New Polynuclear Nickel Complexes with a Variety of Pyridonate and Carboxylate Ligands

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A general synthetic strategy for making, and structures and some properties of, several new polynuclear nickel complexes of pyridonate ligands are reported: these complexes include a linear trinuclear complex $[Ni_3(chp)_4(O_2CMe)_2(MeOH)_6]$, a tetranuclear cubane $[Ni_4(OMe)_4(\eta\text{-}chp)(chp)_3(MeOH)_7]$ and two undecanuclear complexes $[Ni_{11}(\mu_3\text{-}OH)_6(O_2CMe)_6(mhp)_9(H_2O)_3]_2[CO_3]$ and $[Ni_{11}(\mu_3\text{-}OH)_6(O_2CMe)_7(mhp)_9(Hmhp)_2]$ (Hchp and Hmhp = 6-chloro- and 6-methyl-2-pyridone respectively).

One of the goals in the area of polynuclear coordination chemistry is to control the nature of the final product and to escape from reliance on 'spontaneous self-assembly'. The elegant work of Christou and coworkers coupling tetramanganese fragments to make larger assemblies[1] is a rare example of where such designed synthesis has been possible. In many cases the complex reaction products are unexpected.

In 1983 Garner and coworkers. reported that the dodecanuclear cobalt complex $[Co_{12}(OH)_6(O_2CMe)_6(mhp)_{12}]$ **1** was formed, unexpectedly, from reaction of cobalt acetate with Hmhp.[2] We recently extended this work to give octanuclear copper complexes[3] and a novel cyclic dodecanuclear nickel complex[4] $[Ni_{12}(chp)_{12}(O_2CMe)_{12}(H_2O)_6(THF)_6]$ **2**. The presence of pyridonate, carboxylate and solvent molecules in **2** suggested that the nuclearity of the final complex could be controlled by modification of each component in turn.

The reaction of hydrated nickel acetate (6.8 mmol) with excess Hchp (14.2 mmol) at 130 °C for 1 h, followed by removal of unreacted Hchp and acetic acid formed during the reaction, gives a bright green solid. Extraction of this mixture with THF leads to **2**,[4] while extraction with methanol gives a green solution which on slow evaporation results in green needles in 40% yield.† Structure solution‡ revealed a trimeric complex of stoichiometry $[Ni_3(chp)_4(O_2CMe)_2(MeOH)_6]$ **3** (Fig. 1). The central nickel atom, which lies on an inversion centre, is bridged to the external nickel [Ni(2)] by two μ-oxygens from chp ligands and by a 1,3-bridging acetate ligand. Ni(2) is further bound to three molecules of methanol. Both nickel sites have six oxygen donors arranged in a nearly octahedral array. There are strong hydrogen bonds between the methanol groups and the N-atoms of the bridging chp ligands.

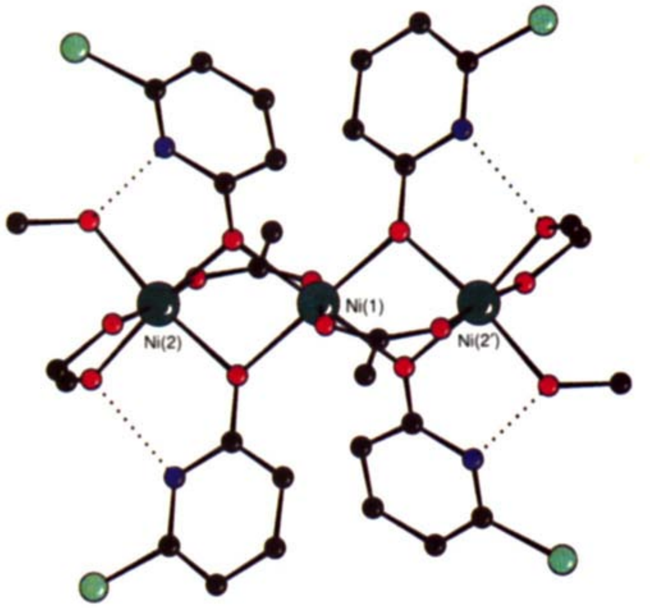

Fig. 1 The structure of the trinuclear complexes $[M_3(chp)_4(O_2CMe)_2(MeOH)_6]$ (M = Ni **3**, Co **4**). Hydrogen bonds with O···N distances in the range 2.654–2.698 Å shown as dotted lines. Bond length ranges (Å): for **3** Ni–O 2.034–2.075 [av. e.s.d. 0.002 Å]; for **4** Co–O 2.055–2.139 [av. e.s.d. 0.008 Å]. [C, black; Cl, light green; N, blue; Ni, dark green; O, red. All figures produced with CAMERON, L. J. Pearce, C. K. Prout and D. J. Watkin, University of Oxford, 1994].

Similar complexes of general formulae $[Ni_3(chp)_4(O_2CR)_2(R'OH)_6]$, where R = Me or Ph, R′ = Me or Et, have also been prepared starting from the relevant nickel carboxylate and recrystallised from the respective alcohol. Several of these complexes have been structurally characterised[5] and the Ni(1)···Ni(2) contacts are found to be in the range 3.087–3.118(2) Å. The series can be yet further extended by using cobalt in place of nickel. $[Co_3(chp)_4(O_2CMe)_2(MeOH)_6]$ **4** can be prepared in yields of around 50% and exhibits a Co(1)···Co(2) separation of 3.164(2) Å, longer than the metal–metal contact in any of the trinuclear nickel species.

In these trinuclear species both carboxylate and alcohol solvate are intimately involved in the final product. However using $Ni(O_2CCCl_3)_2$ as the substrate leads smoothly, on recrystallisation from methanol, to a product which does not contain carboxylate. Structural studies of the green crystalline product‡ show a compound of stoichiometry $[Ni_4(\mu_3\text{-}OMe)_4(\eta\text{-}chp)(chp)_3(MeOH)_7]$ **5** (Fig. 2). The molecule consists of a Ni_4O_4 cube, with the oxygen atoms derived from methoxide units. Each nickel atom is six-coordinate, with its coordination

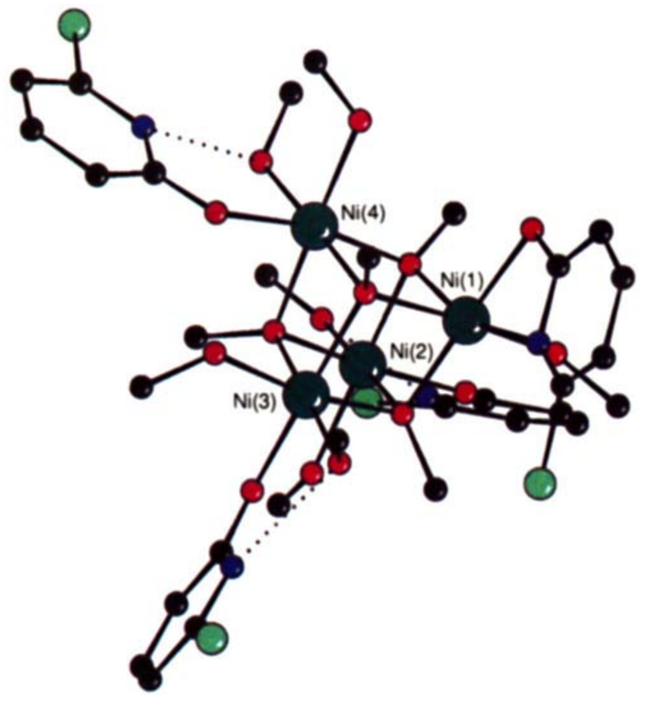

Fig. 2 The structure of the tetranuclear complex $[Ni_4(\mu_3\text{-}OMe)_4(\eta\text{-}chp)(chp)_3(MeOH)_7]$ **5** hydrogen bonds with O···N distances in the range 2.614–2.660 Å shown as dotted lines. Bond length ranges (Å): Ni–O (μ_3-OMe) 2.023–2.074, Ni–O (chp) 2.062–2.091, Ni–O (MeOH), 2.068–2.115, Ni–N 2.211 Å (av. e.s.d. 0.003 Å).

sphere completed by methanol or chp ligands. One of the four chp units is chelating, the remaining are monodentate through the O-atom. As in **3** there is extensive hydrogen bonding between methanol and chp. A number of nickel cubanes involving bridging methoxides or hydroxides have been previously reported.[6–8] It is significant that no carboxylate is found in **5**, indicating that trichloroacetate acts as an efficient leaving group leading to a different nuclearity for the coordination assembly.

The final reagent which can be modified is the pyridone. Reaction of 2 equiv. of Na(mhp) with nickel acetate in THF gives a green precipitate which can be used as a starting material for reaction with molten Hmhp under similar conditions to those mentioned above. Recrystallisation of the green solid from CH_2Cl_2–diethyl ether gives green crystals‡ containing $[Ni_{11}(\mu_3\text{-}OH)_6(\mu\text{-}O_2CMe)_6(mhp)_9(H_2O)_3]_2[CO_3]$ **6** (Fig. 3). The same reaction sequence, with the first step carried out in methanol, gives a related complex, $[Ni_{11}(\mu_3\text{-}OH)_6(\mu\text{-}O_2CMe)_6(mhp)_9(Hmhp)_2(O_2CMe)]$ **7**, after recrystallisation. The crystalline yield of both these compounds is currently low, but the syntheses are reproducible.

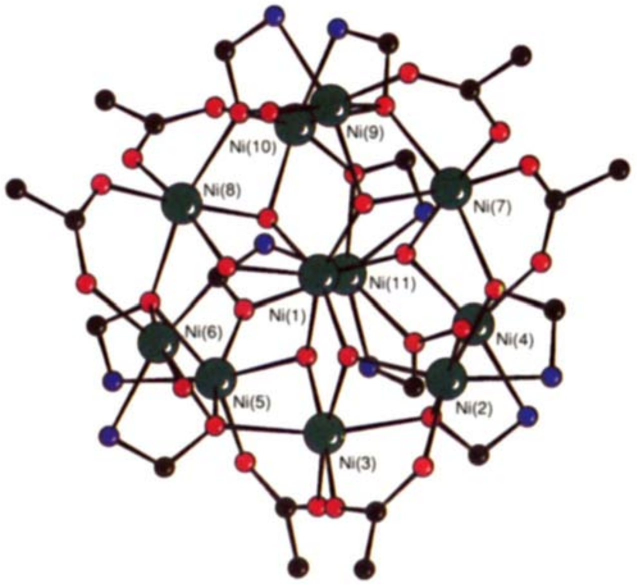

Fig. 3 The structure of the undecanuclear cation of **6** $[Ni_{11}(\mu_3\text{-}OH)_6(O_2CMe)_6(mhp)_9(H_2O)_3]^+$. Bond length ranges: Ni(1)–O (from OH) 2.057–2.096, other Ni–O (from OH) 1.935–2.087, Ni–O (mhp) 2.094–2.247, Ni–O (acetate) 1.980–2.038, Ni–N 2.010–2.080 Å (av. e.s.d. 0.012 Å). Atoms not involved in metal atom bridging are excluded for clarity.

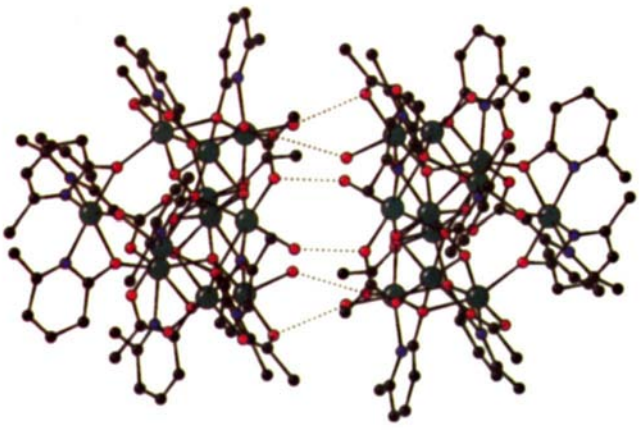

Fig. 4 The hydrogen bonded dimer of undecameric cations in **6**. Hydrogen bonds with O···O distances of 2.565–2.896(12) Å are shown as dotted lines.

In both structures a central Ni atom [Ni(1)] is coordinated to six μ_3-OH groups arranged in a distorted octahedron and shared with nine further nickel atoms. Three of these nickels are each bound to two of the μ_3-hydroxides, forming Ni_2O_2 rings involving the central Ni atom. The other six nickels are each bound to only one of the μ_3-OH groups, and describe a somewhat twisted trigonal prism centred on Ni(1), with the former three Ni atoms at the centres of the 'square' faces of the prism. These nine Ni atoms are additionally bridged by peripheral μ_3-mhp and μ-O_2CMe ligands. The final nickel atom, which is bound to three chelating mhp ligands, caps a triangular face of the trigonal prism, and is attached to the assembly *via* μ-O-atoms from the chelating mhp groups. There are two such capping sites in the molecule; in the cobalt dodecamer, **1**, both sites are occupied.[2] Here the second site is vacant and this region of the complex contains either three H_2O groups in **6**, or two Hmhp and an acetate in **7**. In both cases there are strong hydrogen bonds, in **7** these are exclusively intramolecular, but in **6** the hydrogen bonds are intermolecular, producing an hydrogen-bonded dimer of undecamers similar in appearance to an egg cracked across the centre (Fig. 4). This last feature is intriguing—an assembly lacking both caps is conceivable and might crystallise as a hydrogen-bonded stack of decamers.

Alteration of the pyridone from Hchp to Hmhp produces dramatic changes in the nature of the product. Chief among these is that in **6** and **7** both the O- and N-atoms of mhp are bound to metal atoms, whereas in general in the complexes of chp only the exocyclic O-atom is involved in nickel ligation. A similar effect was found in mixed pyridone–bipyridyl complexes of copper[9] and can be related to the position of the tautomeric equilibrium in these ligands.

Preliminary magnetic studies of **3** and **5** have been carried out.§ In **3** the behaviour is consistent with antiferromagnetic coupling of $-2.3\ cm^{-1}$ between the central and the terminal nickels, with a weak ferromagnetic coupling of $1.3\ cm^{-1}$ between the terminal Ni atoms ($g = 2.1$). For **5** the magnetic moment rises from 6.94 μ_B at 290 K to a maximum of 8.5 μ_B at 11 K. Ni_4O_4 cubanes have been studied previously[6,7] and using a method derived by Gray and coworkers[6] we can model our magnetic data adequately with three Ni–Ni exchange parameters, two of which represent ferromagnetic interactions and one an antiferromagnetic exchange ($J_1 = 7.8, J_2 = 13.0, J_3 = -9.6\ cm^{-1}$, $g = 2.15$). The magnitude of these interactions are similar to those reported previously.[6–8]

While subtle changes in the ligands can have a profound effect on the nuclearity of the complex formed, the structural analogies between **1**, **6** and **7**, and **3** and **4** suggests a consistent pattern of reactivity of pyridone ligands amongst these 3d-metals, and hints, for example, that a cyclic dodecanuclear cobalt complex similar to **2** should be attainable. We have also shown that trichloroacetate can act as an efficient leaving group, implying a promising strategy for the synthesis of homoleptic pyridone complexes. Finally, this work demonstrates that the activity of the N- and O-donors in pyridones may be controlled by careful choice of the substituent group.

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Footnotes

† Satisfactory elemental analyses were obtained for all compounds.

‡ *Crystal data* for $C_{30}H_{42}Cl_4N_4Ni_3O_{14}\cdot 2MeOH$ **3**; $M = 1064.7$, monoclinic, space group $C2/c$, $a = 25.866(12)$, $b = 9.333(5)$, $c = 20.383(12)$ Å, $\beta = 112.28(3)°$, $V = 4533$ Å^3 [from 2θ values of 30 reflections measured at $\pm\omega$ ($26 \leq 2\theta \leq 36°$), $\lambda = 0.71073$ Å], $Z = 4$ (the molecule lies on an inversion centre), $D_c = 1.55\ g\ cm^{-3}$, $T = 150.0(2)$ K, green block, $\mu =$

1.53 mm^{-1}. For $C_{30}H_{42}Cl_4Co_3N_4O_{14}\cdot 2MeOH$ **4**; M = 1065.4, monoclinic, space group $C2/c$, a = 26.189(13), b = 9.329(6), c = 26.361(18) Å, β = 134.20(2)°, V = 4617 Å^3 [from 2θ values of 30 reflections measured at $\pm\omega$ ($26 \leqslant 2\theta \leqslant 31°$), λ = 0.71073 Å], Z = 4 (the molecule lies on an inversion centre), D_c = 1.53 g cm^{-3}, T = 150.0(2) K, misshapen pink block, μ = 1.36 mm^{-1}. For $C_{31}H_{52}Cl_4Ni_4N_4O_{15}\cdot MeOH$ **5**; M = 1129.5, triclinic, space group $P\bar{1}$, a = 12.795(6), b = 14.129(7), c = 14.191(7) Å, α = 91.60(4), β = 101.20(3), γ = 111.81(3)°, V = 2322 Å^3 [from 2θ values of 38 reflections measured at $\pm\omega$ ($31 \leqslant 2\theta \leqslant 36°$), λ = 0.71073 Å], Z = 2, D_c = 1.62 g cm^{-3}, T = 150.0(2) K, pale green lath, μ = 1.89 mm^{-1}. For $C_{66}H_{84}N_9Ni_{11}O_{30}\cdot 0.5CO_3\cdot 2H_2O\cdot 0.5C_4H_{10}O$ **6**; M = 2228.3, monoclinic, space group $C2/c$, a = 39.931(13), b = 25.516(10), c = 22.43(2) Å, β = 120.2(3)°, V = 19751 Å^3 [from 2θ values of 28 reflections measured at $\pm\omega$ ($28 \leqslant 2\theta \leqslant 38°$), λ = 0.71073 Å], Z = 8, D_c = 1.50 g cm^{-3}, T = 150.0(2) K, irregular green wedge, μ = 2.12 mm^{-1}. For $C_{80}H_{95}N_{11}Ni_{11}O_{31}\cdot 2.18CH_2Cl_2\cdot 0.75C_4H_6\cdot 0.61H_2O$ **7**; M = 2605.13, triclinic, space group $P\bar{1}$, a = 15.223(7), b = 16.362(7), c = 24.052(12) Å, α = 78.39(5), β = 83.27(2), γ = 72.30(2)°, V = 5580 Å^3 [from 2θ values of 26 reflections measured at $\pm\omega$ ($25 \leqslant 2\theta \leqslant 28°$), λ = 0.71073 Å], Z = 2, D_c = 1.55 g cm^{-3}, T = 150.0(2) K, green lath, μ = 1.99 mm^{-1}.

Data were collected and processed using a Stoë STADI-4 four-circle diffractometer with an Oxford Cryosystems low-temperature device (J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105), graphite-monochromated Mo-Kα X-radiation, ω-2θ scans with learnt-profile (W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22) for **3** and **5**, ω-scans for **4**, **6** and **7**. All data were corrected for Lorentz and polarisation effects. Data for **3**, **5** and **7** were corrected for absorption. All structures were solved by direct methods using SHELXS-86 (G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467). The structures of both **6** and **7** contain various fragments in addition to the nickel complexes. In **7** the site occupancies of these fragments were refined; in **6** one of the fragments refines best as a CO_3 unit. Refinement was on F^2 with all non-H atoms anisotropic (except for solvent and anion fragments in **6** and **7**) to give: for **3** for 313 parameters $R1$ = 0.0336 for 4434 data with $F > 4\sigma(F)$, $wR2$ = 0.0843 for all 5232 independent reflections ($2\theta \leqslant 55°$); for **4** for 274 parameters $R1$ = 0.1088 for 2448 data with $F > 4\sigma(F)$, $wR2$ = 0.3658 for all 4050 independent reflections ($2\theta \leqslant 50°$); for **5** for 554 parameters $R1$ = 0.0355 for 6221 data with $F > 4\sigma(F)$, $wR2$ = 0.0987 for all 6932 independent reflections ($2\theta \leqslant 50°$); for **6** for 1089 parameters $R1$ = 0.0937 for 6173 data with $F > 4\sigma(F)$, $wR2$ = 0.2866 for all 12879 independent reflections ($2\theta \leqslant 45°$); for **7** for 1338 parameters $R1$ = 0.0703 for 10293 data with $F > 4\sigma(F)$, $wR2$ = 0.2094 for all 14566 independent reflections ($2\theta \leqslant 45°$). All refinements used SHELXL-93 (G. M. Sheldrick, University of Göttingen, Germany 1993).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Variable-temperature magnetic measurements in the region 2–300 K were made on a SQUID magnetometer (Quantum Design) in a field of 1000 G on samples sealed in gelatin capsules. In all cases diamagnetic corrections for the sample holders and samples were applied to the data. The observed and calculated data were fitted using in-house software (J. M. Rawson, The University of Edinburgh, 1994).

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