

Three-dimensional structure of the clathrate complex $[\{\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{dabco})_2\} \cdot \text{dabco}] \cdot 2\text{dmsO}$ obtained from zero valent metal (dabco = 1,4-diazabicyclo[2.2.2]octane and dmsO = dimethyl sulfoxide)

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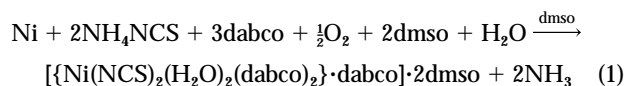
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The new clathrate complex $[\{\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{dabco})_2\} \cdot \text{dabco}] \cdot 2\text{dmsO}$ (dabco = 1,4-diazabicyclo[2.2.2]octane and dmsO = dimethyl sulfoxide), the first example of a compound comprising metal centres and dabco molecules in a 1 : 3 ratio, has been prepared from metal powder; its crystal structure contains $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{dabco})_2]_{\infty}$ square grids linked by hydrogen-bonded dabco molecules to afford a three-dimensional framework, molecules of dmsO occupy square-shaped channels.

Co-ordination compounds with increasing dimensionality may be expected to yield a variety of novel structures and properties of both chemical and physical significance.¹ Our aim was to design and prepare transition-metal compounds possessing extended molecular architectures and our study has focused on the synthesis and structural characterisation of polymeric compounds using 1,4-diazabicyclo[2.2.2]octane (dabco) as a bridging ligand. Bidentate ligands, which do not form chelates but bridges, are of interest with respect to the preparation of unusual co-ordination polymers. The complexes $[\text{NiCl}_3(\text{Hdabco}) \cdot (\text{dabco})]$ and $[\text{Ni}(\text{NCS})_4(\text{Hdabco})_2]$ have been synthesised and are shown to possess chain and layered structures respectively.^{2,3} The compound $[\text{Cd}(\text{Hdabco})_2\{\text{Ni}(\text{CN})_4\}_2] \cdot 4\text{PhNH}_2$ has been reported to have a two-dimensional structure.⁴ We have now succeeded in the preparation of the clathrate complex $[\{\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{dabco})_2\} \cdot \text{dabco}] \cdot 2\text{dmsO}$ (dmsO = dimethyl sulfoxide) with a three-dimensional framework and herein report the synthesis and crystal structure of this compound.[†] To the best of our knowledge, this is the first example of a compound comprising metal centres and dabco molecules in a 1 : 3 ratio.

Conventional synthesis of transition-metal complexes usually involves a metal salt as a starting material. Our synthesis employs unactivated metal powder. The synthesis of a co-ordination compound from a zero valent metal is a fascinating and promising approach to the production of complexes of unusual stoichiometry and structure.⁷ The reaction [summarised in equation (1)] was carried out in air. Nickel powder (1



mmol, NH_4NCS (2 mmol), and dabco (3 mmol) were heated in

dmsO at 50–60 °C and stirred until total dissolution of nickel was observed (ca. 8 h). After cooling, the green microcrystals were collected and washed with dry isopropanol (yield 75%).§

The crystal structure of the compound showed it to contain $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{dabco})_2]_{\infty}$ layers, which are linked by unco-ordinated dabco molecules to afford a three-dimensional framework, and unco-ordinated dmsO molecules occupy square-shaped channels (Fig. 1). All nickel centres have a distorted octahedral environment consisting of two *trans* thiocyanato nitrogens [at 2.040(3) Å], two *trans* water oxygens [at 2.069(3) Å] and two dabco nitrogens [at 2.278(3) Å] occupying axial positions. It should be noted that the axial Ni–N(1) distance is significantly elongated compared to the corresponding value for six-co-ordinate nickel compounds (2.10–2.20 Å),^{9,10} probably because of the existence of strong intermolecular hydrogen bonding $\text{O}(1)\text{--H}(a) \cdots \text{N}(2')$, $\langle x, \frac{1}{2} - y, -\frac{1}{2} + z \rangle$ with an $\text{O}(1) \cdots \text{N}(2')$ distance of 2.809(5) Å and an $\text{O}(1)\text{--H}(a)\text{--N}(2')$ angle of 176(5)°. This bonding results in the generation of infinite square grids perpendicular to the [100] direction.

† Crystal data: $\text{C}_{24}\text{H}_{52}\text{N}_8\text{NiO}_4\text{S}_4$, $M = 703.70$, monoclinic, $a = 11.116(2)$, $b = 12.490(2)$, $c = 13.201(3)$ Å, $\beta = 108.35(3)^\circ$; $U = 1739.6(7)$ Å³ (by least-squares refinement on diffractometer angles from 24 centred reflections, $2\theta < 2\theta < 30^\circ$), $T = 293$ K, space group $P2_1/c$ (no. 14), graphite-monochromated Mo-K α radiation, $\lambda = 0.71073$ Å, $Z = 2$, $D_c = 1.343$ g cm⁻³, $F(000) = 752$, green prism with dimensions $0.44 \times 0.36 \times 0.20$ mm, $\mu = 8.4$ cm⁻¹, absorption correction by the Gaussian method,⁵ A^* (minimum, maximum) = 1.18–1.33; Enraf-Nonius CAD4 diffractometer using ω - 2θ scan mode, $2\theta \leq 48^\circ$, $0 \leq h \leq 12$, $0 \leq k \leq 14$, $-15 \leq l \leq 14$, three standard reflections showed no significant variation in intensity; 3039 reflections measured, 2726 unique ($R_{\text{int}} = 0.026$) and of these 2016 had $I > 3.00\sigma(I)$ and were considered to be observed. The structure was solved by direct methods and subsequent Fourier-difference techniques, and refined anisotropically, by atom-block matrix least squares, on F (program XTAL 3.4⁶). The weighting scheme was based on $\sigma^2(I) = \sigma^2(I)_{\text{diff}} + n\sigma^4(I)_{\text{diff}}$, $n = 4 \times 10^{-4}$. The final R , R' were 0.046 and 0.055 respectively for 234 parameters and 12 restraints (to bond lengths and angles of dmsO molecules), goodness of fit = 2.046. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/505.

§ Satisfactory elemental analyses were obtained (Found: C, 41.71; H, 7.67; N, 16.31; Ni, 8.80. Calc. for $\text{C}_{24}\text{H}_{52}\text{N}_8\text{NiO}_4\text{S}_4$: C, 42.03; H, 7.66; N, 16.34; Ni, 8.56%). The IR spectra (KBr) showed a very strong characteristic absorption band at 2090 cm⁻¹ (ν_{CN}) and a broad absorption in the range 3000–3200 cm⁻¹ corresponding to hydrogen bonds. The reflectance spectrum exhibited three bands at 29 000, 24 800 and 15 200 cm⁻¹ in the range 30 000–12 200 cm⁻¹. This is in agreement with the symmetry of the metal complex being lowered from O_h to D_{4h} .⁸

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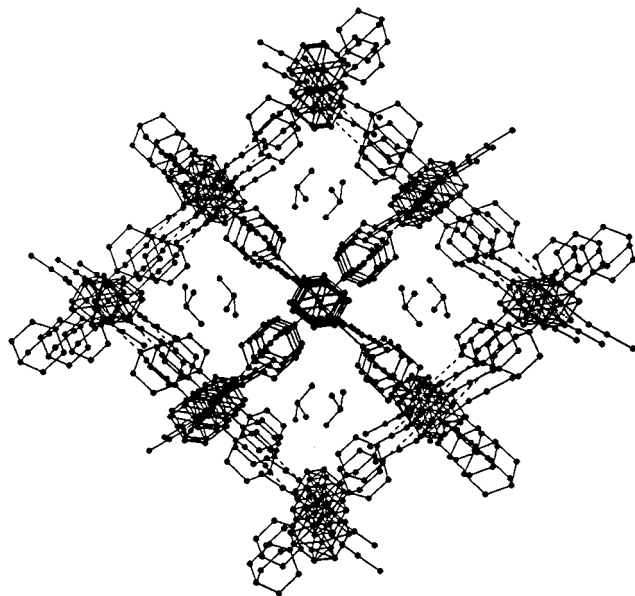


Fig. 1 Perspective packing diagram viewed down the *a* axis revealing the square-shaped channels with unco-ordinated dmsu

Within each grid all nickel centres are coplanar. The other bond distances and angles of the $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{dabco})_2]$ unit are within the expected range.

There is a principal difference in structural function of the unco-ordinated dabco and dmsu molecules in this structure. No contact distances significantly less than that determined from van der Waals radii are observed for dmsu, while there is quite strong hydrogen bonding between the unco-ordinated dabco and the water molecules with the $\text{O}(1) \cdots \text{N}(11)$ distance of 2.745(5) Å and $\text{O}(1)-\text{H}(\text{b})-\text{N}(11)$ angle of 175(5)° (Fig. 2). Inter-layer linkages are made *via* this bonding in such a way that large channels extending along the [100] direction occur (Fig. 1). Their dimensions can be easily calculated from the unit cell parameters (approximately 13 Å diagonally).

It should be noted that the compound possesses high stability and is insoluble in water and common organic solvents, which seems to be attributed to the strong hydrogen bonding to unco-ordinated dabco. Moreover, we presume that these dabco molecules form a supramolecular arrangement which stabilises the metal complex entity itself and can be illustrated by the failure to isolate the pure complex $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{dabco})_2]$.²

Acknowledgements

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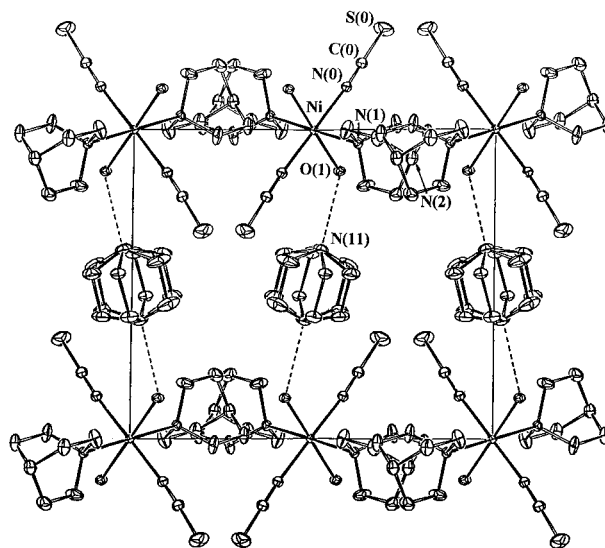


Fig. 2 Projection of the unit cell onto the *ab* plane. All atoms are represented by their 20% probability ellipsoids. Selected interatomic distances (Å) and angles (°): Ni–O(1) 2.069(3), Ni–N(0) 2.040(3), Ni–N(1) 2.278(3); O(1)–Ni–N(0) 90.5(1), O(1)–Ni–N(1) 87.7(1), N(0)–Ni–N(1) 87.2(1). Hydrogen atoms and dmsu molecules are omitted for clarity

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