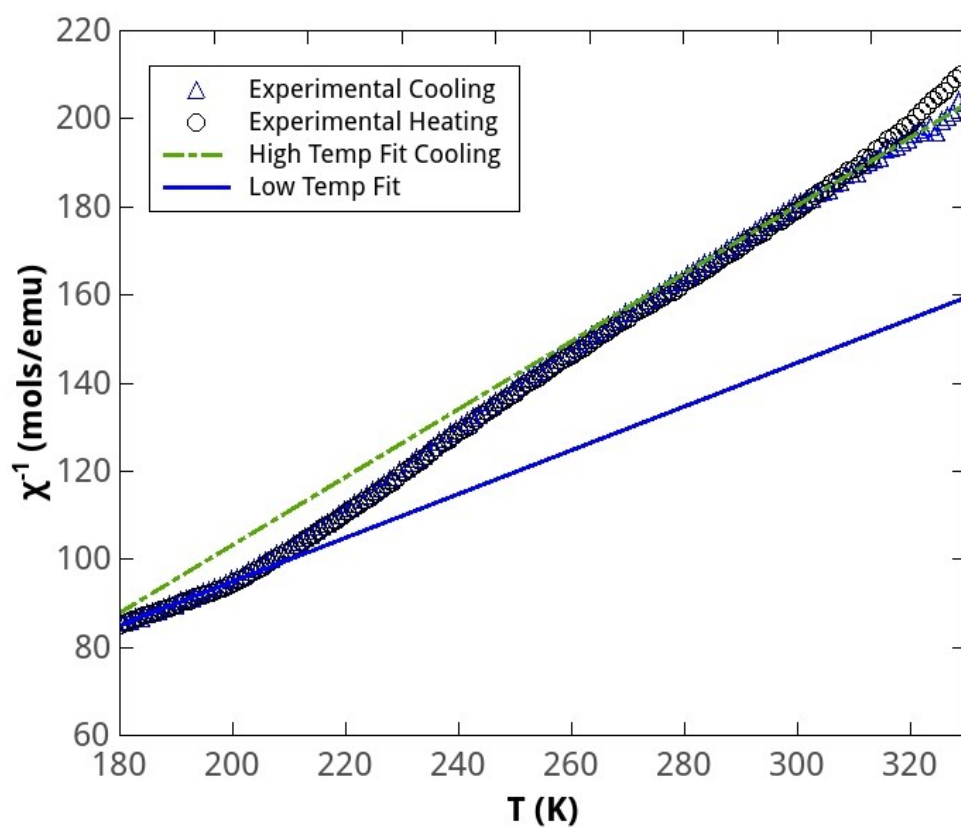
Figure 4-SI: Magnetic susceptibility measurements for sample (**2**) in the temperature range from 180 K to 330 K. The circles and triangles represent the experimental data collected on heating and cooling, and the lines show the Curie-Weiss fits used to determine the effective magnetic moments.

The thermochromism has not been observed for the systems (**1**) and (**2**) in the presence of the solvents water, methanol, ethanol and acetonitrile.
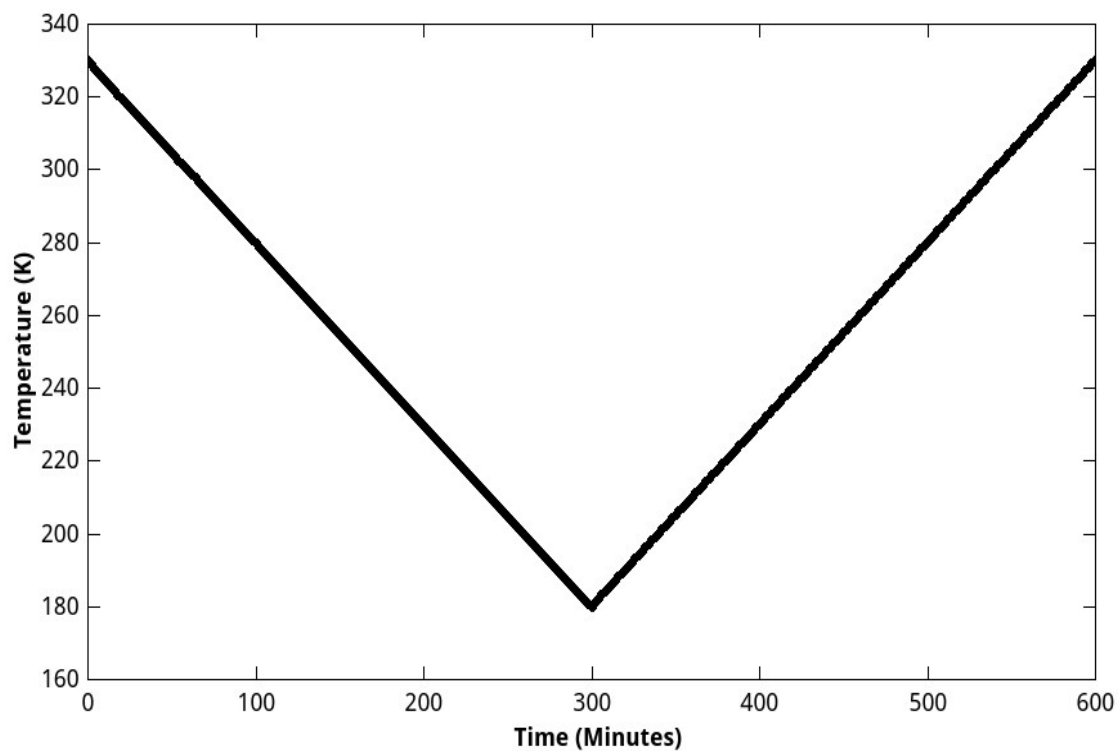
Figure 5-SI : Cooling and heating profile during magnetic measurement of cobalt(II) thiocyanate dissolved in 1-ethyl-3-methylimidazolium thiocyanate, [C$_4$mim][SCN]. Measurement begins at 330 K proceeds with a rate of 0.5 K min^{-1}, down to 180 K and then back to 330 K.

The diamagnetic contribution was calculated for the samples using the Pascal's constants method. This resulted in a correction factor of 0.07 µB, less than our quoted uncertainty.