Paramagnetic Dithiolene Complexes as Metallo-ligands: Ether/Thioether Coordination

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SUPPLEMENTARY MATERIAL

Syntheses

*Dithiocarbonate **3b***. The trithiocarbonate[i] **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 $CH_3COOH/CHCl_3$ (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_2O, 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). ^1H NMR ($CDCl_3$, TMS) δ: 4.05 (t, 2H); 2.98 (t, 2H) ppm. IR (KBr) $\nu_{C=O}$ = 1658 cm^{-1}. Elem. Anal. Calc. for $C_7H_8O_2S_4$ (Found) : 33.31 (33.20), 3.19 (3.22) %.

*(nBu_4N)(**1**)•DMF*. To a solution of dithiocarbonate **3b** (0.1179 g, 0.48 mmol) in distilled MeOH (20 ml) is added Bu_4NOH 1M (1.05 ml, 1.05 mmol). After stirring for 1h, $NiCl_2•6H_2O$ (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_3CN, CH_2Cl_2 and DMF. Recrystallization by Et_2O vapour diffusion on a DMF solution afforded the $n\mathrm{Bu}_4\mathrm{N}^+$ salt as DMF solvate, (nBu$_4$N)(**1**)•DMF (0.195 g, 75%). Elem. Anal. Found: C, 45.32; H, 7.18; N, 2.95. $C_{31}H_{59}N_2NiO_3S_8$ (MW = 823.04 g/mol) requires C, 45.24; H, 7.23, N, 3.40 %. UV-vis (CH_2Cl_2): λ_{max} = 900 nm.

*[Ni(DMF)$_6$][**1**]$_2$*. A solution a (nBu$_4$N)(**1**)•DMF (10.0 mg, 0.012 mmol) in CH_3CN (2.0 ml) is added to a solution of $Ni(ClO_4)_2•6H_2O$ (31.3 mg, 0.08 mmol) in CH_3CN (2.0 ml) and left unstirred for one day. The black precipitate is filtered and washed with CH_3CN. Recrystallization by Et_2O vapour diffusion on a DMF solution afforded needle-shaped crystals which analyse as [Ni(DMF)$_6$][**1**]$_2$. Elem. Anal. Found: C, 33.24; H, 4.86; N, 5.48. $C_{42}H_{70}N_6Ni_3O_{10}S_{16}$ (MW = 1508.1780 g/mol) requires C, 33.45; H, 4.68; N, 5.57 %.

*[NiCl(DMF)$_2$] [**1**]•(2DMF,Et$_2$O).* A solution of (*n*Bu$_4$N)(**1**)•DMF (10.0 mg, 0.012 mmol) in CH$_3$CN (2 ml) is mixed with a solution of NiCl$_2$•6H$_2$O (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 CH$_3$CN. Recrystallization by Et$_2$O vapour diffusion on a DMF solution afforded prismatic crystals (11.4 mg, 55%), identified from X-ray diffraction as a DMF/Et$_2$O solvate formulated as [NiCl(DMF)$_2$][**1**]•(2DMF,Et$_2$O). Elem. Anal. Found: C, 32.45; H, 5.16; N, 6.04, compatible with the loss of Et$_2$O molecule. [NiCl(DMF)$_2$][**1**]•2DMF: $C_{24}H_{44}ClN_4Ni_2O_6S_8$ (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) by full-matrix least-squares methods,[iv] as implemented in the WinGX software package.[v] 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)$_6$](**1**)$_2$ (3.6 mg) and [NiCl(DMF)$_2$](**1**) (2.2 mg). The magnetic data were corrected for the sample holder and the diamagnetic contributions.

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[iii] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, *32*, 115.

[iv] SHELX97 - Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, (1998).

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