Synthesis and crystal structure of bis(ethylenediamine)-diisothiocyanatonickel(II)–benzene: a new 'Werner-type' clathrate compound

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The purple complex clathrate [Ni(en)$_2$(NCS)$_2$]·C$_6$H$_6$ is the first example of an inclusion compound based on a bis(bidentate amine) octahedral complex host.

A large number of inclusion compounds of the general formula [MA$_4$X$_2$]·*x*G have been reported over the past four decades.[1] In these materials, M is a divalent transition-metal ion, A is a neutral monodentate amine ligand, X is a monoanionic ligand, and G is a neutral guest molecule. Among the most heavily studied systems have been those based on neutral octahedral complexes of *trans*-diisothiocyanatonickel(II) with substituted pyridine[2] or α-arylalkylamine[3] ligands, [Ni(am)$_4$(NCS)$_2$]. These complexes have been shown to form inclusion compounds with a variety of substituted benzene and naphthalene molecules. To date, no analogous inclusion compounds have been found for complexes of bidentate amines. We report here the synthesis and characterization of [Ni(en)$_2$(NCS)$_2$]·C$_6$H$_6$ **1**, the first member of a new family of inclusion compounds based on a bidentate amine complex host.

The synthesis of **1** was carried out as follows: Ni(NO$_3$)$_2$·6H$_2$O (2.92 g, 10 mmol) and KSCN (4.05 g, 40 mmol), each dissolved in 10 ml of water, were mixed. To the stirring emerald green solution were added dropwise 1.5 ml of neat ethylenediamine; the solution changed to blue and then dark purple. After most of the ethylenediamine had been added a fine light purple precipitate formed and the pH of the solution was 10. To this mixture, 2-aminoethanol was added dropwise (*ca.* 25–30 drops) until the precipitate had completely dissolved, raising the pH to 11.2. The dark blue–purple solution was diluted with water to a total volume of approximately 45 ml. Solid citric acid was added in small portions until the pH fell to 7.9. A 15 ml sample of this solution was placed in a 50 ml vial and *ca.* 2 ml of benzene was placed on top of the aqueous layer. A light purple, microcrystalline precipitate immediately began to form at the interface between the liquid phases, growing downward into the aqueous layer. Within a few hours, a large cloud-shaped mass (*ca.* 1–2 cm in height) had formed and the colour of the solution had lightened considerably. On standing for several days at room temperature, large purple slabs up to 3 mm in diameter grew on the bottom of the solid mass which was floating in the solution. These larger crystals are moderately air stable with respect to loss of benzene, while the microcrystalline material decomposes, turning to a lighter purple, within minutes of removal from the solution. All characterization was carried out on crystals that were harvested by hand and washed with ethanol.† The formation of the inclusion compound **1** is sensitive to the pH and concentration of the aqueous solution. At pH 9, **1** forms much more slowly and in lesser amounts than at pH 8. When the synthesis was attempted with the concentrations of the inorganic reagents reduced by 75%, **1** was not formed even after one month.

The crystal structure of **1**‡ shows that there is one guest benzene molecule per nickel complex (Fig. 1). Both molecules reside on centres of inversion. The complex has two nearly linear *trans* isothiocyanato ligands bound to the nickel in a modestly bent arrangement [Ni–N(1)–C(1) 166°]. The deviation from linear ligation is actually substantially less than the complex displays in its pure crystalline state [Ni–N–C 143.0(2)°].[4] The ability of the isothiocyanate ligand to vary its angle of coordination over such a wide range undoubtedly plays a large role in the ability of these complexes to form inclusion compounds with many different guests.[2] The unit cell of **1** (Fig. 2) shows a primitive lattice of nickel complexes with the benzene molecules in the centres of the *c* faces. The extended structure has alternating layers of complexes and benzene molecules in the *ac* plane stacking in the *b* direction. At the same time, layers containing both molecules in the *ab* plane stack in the *c* direction. This packing scheme may be unique to this system as the complexes in pure form[4] pack in a pseudo-body-centred array in the monoclinic space group $P2_1/n$, while our preliminary results indicate that the toluene and aniline clathrates have different structures as well. The guest benzene molecules display little thermal motion as evidenced by the small, regular displacement parameters of the C atoms and the well defined H atom positions of the benzene molecule. This, as well as the thermal stability of the compound, indicates that the molecules are tightly packed together. The volume expansion due to the benzene molecule (and, in part, to the change in ligation of the NCS) is approximately 125 Å^3, as compared with the volume of a benzene molecule in crystalline benzene of about 127 Å^3 at 270 K.[5]

TG of crystals of **1** (lightly ground) shows a single-step mass loss of 19.6% centred at 392 K (onset 357 K, completion 407 K), which is in good agreement with the theoretical loss of 20.9% for one mole of benzene. Presumably, a small amount of the guest was lost from the sample during the few minutes it

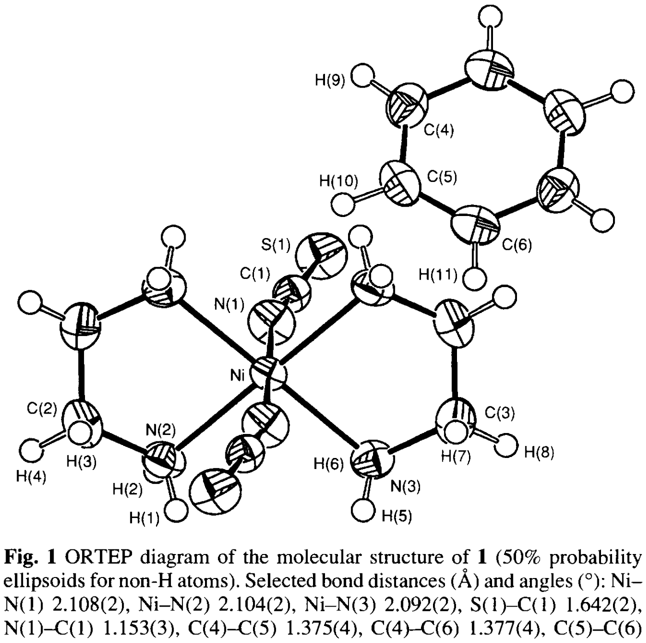

Fig. 1 ORTEP diagram of the molecular structure of **1** (50% probability ellipsoids for non-H atoms). Selected bond distances (Å) and angles (°): Ni–N(1) 2.108(2), Ni–N(2) 2.104(2), Ni–N(3) 2.092(2), S(1)–C(1) 1.642(2), N(1)–C(1) 1.153(3), C(4)–C(5) 1.375(4), C(4)–C(6) 1.377(4), C(5)–C(6) 1.372(4), N(1)–Ni–N(2) 91.71(8), N(1)–Ni–N(3) 90.48(8), N(2)–Ni–N(3) 97.04(8), Ni–N(1)–C(1) 165.9(2), S(1)–C(1)–N(1) 178.6(2), C(5)–C(4)–C(6) 120.0(2), C(4)–C(5)–C(6) 120.3(2), C(4)–C(6)–C(5) 119.7(2).

took to grind the sample and load it into the balance. The material retains its purple colour following this mass loss and is stable to *ca.* 493 K, at which point a large endotherm occurs centred at 503 K accompanied by a slight mass loss. It was verified independently that this is the melting of the nickel complex. Final decomposition of the complex begins at *ca.* 541 K. These data indicate that the benzene can be removed while leaving the complex intact. Crystals of the pure complex§ melt at the same temperature as the desorbed clathrate. Powder X-ray diffraction reveals that the structure of the desorbed clathrate (obtained by heating **1** at 130 °C for several hours) is different from that of the pure complex as grown from solution (Fig. 3). The desorbed material, when placed in contact with an atmosphere of benzene vapour for *ca.* 12 h, absorbs about 1.5 moles of benzene per mole of complex. The powder pattern of the resulting crystalline inclusion compound is different from that of **1**. This solid state desorption/reabsorption is reversible for these two phases which have different structures from those grown in solution.

In conclusion, we have synthesized and characterized the first inclusion compound of a bis(bidentate amine) octahedral complex **1**, $[Ni(en)_2(NCS)_2]\cdot G$ where G = benzene. In addition to **1**, toluene, aniline and fluorobenzene inclusion compounds of this complex have been prepared. Preliminary single crystal X-ray studies show that the toluene and aniline compounds are isostructural, but different from **1**. They are monoclinic, probable space group *C*2/*c*. In both cases, the guest resides on a symmetry element that requires the substituent to be disordered. In neither compound is the position of the guest as well defined as in **1**. Our results so far indicate that **1** represents the first member of a new family of inclusion compounds whose chemistry differs from that of previously studied monodentate amine complexes.[6–13]

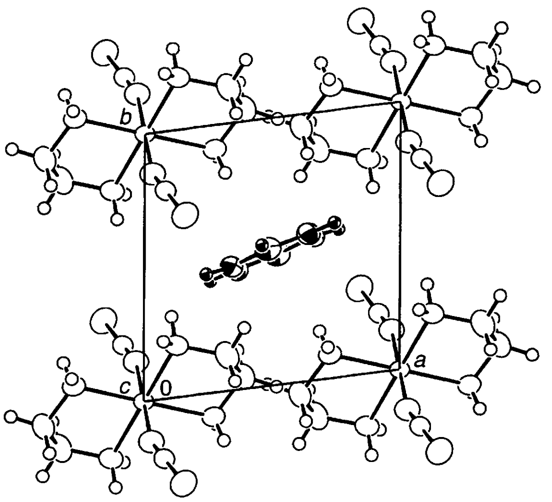

Fig. 2 ORTEP packing diagram of **1** projected on the *ab* plane (50% probability ellipsoids for non-H atoms). Unit cell outline is shown. Selected intermolecular contacts (Å) with symmetry operations: C(4)···H(6) (*x*, *y*, *z* − 1) 2.76(2), C(4)···H(7) (*x*, *y* + 1, *z* − 1) 2.97(3), C(5)···H(6) (*x*, *y*, *z* − 1) 2.89(2), C(6)···H(6) (− 1 − *x*, 1 − *y*, − 1 − *z*) 2.84(2), H(3)···H(3) (1 − *x*, −*y*, 1 − *z*) 2.30(5), H(4)···H(11) (− *x*, 1 − *y*, − *z*) 2.54(4), H(4)···H(10) (− *x*, 1 − *y*, − *z*) 2.71(4), H(7)···H(9) (*x*, *y* − 1, *z* + 1) 2.70(4).

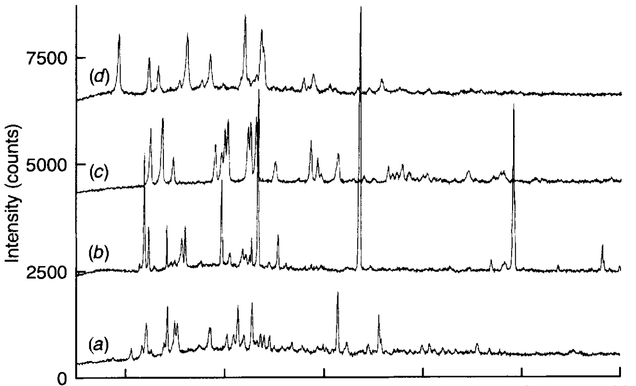

Fig. 3 Powder X-ray diffraction patterns of (*a*) $[Ni(en)_2(NCS)_2]$ crystals grown from solution, (*b*) **1** grown from solution, (*c*) $[Ni(en)_2(NCS)_2]$ obtained by desorption of **1** and (*d*) $[Ni(en)_2(NCS)_2]\cdot xC_6H_6$ obtained by reabsorption of benzene vapour

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Footnotes

† Anal. Found: C, 36.55; H, 5.67; N, 22.79. Calc. For $C_{12}H_{22}N_6S_2Ni$: C, 38.62; H, 5.94; N, 22.52. The low values for C and H are consistent with loss of a small amount of the guest during sample handling. Thermogravimetric analysis: data were obtained on a computer-automated Seiko Instruments TGA–DTA–DSC unit from 313 K to 573 K at a heating rate of 10 K min^{-1} in air.

‡ *Crystal data* for $[Ni(en)_2(NCS)_2]\cdot C_6H_6$: $C_{12}H_{22}N_6NiS_2$, M = 373.17. Colour, habit: purple, slab. Triclinic, space group $P\bar{1}$, a = 8.084(3), b = 8.250(2), c = 8.016(2) Å, α = 112.21(2), β = 115.72(2), γ = 74.38(2)°, U = 442.3(5) Å^3, Z = 1, D_c = 1.401 g cm^{-3}, μ(Mo-Kα) = 13.3 cm^{-1}. Crystal dimensions: 0.30 × 0.28 × 0.24 mm. The crystal was coated with epoxy cement prior to mounting. Data were measured to 60° 2θ at 293 K on a Rigaku AFC5 diffractometer using ω–2θ scans with graphite-monochromated Mo-Kα radiation. A total of 2739 reflections were collected of which 2569 were unique (R_{int} = 0.012). The structure was solved by the Patterson method and refined using data corrected for absorption (ψ-scans) and secondary extinction to give R = 0.034 (R_w = 0.032) for 2116 independent observed reflections [$I > 3\sigma(I)$] and 131 parameters. All nonhydrogen atoms were refined anisotropically and all hydrogen atoms were positionally refined with fixed isotropic B values. 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 182/271.

§ Large (up to 5 mm) six-sided elongated purple slabs (mp 499–501 K) of composition $[Ni(en)_2(NCS)_2]$ grow within a few days from the aqueous solution described above if a suitable guest is not added.

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