Supplementary Material

Syntheses

Dithiocarbonate 3b. The trithiocarbonate\(^1\) 3a (0.3130 g, 1.16 mmol) is added to a solution of mercuric acetate (0.8070 g, 2.54 mmol) in a mixture of CH\(_3\)COOH/CHCl\(_3\) (3/1 v/v, 17.0 ml) and the solution stirred for 2.5h at rt. The white suspension is filtered on Celite and the filtrate evaporated under vacuum to afford a white solid, dissolved in CHCl\(_3\). The chloroform solution is extracted with H\(_2\)O, dried on MgSO\(_4\) and concentrated, affording 3b as white crystals (0.2447 g, yield 85%), m.p. 137–138°C (Litt.\(^{ii}\) 138–140°C). \(^1\)H NMR (CDCl\(_3\), TMS) \(\delta\): 4.05 (t, 2H); 2.98 (t, 2H) ppm. IR (KBr) \(\nu\)C=O = 1658 cm\(^{-1}\). Elem. Anal. Calc. for C\(_7\)H\(_8\)O\(_2\)S\(_4\) (Found) : 33.31 (33.20), 3.19 (3.22) %.

\((nBu_4N)(I)\)•DMF. To a solution of dithiocarbonate 3b (0.1179 g, 0.48 mmol) in distilled MeOH (20 ml) is added Bu\(_4\)NOH 1M (1.05 ml, 1.05 mmol). After stirring for 1h, NiCl\(_2\)•6H\(_2\)O (55.6 mg, 0.24 mmol) is added. The suspension is stirred for 10 mn and filtered. The brown solid is washed with MeOH and dried. It is soluble in CH\(_3\)CN, CH\(_2\)Cl\(_2\) and DMF. Recrystallization by Et\(_2\)O vapour diffusion on a DMF solution afforded the \(nBu_4N^+\) salt as DMF solvate, \((nBu_4N)(I)\)•DMF (0.195 g, 75%). Elem. Anal. Found: C, 45.32; H, 7.18; N, 2.95. C\(_{31}\)H\(_{59}\)N\(_2\)NiO\(_3\)S\(_8\) (MW = 823.04 g/mol) requires C, 45.24; H, 7.23, N, 3.40 %. UV-vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}}\) = 900 nm.

\([Ni(DMF)_6][I]\)\(_2\). A solution a \((nBu_4N)(I)\)•DMF (10.0 mg, 0.012 mmol) in CH\(_3\)CN (2.0 ml) is added to a solution of Ni(ClO\(_4\))\(_2\)•6H\(_2\)O (31.3 mg, 0.08 mmol) in CH\(_3\)CN (2.0 ml) and left unstirred for one day. The black precipitate is filtered and washed with CH\(_3\)CN. Recrystallization by Et\(_2\)O vapour diffusion on a DMF solution afforded needle-shaped crystals which analyse as \([Ni(DMF)_6][I]\)\(_2\). Elem. Anal. Found: C, 33.24; H, 4.86; N, 5.48. C\(_{42}\)H\(_{70}\)Ni\(_5\)O\(_{10}\)S\(_{16}\) (MW = 1508.1780 g/mol) requires C, 33.45; H, 4.68; N, 5.57 %.

Electronic Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry 2011
[NiCl(DMF)₂][I]•(2DMF,Et₂O). A solution of (nBu₄N)(I)•DMF (10.0 mg, 0.012 mmol) in CH₃CN (2 ml) is mixed with a solution of NiCl₂•6H₂O (10.5 mg, 0.042 mmol) in MeOH (0.5 ml). The filtered solution was left for two days while a black precipitate appears. The black precipitate is filtered and washed with CH₃CN. Recrystallization by Et₂O vapour diffusion on a DMF solution afforded prismatic crystals (11.4 mg, 55%), identified from X-ray diffraction as a DMF/Et₂O solvate formulated as [NiCl(DMF)₂][I]•(2DMF,Et₂O). Elem. Anal. Found: C, 32.45; H, 5.16; N, 6.04, compatible with the loss of Et₂O molecule. [NiCl(DMF)₂][I]•2DMF: C₂₄H₄₄ClN₄Ni₂O₆S₈ (MW = 893.9976 g/mol) requires C, 32.24; H, 4.96; N, 6.27 %.

X-ray Diffraction Studies. Data were collected on a Nonius KappaCCD or APEXII Bruker AXS Diffractometers with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Structures were solved by direct methods (SHELXS-97, SIR97)iii and refined (SHELXL-97)iv by full-matrix least-squares methods, as implemented in the WinGX software package. Absorption corrections were applied. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined.

Magnetic properties. The magnetic susceptibility measurements were obtained from a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from –5 to 5 T. Measurements were performed on polycrystalline samples of [Ni(DMF)₆](I)₂ (3.6 mg) and [NiCl(DMF)₂](I) (2.2 mg). The magnetic data were corrected for the sample holder and the diamagnetic contributions.

---


