Synthesis and structure of a new nickel(II) complex $[NBu_4]_2[Ni\{Se_2C_2(CN)_2\}_2]$

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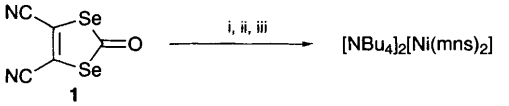
The synthesis of a new nickel(II) complex, $[NBu_4]_2[Ni\{Se_2C_2(CN)_2\}_2]$, and its structure are described.

The *cis*-2,3-disulfanylbut-2-enedinitrile or maleonitriledithiolate (mnt) ligand has been used for a long time in the preparation of transition-metal complexes, $[M(mnt)_n]^{z-}$, allowing the stabilisation of several oxidation states for the transition metal, M. Depending on the metal and on the oxidation state, these complexes can be either diamagnetic or paramagnetic, and special emphasis has been given to the use of trivalent transition-metal complexes as counter ions in low-dimensional organic conductors, such as $[M(mnt)_2(perylene)_2]$ and in salts that exhibit ferromagnetic interactions at low temperatures.[3,4] Conductivity along stacks of $M(mnt)_2$ units has also been achieved in $A_x[M(mnt)_2]$ compounds (A = Na, K, Cs).[5] Although the preparation of mnt, from carbon disulfide, is easy to perform[6] and proceeds with reasonably high yield, the similar reaction between carbon diselenide and sodium cyanide does not give the expected selenium analogue, the preparation of which, until now, was unreported. Here, we report the preparation of this selenium analogue, maleonitrilediselenolate (mns), for which the nickel(II) complex $[Ni(mns)_2]^{2-}$ was isolated as the tetrabutylammonium salt $[NBu_4]_2[Ni(mns)_2]$. The synthetic route is based on the nucleophilic ring opening of 4,5-dicyano-1,3-diselenole-3-one **1**, prepared as described by Poleschner and Fanghänel,[7] and subsequent complexation with Ni as shown in Scheme 1. The FTIR spectrum of $[NBu_4]_2$-$[Ni(mns)_2]$ shows a band at 432 cm^{-1} which corresponds to the band occurring at 357 cm^{-1} for $[NBu_4]_2[Ni(mnt)_2]$ and is assigned to the Ni–S stretching vibration (with contribution from the ring deformation).[8]



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Scheme 1 *Reagents*: i, EtONa, EtOH; ii, $NiCl_2{\cdot}6H_2O$; iii, NBu_4Br

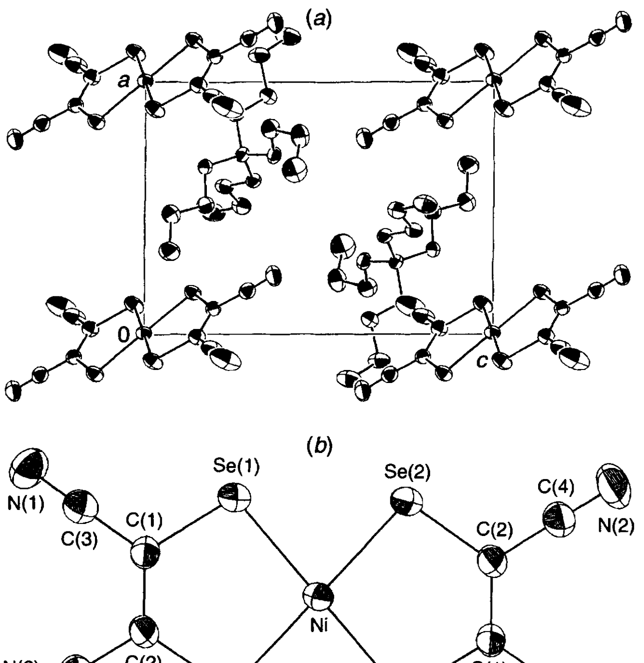

Fig. 1 Crystal structure of $[NBu_4]_2[Ni(mns)_2]$; (*a*) ORTEP projection on the *ac* plane (cations on the near side of the layer are omitted for clarity), (*b*) top view of the $[Ni(mns)_2]$ molecule showing labelling scheme for the atoms

The crystal structure of $[NBu_4]_2[Ni(mns)_2]$ derived from single-crystal X-ray diffraction data (Fig. 1) was solved in a triclinic unit cell, space group $P\bar{1}$, and is isomorphous to $[NBu_4]_2[Ni(mnt)_2]$.

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Footnotes

† All the compounds gave satisfactory elemental analysis results.

‡ *Crystal data* for $[NBu_4]_2[Ni(mns)_2]$: $C_{40}H_{72}N_6NiSe_4$, M_w = 505.79, triclinic, space group $P\bar{1}$, a = 9.8809(9), b = 10.8511(8), c = 12.4561(13) Å, α = 85.646(7), β = 87.970(8), γ = 65.542(7)°, U = 1212.2(2) $Å^3$, Z = 1, D_c = 1.386 Mg m^{-3}, $F(000)$ = 518. X-Ray data were collected at room temp. on an Enraf-Nonius CAD-4 automatic diffractometer using graphite-monochromated Mo-Kα (λ = 0.71069 Å, 50 kV, 26 mA) radiation up to 2θ = 56°. Unit-cell dimensions and the orientation matrix were obtained from least-squares refinement of the setting angles of 25 reflections in the range $24 < 2\theta < 34°$. The data set was collected in the ω–2θ scan mode [$\Delta\omega$ = $(0.85 + 0.35 \tan\theta)°$]. The intensities were corrected for Lorentz, polarisation and absorption effects by empirical corrections based on ψ-scans (maximum and minimum transmission factors were 0.9999 and 0.8139), using the Enraf–Nonius reduction program, MoLEN.[9] The structure was solved by direct methods using SHELX-86[10] and subsequently completed by Fourier recycling using SHELXL-93.[11] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions. Final refinement on F^2 for all reflections by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms converged at R = 0.0403, wR = 0.0815, [the observed criterion $I > 2\sigma(I)$ for 3205 reflections was used only for calclating R factors], S = 1.059 for 234 parameters. A difference Fourier synthesis revealed residual densities between −0.384 and 0.411 e $Å^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/158.

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