Aufbau synthesis of a mixed-metal anion receptor cage

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Received (in Basel, Switzerland) 26th October 1998, Accepted 8th December 1998

The isolation and structural characterisation of square planar [Ni(atu)$_2$] (Hatu = amidinothiourea) has provided a rational basis to synthesise the novel mixed-metal cage compounds [Ni$_4$Pd$_2$(atu)$_8$X]X$_3$ (X = Cl, Br); one of these cages (when X = Cl) has been crystallographically characterised showing that the chloride anion is encapsulated in the centre of the cage forming eight hydrogen-bonds with N–H groups from the ligands and two Lewis acid–base interactions with two palladium(II) ions.

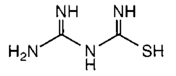
The inclusion of guest molecules into host structures has attracted great interest over the past two decades.[1] This interest has been stimulated by the potential properties of these supermolecules as chemical sensors,[2] nanoscale devices[3] and systems with biological markers.[4] Whilst the supramolecular chemistry of cationic or neutral guests has been widely studied,[5] that of anions has received much less attention.[6] Examples of molecular containers (such as squares and cages) have been reported to selectively encapsulate anionic guests.[7] The incorporation of transition metal centres into such molecular containers may either enhance their Lewis acidity or introduce magnetic, electrochemical and luminescent properties into the host molecules.[8]

Recently we have reported the selective encapsulation of anions (Cl **1**, Br **2**) inside the hexanuclear nickel cages [Ni$_6$(atu)$_8$]$^{4+}$ (Hatu = amidinothiourea and atu is its deprotonated form).[9] These cages self-assemble according to eqn. (1) only in the presence of the templating anions F$^-$, Cl$^-$ and Br$^-$.

$$4\,\mathrm{Ni(ClO_4)_2} + 8\,\mathrm{Hatu} \longrightarrow 4\,[\mathrm{Ni(atu)_2}] \xrightarrow{2\,\mathrm{NiX_2}} [\mathrm{Ni_6(atu)_8X}]\mathrm{X_3} \qquad (1)$$

X = Cl **1**, Br **2**

Hatu =



Here, we report the synthesis and structural characterisation of the square planar precursor [Ni(atu)$_2$] **3**. The isolation of this complex has made it possible to rationally synthesise the new mixed-metal cage compounds [Ni$_4$Pd$_2$(atu)$_8$X]X$_3$ (X = Cl **4**, X = Br **5**) which retain the basic octahedral metal framework observed in **1** and **2** but selectively include the palladium ions in *trans*-positions. Although there are a number of examples of anion encapsulation by homonuclear cages, few examples of mixed metal cages have previously been reported.

When a solution of Ni(ClO$_4$)$_2$ in methanol was mixed with 2 equivalents of amidinothiourea [Hatu = H$_2$NC(=NH)-NHC(=NH)SH] a dark orange solution was obtained from which a crystalline material was separated after addition of diethyl ether. A single crystal analysis of the compound confirmed its formulation as *trans*-[Ni(atu)$_2$] (Fig. 1).

Amidinothiourea can coordinate to metal centres using either two nitrogens (N,N) or one nitrogen and one sulfur (N,S). The molecular structure of **3** reveals the coordination mode to be N,N′. This is in striking contrast to what is observed in the only other structurally characterised complex of this ligand, with palladium, where N,S coordination occurs.[10] This suggested that the non-coordinated sulfur atoms in **3** are available for coordination to additional metal centres. This was partially corroborated when addition of NiX$_2$ salts (X = Cl, Br) to this solution yielded the recently reported hexanickel cages **1** and **2**, albeit with an isomerisation of the square-planar complex from *trans*- to *cis*-.

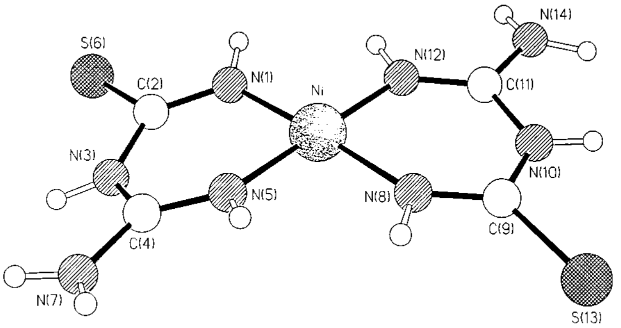


Fig. 1 The molecular structure of one of the independent molecules present in the crystals of **3**. Ni–N distances are in the range 1.843(5)–1.872(4) Å.

When a solution of [Pd(PhCN)$_2$Cl$_2$] in CH$_2$Cl$_2$ was added to a solution of **3** in methanol (in a 1 : 2 ratio) a change in colour to a brighter orange was immediately observed. After 2 h the volume of methanol was reduced and diethyl ether added. A crystalline material precipitated and was formulated as [Ni$_4$Pd$_2$(atu)$_8$Cl]Cl$_3$ **4** on the basis of spectroscopic and elemental analyses.† Crystals suitable for crystallographic analysis were obtained by slow evaporation of diethyl ether into a methanol solution of **4**. The molecular structure of **4** is shown in Fig. 2.

The X-ray analysis‡ revealed the presence of an octahedral Ni$_4$Pd$_2$ mixed-metal cage complex with one of the chloride anions encapsulated at its centre. The overall geometry is very similar to that of the all-nickel counterpart **1**,[9] but with the nickel atoms in the *trans*-positions replaced by palladium atoms (*vide infra*). The geometry at each nickel centre is square-planar with Ni–N distances ranging between 1.847(5) and 1.887(9) Å,

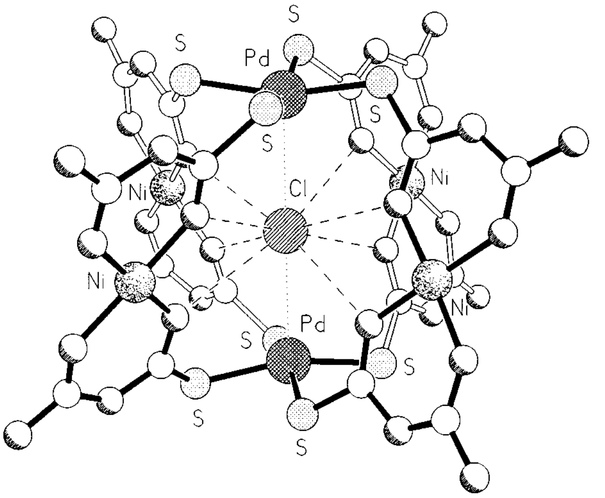


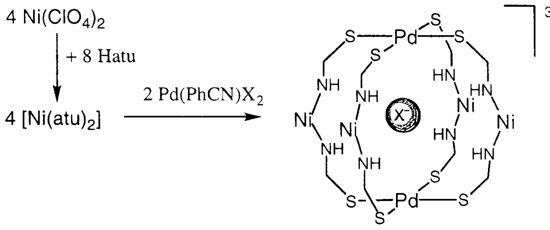
Fig. 2 The molecular structure of the mixed-metal cage cation **4** showing the encapsulation of a chloride anion. The Ni–N distances are in the range 1.847(5)–1.887(9) Å, Pd–S between 2.315(2) and 2.323(2) Å and N···Cl 3.29–3.39 Å; the Pd···Cl distances are 3.169(2) and 3.190(2) Å.

whereas that at the palladium centres is distinctly pyramidal, the palladium atoms lying *ca.* 0.31 Å out of the planes of their substituents towards the encapsulated chloride anion [the Pd–S distances range between 2.315(2) and 2.323(2) Å]. As in **1** the anion is displaced slightly towards one of the MS_4 metal atoms, the Pd···Cl distances being 3.169(2) and 3.190(2) Å. The 'retaining' N–H···Cl hydrogen-bonds have N···Cl distances ranging between 3.29 and 3.39 Å. The cage as a whole exhibits a small helical twist with the north and south PdS_4 units being rotated by *ca.* 17° with respect to each other about the Pd···Pd vector. Although the cage has helicity, the crystals are racemic, there being equal numbers of Δ and Λ forms present. The 'non-encapsulated' chloride anions link adjacent cages *via* additional N–H···Cl hydrogen-bonds, with the voids formed between the cages being filled by the methanol and diethyl ether solvent molecules.

An intriguing difference between the hexanickel cages **1** and **2**,[9] and the mixed-metal Ni–Pd cages reported in this paper (**4** and **5**) is their colour: the former are dark green while the later are dark orange. Ni(II) square planar complexes are generally red or orange. However, the coordination of ligands above or below the square-plane commonly results in a change in their colour to dark green or blue.[11] This has been attributed to interactions between these ligands and the metal d_{z^2} orbital in the axial positions of the square planar unit. The change in colour for **1** and **2** underlines the importance of the acceptor–donor interaction between the NiS_4 units and the encapsulated halide.

The generality of the *aufbau* process for the synthesis of **4** is supported by the ability to synthesise the analogous bromide species. When a mixture of $Ni(ClO_4)_2$/2 Hatu was reacted with $[Pd(PhCN)_2Br_2]$ an orange product was obtained. This product was recrystallised from methanol–diethyl ether and was formulated on the basis of IR, ^1H NMR and elemental analyses as the cage compound $[Ni_4Pd_2(atu)_8Br]Br_3$ **5**.

The formation of the above complexes can be rationalised on the basis of the sequence of reactions shown in eqn. (2).



(2)

X = Cl **4**, Br **5**

These results have demonstrated that the formation of octahedral cage complexes of amidinothiourea, which are capable of encapsulating halide anions, are not limited to the self-assembly processes but can be built up using well defined coordination chemistry principles. The isolation of mixed-metal cages such as those described above, open up the possibility of fine tuning the chemical and spectroscopic properties of this interesting class of anion receptor molecules.

We thank EPSRC for financial support and BP plc for endowing D. M. P. M's chair.

Notes and references

† **4**: yield (crystalline material): 37% [based on the initial $Ni(ClO_4)_2$]; ^1H NMR (CD_3OD) δ 7.9 (br, NH). IR(KBr): ν/cm^{-1} 3434m, 3332m (N–H), 1658vs (C–N), 1598s (C–S), 1174s. Electronic spectrum (MeOH): λ_{max} = 441 nm; Anal. Calc. for $C_{16}H_{40}N_{32}S_8Ni_6Cl_4\cdot5H_2O\cdot0.5CH_2Cl_2$: C, 12.3; H, 3.1; N, 26.9; Cl, 10.6. Found: C, 12.0; H, 3.1; N, 26.4; Cl, 9.5%.

5: yield (crystalline material): 46% [based on the initial $Ni(ClO_4)_2$]; ^1H NMR (CD_3OD) δ 8.0 (br, NH). IR(KBr): ν/cm^{-1} 3434m, 3332m (N–H), 1658vs (C–N), 1598s (C–S), 1174s. Electronic spectrum (MeOH): λ_{max} = 445 nm; Anal. Calc. for $C_{16}H_{40}N_{32}S_8Ni_6Br_4\cdot CH_3OH$: C, 11.7; H, 2.5; N, 25.8; Br, 18.5. Found: C, 11.2; H, 2.8; N, 23.8; Br, 18.7%.

‡ *Crystal data*: for **3**: $C_4H_{10}N_8S_2Ni\cdot0.67Me_2SO$, M = 345.1, monoclinic, space group $P2_1/c$ (no. 14), a = 8.776(1), b = 12.142(1), c = 18.806(1) Å, β = 99.77(1)°, V = 1974.9(3) Å^3, Z = 6 (one of the two independent molecules has C_i symmetry), D_c = 1.741 g cm^{-3}, μ(Cu-Kα) = 61.0 cm^{-1}, $F(000)$ = 1068, T = 173 K; yellow plates, 0.20 × 0.12 × 0.03 mm, Siemens P4/RA diffractometer, ω-scans, 2678 independent reflections. The structure was solved by direct methods and the major occupancy non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give R_1 = 0.047, wR_2 = 0.103 for 2136 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$] and 306 parameters.

For **4**: $C_{16}H_{40}Cl_4N_{32}S_8Ni_4Pd_2\cdot6.5CH_3OH\cdot Et_2O$, M = 1809.1, monoclinic, $P2_1/c$ (no. 14), a = 19.271(2), b = 15.586(2), c = 25.250(4) Å, β = 104.10(1)°, V = 7356(2) Å^3, Z = 4, D_c = 1.634 g cm^{-3}, μ(Cu-Kα) = 89.4 cm^{-1}, $F(000)$ = 3676, T = 183 K; orange prisms, 0.42 × 0.33 × 0.23 mm, Siemens P4/RA diffractometer, ω-scans, 10 934 independent reflections. The structure was solved by direct methods and the major occupancy non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give R_1 = 0.053, wR_2 = 0.135 for 8789 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$] and 831 parameters. CCDC 182/1122.

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Communication 8/08303G