Heterobimetallic nickel–sodium and cobalt–sodium complexes of pyridonate ligands

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Seven new mixed-metal complexes have been prepared and their structures determined. Reaction of anhydrous nickel(II) chloride with Na(xhp) (xhp = 6-methyl- or 6-chloro-2-pyridonate, mhp or chp respectively) produced the discrete polynuclear complexes $[Ni_4Na_4(mhp)_{12}(Hmhp)_2]$ **1** and $[Ni_2Na_2(chp)_2(H_2O)(MeCN)_4]$ **2**, depending on the pyridonate derivative used. A closely related complex $[Ni_2Na_2(chp)_6(H_2O)_2(MeCN)_4]$ **3** cocrystallised with **2** from a reaction scheme involving phenylacetate. A polymeric complex $[\{Ni_2Na_2(chp)_6(H_2O)\}_n]$ **4** can be isolated from a similar reaction to that which gave **2** but by recrystallisation from ethyl acetate rather than the co-ordinating solvent MeCN. The cobalt analogue of **4**, $[\{Co_2Na_2(chp)_6(H_2O)\}_n]$ **5** was also prepared and a closely related cobalt–sodium polymer, $[\{Co_2Na_2(chp)_6\}_n]$ **6**, crystallised from ethyl acetate. A further polymer featuring the mhp ligand, $[\{Co_2Na_2(mhp)_6(Hmhp)(H_2O)\}_n]$ **7**, was produced from reaction of anhydrous cobalt(II) acetate with Na(mhp) followed by recrystallisation from toluene. The structures of the molecular species **1**, **2** and **3** can be rationalised as co-ordination of Na by $[Ni(xhp)_3]^-$ 'complex ligands' in which the nickel centres are surrounded by three chelating pyridonates. In the polymeric species **4**, **5**, **6** and **7** the structures can be viewed as involving co-ordination of Na by $[M_2(xhp)_6]^{2-}$ complex ligands. In **6** the absence of any additional solvent molecules leads to interaction of the sodium site with Cl-donors.

We have been exploring routes to high nuclearity co-ordination complexes using mixtures of 1,3-bridging ligands to stabilise the polynuclear arrays. During this work we have occasionally noticed involvement of sodium as a structural element, for example as a nucleation centre in the 'metallocrown' $[Cu_6-Na(mhp)_{12}][NO_3]$ [1] (mhp = 6-methyl-2-pyridonate) or as an anchoring point in the 'supra-cage assembly' $[Ni_{16}Na_6(chp)_4-(phth)_{10}(Hphth)_2(MeO)_{10}(OH)_2(MeOH)_{20}]$ (chp = 6-chloro-2-pyridonate, phth = phthalate).[2] Here we report seven further examples of the co-ordination of sodium by a 3d-metal complex.

Experimental

Preparations

All reagents, metal salts and ligands were used as obtained from Aldrich. Sodium salts of pyridone ligands were obtained by deprotonation of the ligand in MeOH using Na(OMe) followed by evaporation to dryness. Analytical data were obtained on a Perkin-Elmer 2400 Elemental Analyser by the University of Edinburgh Microanalytical Service and are given in Table 1. Mass spectra were obtained by fast atom bombardment (FAB) of samples in a 3-nitrobenzyl alcohol matrix on a Kratos MS50 spectrometer.

$[Ni_4Na_4(mhp)_{12}(Hmhp)_2]$ **1**. The salt Na(mhp) (0.506 g, 3.86 mmol) was added to a stirred solution of anhydrous nickel(II) chloride (0.250 g, 1.93 mmol) in MeOH (30 cm^3). After 24 h the green solution was filtered and the filtrate evaporated to dryness under reduced pressure, leaving a green paste. Recrystallisation of this paste from acetonitrile or ethyl acetate produced green crystals of complex **1**. FAB mass spectra (significant peaks, possible assignments): m/z 1843, $[Ni_4Na_4(mhp)_{12}(Hmhp)_2]^+$; 1734, $[Ni_4Na_4(mhp)_{12}(Hmhp)]^+$; 1625, $[Ni_4Na_4(mhp)_{12}]^+$; 1409, $[Ni_4Na_4(mhp)_{10}]^+$; 1326, $[Ni_3Na_3(mhp)_{10}]^+$; 704, $[Ni_2Na_2-(mhp)_6]^+$; 596, $[Ni_2Na_2(mhp)_4]^+$; 537, $[NiNa_2(mhp)_4]^+$; 429, $[NiNa_4(mhp)_3]^+$; 406, $[NiNa(mhp)_3]^+$; and 298, $[NiNa(mhp)_2]$.

$[Ni_2Na_2(chp)_6(H_2O)(MeCN)_4]$ **2**. This was prepared in a similar fashion to that of complex **1** using Na(chp) in place of Na(mhp). Recrystallisation from MeCN gave green crystals of **2**. FAB mass spectrum (significant peaks, possible assignments): m/z 1117, $[Ni_2Na_2(chp)_6(MeCN)_4(H_2O)]^+$; 806, $[Ni_2-Na_2(chp)_6]^+$; 655, $[Ni_2Na(chp)_4]^+$; and 339, $[NiNa(chp)_2]^+$.

$[Ni_2Na_2(chp)_6(H_2O)(MeCN)_4]\cdot[Ni_2Na_2(chp)_6(H_2O)_2(MeCN)_4]$ **2.3**. The salt Na(chp) (0.318 g, 2.10 mmol) was added to a stirred solution of hydrated nickel(II) chloride (0.250 g, 1.05 mmol) and Na(O$_2$CCH$_2$Ph) (0.166 g, 1.05 mmol) in MeOH (30 ml). The solution was stirred for 24 h, filtered and evaporated to dryness, leaving a green paste. Crystallisation from MeCN produced crystals of complex **2.3**. FAB mass spectrum (significant peaks, possible assignments): m/z 1117, $[Ni_2Na_2(chp)_6(MeCN)_4-(H_2O)]^+$; 806, $[Ni_2Na_2(chp)_6]^+$; 655, $[Ni_2Na(chp)_4]^+$; and 339, $[NiNa(chp)_2]^+$.

$[\{Ni_2Na_2(chp)_6(H_2O)\}_n]$ **4**. This was prepared in a similar fashion to that of complex **1** using Na(chp) in place of Na(mhp). Recrystallisation from ethyl acetate gave green crystals of **4**. FAB mass spectrum (significant peaks, possible assignments): m/z 766, $[NiNa_2(chp)_4(H_2O)]^+$; 614, $[NiNa(chp)_4-(H_2O)]^+$; 485, $[NiNa(chp)_3(H_2O)]^+$; 444, $[Ni(chp)_3]^+$; 303, $[Na_2(chp)_2]^+$; 280, $[Na(chp)_2]^+$; 210, $[NiNa(chp)]^+$; 187, $[Ni-(chp)]^+$; and 152, $[Na(chp)]^+$.

$[\{Co_2Na_2(chp)_6(H_2O)\}_n]$ **5**. This was prepared in a similar fashion to that of complex **1** using Na(chp) in place of Na(mhp) and anhydrous cobalt(II) chloride in place of anhydrous nickel(II) chloride. Recrystallisation from MeCN gave pink crystals of **5**. No significant FAB mass spectral peaks.

$[\{Co_2Na_2(chp)_6\}_n]$ **6**. Anhydrous cobalt(II) chloride (0.25 g, 1.9 mmol) and Na(chp) (0.59 g, 3.9 mmol) were added to a solution of sodium formate (0.14 g, 1.9 mmol) dissolved in MeOH (40 ml), and the reaction mixture stirred for 24 h. The solution was then filtered and evaporated to dryness producing a purple

Table 1 Analytical data * for compounds **1** to **7**

Complex		Analysis (%)			
		C	H	N	Yield (%)
1	[Ni$_4$Na$_4$(mhp)$_{12}$(Hmhp)$_2$]	54.6 (54.7)	4.6 (4.7)	10.5 (10.6)	70
2	[Ni$_2$Na$_2$(chp)$_6$(H$_2$O)(MeCN)$_4$]	40.6 (40.8)	2.9 (2.9)	12.1 (12.5)	75
2.3	[Ni$_2$Na$_2$(chp)$_6$(H$_2$O)(MeCN)$_4$]·	40.6 (40.5)	2.7 (2.9)	11.9 (12.4)	6
	[Ni$_2$Na$_2$(chp)$_6$(H$_2$O)$_2$(MeCN)$_4$]				
4	[{Ni$_2$Na$_2$(chp)$_6$(H$_2$O)}$_n$]	37.8 (37.8)	2.1 (2.1)	8.8 (8.8)	38
5	[{Co$_2$Na$_2$(chp)$_6$(H$_2$O)}$_n$]	37.8 (37.8)	2.0 (2.1)	8.6 (8.8)	10
6	[{Co$_2$Na$_2$(chp)$_6$}$_n$]	38.4 (38.5)	1.9 (1.9)	8.8 (9.0)	8
7	[{Co$_2$Na$_2$(mhp)$_6$(Hmhp)(H$_2$O)}$_n$]	54.4 (53.7)	5.4 (4.8)	9.7 (10.4)	12

* Calculated values are given in parentheses.

paste which was dried under vacuum overnight. The paste was extracted with ethyl acetate (15 ml) and purple crystals of **6** formed after 1 d. FAB mass spectrum (significant peaks, possible assignments): *m/z* 806, [Co$_2$Na$_2$(chp)$_5$]$^+$; 655, [Co$_2$Na(chp)$_4$]$^+$; 504, [Co$_2$(chp)$_3$]$^+$; 339, [CoNa(chp)$_2$]$^+$; and 303, [Na$_2$(chp)$_2$]$^+$.

[{Co$_2$Na$_2$(mhp)$_6$(Hmhp)(H$_2$O)}$_n$] **7**. Anhydrous cobalt(II) acetate (0.34 g, 1.9 mmol) and Na(mhp) (0.55 g, 4.2 mmol) were stirred together in dry CH$_2$Cl$_2$ under N$_2$ for 24 h during which time the solution became very dark purple. It was filtered and the filtrate evaporated to dryness under reduced pressure, leaving a purple paste. The paste was dissolved in toluene and placed at −5 °C. A small number of pink crystals grew over a period of 4 weeks. No significant FAB mass spectral peaks.

Crystallography

Crystal data and data collection and refinement parameters for compounds **1**–**7** are given in Table 2, selected bond lengths and angles in Tables 3–7.

Data collection and processing. Data were collected on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device,[3] using graphite-monochromated Cu-Kα radiation for complexes **1**, **2**, **2.3**, **4** and **5**, and Mo-Kα radiation for **6** and **7**; ω–θ scans for **1**, **2** and **6**, ω scans for **2.3** and **5**, and ω–2θ scans for **4** and **7**. Data were corrected for Lorentz-polarisation factors. Semiempirical absorption corrections based on azimuthal measurements[4] were applied to data for **2**, **2.3** and **7**; lower crystal quality led to an absorption correction using DIFABS[5] being applied to data for **1** and **4**. Complex **5** crystallised as very thin plates and the crystal was mounted on a short length (0.2 mm) of glass wool in order to minimise background scatter. Although it is not normally advisable for cobalt compounds, Cu-Kα radiation was used for data collection for **5** because of its higher intensity relative to Mo-Kα; peak profiles were broad and ω scans of width (2.2 + 0.15 tan θ) were used. The data for **5** were corrected for absorption by numerical integration based on face-indexing.

Structure analysis and refinement. All structures were solved by direct methods using SHELXS 86[6] or SIR 92[7] and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement. In **7** one of two dicobalt moieties in the polymer is disordered about a crystallographic inversion centre. All non-H atoms were refined anisotropically with global rigid body and rigid bond restraints applied to the ligands in **5** and **7**. Pyridone ligands were also restrained to have similar geometries in **5** and **7**. Fourier-difference syntheses were employed in positioning idealised methyl-hydrogen atoms which were assigned isotropic thermal parameters [U(H) = 1.5 U_{eq}(C)]. Ring H atoms were included in idealised positions, allowed to ride on their parent C atoms (C–H 0.93 Å), and
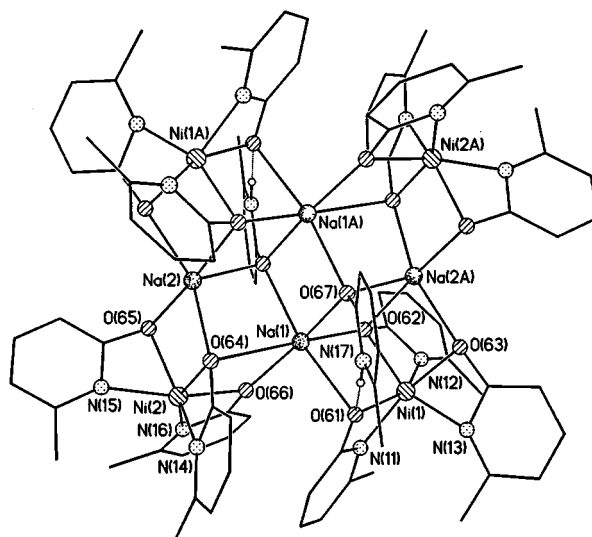
Fig. 1 Structure of complex **1** in the crystal, showing the atom-numbering scheme. The molecule lies disposed about an inversion centre

assigned isotropic thermal parameters [U(H) = 1.2 U_{eq}(C)]. All refinements were against F^2 and used SHELXL 93.[8]

CCDC reference number 186/1042.

See http://www.rsc.org/suppdata/dt/1998/2657/ for crystallographic files in .cif format.

Results

Reaction of nickel(II) chloride with 2 equivalents of Na(mhp) leads, after recrystallisation from either MeCN or ethyl acetate, to [Ni$_4$Na$_4$(mhp)$_{12}$(Hmhp)$_2$] **1** in moderate yield. Diffraction studies reveal a centrosymmetric structure containing four chemically identical [Ni(mhp)$_3$]$^-$ units surrounding a central sodium 'chair' (Fig. 1). Each nickel is co-ordinated to three chelating mhp ligands, two of which also bind to one sodium through their exocyclic oxygen atoms, which are thus μ-bridging. The oxygen atom of the third chelating mhp binds to two further sodiums, and hence is μ$_3$-bridging. Two Hmhp ligands are also found in the structure and show a novel binding mode, each bridging three Na atoms through the exocyclic oxygen atom alone. This mode has not to our knowledge previously been reported either for Hxhp (6-substituted 2-pyridone) or xhp ligands and represents bridging by the keto-tautomer of the pyridonate ligand as the ring N atom is protonated.

The nickel centres in complex **1** have distorted octahedral co-ordination geometries as a result of the small bite angles of the chelating mhp ligands (Table 3). The Ni–N bond lengths are slightly shorter than the Ni–O bonds, although the two bond length ranges overlap allowing for statistical significance. The two crystallographic unique sodium sites show distinct geometries: Na(1) has five contacts to O-donors between 2.230 and

Table 2 Experimental data for the X-ray diffraction studies of compounds **1**, **2**, **2.3**, **3**, **4**, **5**, **6** and **7**

	1	**2**	**2.3**	**4**	**5**	**6**	**7**
Formula	$C_{84}H_{86}N_{14}Na_4Ni_4O_{14}$	$C_{38}H_{32}Cl_6N_{10}Na_2Ni_2O_7$	$C_{38}H_{32}Cl_6N_{10}Na_2Ni_2O_7 \cdot$ $C_{38}H_{34}Cl_6N_{10}Na_2Ni_2O_8$	$C_{30}H_{20}Cl_6N_6Na_2Ni_2O_7$	$C_{30}H_{20}Cl_6Co_2N_6Na_2O_7$	$C_{15}H_9CoN_3NaO_3$	$C_{42}H_{45}Co_2N_7Na_2O_8$
M	1842.5	1116.8	2251.7	952.6	953.1	467.5	939.7
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$I2$	$P2/c$	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a/Å	10.818(4)	15.667(2)	16.4177(15)	21.407(6)	21.582(5)	7.261(2)	11.618(5)
b/Å	14.336(5)	9.1628(5)	9.1699(5)	11.860(3)	11.898(3)	11.316(2)	12.931(5)
c/Å	16.281(6)	16.4418(11)	31.597(2)	13.912(2)	13.873(3)	12.105(3)	17.540(6)
α/°	109.90(2)					112.204(10)	87.86(10)
β/°	100.46(2)	90.525(10)	91.096(11)	91.04(2)	91.45(2)	93.119(14)	71.45(10)
γ/°	107.50(2)					105.192(13)	64.36(10)
U/Å³	2147.8	2360.1	4756.0	3531.5	3561.2	875.5	2236.6
T/K	150.0(2)	220.0(2)	220.0(2)	220.0(2)	220.0(2)	220.0(2)	293
Z	1[a]	2[b]	2	4	4	2	2
D_c/g cm⁻³	1.424	1.572	1.572	1.792	1.778	1.773	1.395
Crystal shape and colour	Green plate	Green block	Green block	Green lath	Purple rod	Purple plate	Pink block
Crystal size/mm	0.39 × 0.35 × 0.12	0.27 × 0.23 × 0.23	0.27 × 0.16 × 0.10	0.35 × 0.16 × 0.08	0.66 × 0.27 × 0.21	0.35 × 0.18 × 0.08	
μ/mm⁻¹	1.764	4.791	4.768	6.243	1.463	1.484	0.819
Unique data	6251	2929	6939	2584	3134	3100	5783
Observed data ($F_o > 4\sigma F_o$)	4727	2751	4810	1414	2259	1959	3455
Parameters	548	294	591	240	240	235	838
Maximum Δ/σ ratio	0.006	0.001	0.012	0.001	0.001	0.001	−0.001
$R1$, $wR2$[c]	0.0512, 0.1450	0.0338, 0.0882	0.0534, 0.1263	0.0515, 0.1091	0.0438, 0.1084	0.0538, 0.1196	0.0478, 0.1453
Weighting scheme,[d] w^{-1}	$\sigma^2(F_o^2) + (0.097P)^2$	$\sigma^2(F_o^2) + (0.0633P)^2$	$\sigma^2(F_o^2) + (0.0316P)^2 + 8.23P$	$\sigma^2(F_o^2) + (0.0358P)^2$	$\sigma^2(F_o^2) + (0.0612P)^2$	$\sigma^2(F_o^2) + (0.0502P)^2$	$\sigma^2(F_o^2) + (0.0504P)^2 + 4.93P$
Goodness of fit	1.013	1.038	1.051	0.966	1.013	0.981	1.012
Largest residuals/e Å⁻³	+0.404, −0.439	+0.238, −0.483	+0.284, −0.363	0.305, −0.289	0.620, −0.595	0.529, −0.613	0.308, −0.537

[a] The molecule lies on an inversion centre. [b] The molecule lies on a two-fold axis. [c] $R1$ based on observed data, $wR2$ on all unique data. [d] $P = \frac{1}{3}[\max(F_o^2, 0) + 2F_c^2]$.

**Table 3** Selected bond lengths (Å) and angles (°) for compound **1**

Ni(1)–N(11)	2.044(3)	Ni(2)–N(14)	2.067(3)
Ni(1)–N(12)	2.095(3)	Ni(2)–N(15)	2.074(3)
Ni(1)–N(13)	2.061(3)	Ni(2)–N(16)	2.088(3)
Ni(1)–O(61)	2.144(3)	Ni(2)–O(64)	2.149(3)
Ni(1)–O(62)	2.107(3)	Ni(2)–O(65)	2.117(3)
Ni(1)–O(63)	2.144(3)	Ni(2)–O(66)	2.108(3)
Na(1)–O(66)	2.230(3)	Na(2)–O(64)	2.302(3)
Na(1)–O(62)	2.325(3)	Na(2)–O(65)	2.357(3)
Na(1)–O(67)	2.352(3)	Na(2)–O(63A)	2.269(3)
Na(1)–O(61)	2.487(3)	Na(2)–O(62A)	2.541(3)
Na(1)–O(67A)	2.367(3)	Na(2)–O(67A)	2.327(3)
N(11)–Ni(1)–N(13)	101.34(13)	N(14)–Ni(2)–N(15)	101.93(14)
N(11)–Ni(1)–N(12)	105.24(14)	N(14)–Ni(2)–N(16)	112.80(14)
N(13)–Ni(1)–N(12)	109.91(13)	N(15)–Ni(2)–N(16)	103.60(13)
N(11)–Ni(1)–O(62)	102.73(12)	N(14)–Ni(2)–O(66)	100.83(13)
N(13)–Ni(1)–O(62)	155.93(12)	N(15)–Ni(2)–O(66)	157.00(12)
N(12)–Ni(1)–O(62)	64.00(12)	N(16)–Ni(2)–O(66)	64.02(12)
N(11)–Ni(1)–O(63)	161.27(12)	N(14)–Ni(2)–O(65)	150.29(12)
N(13)–Ni(1)–O(63)	64.01(12)	N(15)–Ni(2)–O(65)	64.05(12)
N(12)–Ni(1)–O(63)	91.31(12)	N(16)–Ni(2)–O(65)	96.36(12)
O(62)–Ni(1)–O(63)	92.29(11)	O(66)–Ni(2)–O(65)	96.85(11)
N(11)–Ni(1)–O(61)	63.73(13)	N(14)–Ni(2)–O(64)	63.88(12)
N(13)–Ni(1)–O(61)	96.77(12)	N(15)–Ni(2)–O(64)	102.72(12)
N(12)–Ni(1)–O(61)	152.94(12)	N(16)–Ni(2)–O(64)	153.53(13)
O(62)–Ni(1)–O(61)	93.26(11)	O(66)–Ni(2)–O(64)	90.23(12)
O(63)–Ni(1)–O(61)	104.76(11)	O(65)–Ni(2)–O(64)	92.56(11)
O(66)–Na(1)–O(62)	109.58(12)	O(63A)–Na(2)–O(64)	151.38(13)
O(66)–Na(1)–O(67)	162.88(12)	O(63A)–Na(2)–O(67A)	105.41(11)
O(62)–Na(1)–O(67)	87.14(11)	O(64)–Na(2)–O(67A)	102.48(12)
O(66)–Na(1)–O(67A)	99.39(11)	O(63A)–Na(2)–O(65)	98.73(11)
O(62)–Na(1)–O(67A)	97.08(11)	O(64)–Na(2)–O(65)	82.84(11)
O(67)–Na(1)–O(67A)	81.59(10)	O(67A)–Na(2)–O(65)	99.39(10)
O(66)–Na(1)–O(61)	93.19(11)	O(63A)–Na(2)–O(62A)	78.29(10)
O(62)–Na(1)–O(61)	79.84(11)	O(64)–Na(2)–O(62A)	99.12(11)
O(67)–Na(1)–O(61)	85.98(10)	O(67A)–Na(2)–O(62A)	82.79(10)
O(67A)–Na(1)–O(61)	167.35(11)	O(65)–Na(2)–O(62A)	176.72(11)

Symmetry transformation used to generate equivalent atoms: A $-x + 1$, $-y$, $-z + 1$.

Fig. 2 Structure of complex **2** in the crystal, showing the atom-numbering scheme. The molecule lies disposed about a two-fold axis

Fig. 3 Structure of complex **3** in the crystal of **2.3**, showing the atom-numbering scheme. The molecule lies disposed about a two-fold axis

2.487 Å with one longer contact of 3.008 Å to O(64); Na(2) has five contacts to O-donors which fall in the range 2.269 to 2.541 Å but no further long contacts. There is no difference between Na–O bonds to mhp or Hmhp ligands which is perhaps surprising. The Na–O (Hmhp) bonds average 2.35 Å which is extremely short for a Na–O (ketone) distance. This is still more surprising considering that this ketone oxygen is bridging three sodium sites, and is therefore formally pentavalent. Only four previous examples [9–12] have been reported of μ_3-oxygen bridges where the O-donor is derived from a ketone. These examples involve lithium [9,10] vanadium [11] and cadmium [12].

The metal polyhedron can be described as four linked cubes with each cube missing a vertex; for example, the cube comprising Na(1), O(67), Na(2a), O(63), Ni(1), O(61) and O(62). Each cube contains one Ni, two Na and four O atoms and is linked to two others, sharing an edge [Na(2), O(67) or symmetry equivalents] with one, and a vertex [Na(1) or Na(1a)] with a second. The average Na · · · Na contact is 3.499 Å, with the closest Ni · · · Ni contact being over 6 Å.

Reaction of nickel(II) chloride with Na(chp) followed by crystallisation from MeCN gives a tetrametallic species [Ni$_2$-Na$_2$(chp)$_6$(H$_2$O)(MeCN)$_4$] **2** which crystallises about a two-fold rotation axis. As in **1** the molecule contains [Ni(xhp)$_3$]$^-$ 'complex ligands' linked to a central sodium core (Fig. 2). Oxygen atoms from two of the chelating chp ligands each bridge to one sodium centre as in **1**, however in **2** the third O atom [O(1R)] is bound only to the Ni, whereas in **1** it is μ_3 bridging. Again the nickel centres have distorted octahedral geometries due to the small bite angle of the chp ligands (Table 4). The sodium is five-co-ordinate, bound to two chp oxygen donors, a μ-bridging water and two molecules of MeCN. The bridging H$_2$O is involved in two strong hydrogen bonds to the non-bridging O
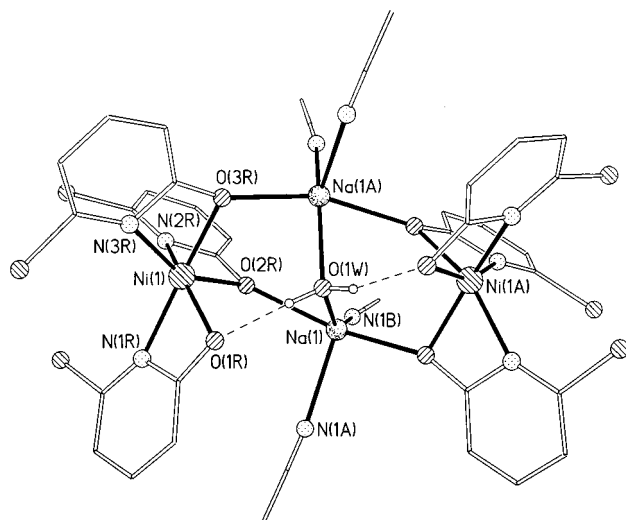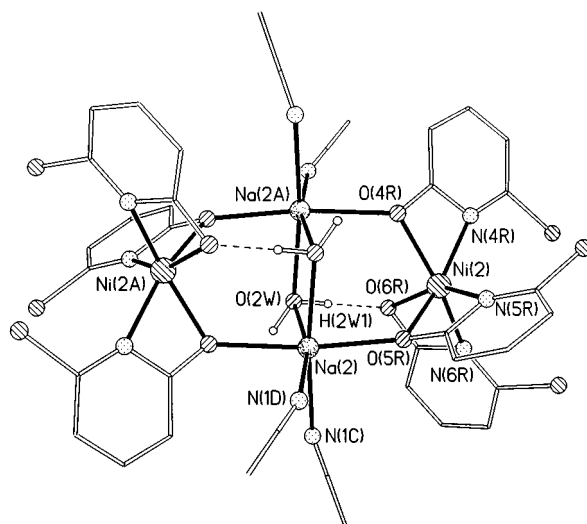
atoms [O(1R) and its symmetry equivalent], [O(W) · · · O(1R) 2.705 Å].

A quite different reaction involving sodium phenylacetate, nickel(II) chloride and Na(chp) also led to a small yield of crystals containing complex **2**, however here **2** was found cocrystallised with a further tetranuclear complex [Ni$_2$Na$_2$(chp)$_6$(H$_2$O)$_2$-(MeCN)$_4$] **3** (Fig. 3). There is a close similarity between **2** and **3**, the significant difference being that two μ-water molecules are found in **3** bridging between the central sodium centres. Each bridging H$_2$O forms only one strong hydrogen bond in **3**, whereas the bridging H$_2$O in **2** formed two. The nickel co-ordination spheres are identical in the two complexes (Table 4) but the sodium environment in **3** is six-co-ordinate, involving two bridging water molecules, two MeCN ligands and two μ-oxygen donors from chp ligands.

Complex **2** is formed from reaction of nickel(II) chloride with Na(chp) followed by recrystallisation of the product from MeCN. If the same product is recrystallised from ethyl acetate a polymeric complex [{Ni$_2$Na$_2$(chp)$_6$(H$_2$O)}$_n$] **4** is obtained (Fig. 4). The change from **2** may be caused by the absence of co-ordinating solvate molecules which lead to quite different metal co-ordination environments. In **4** the nickel site is six-co-ordinate, but there are only two chelating chp ligands bound to the metal with the remaining two sites occupied by two μ-oxygen donors [O(23) and its symmetry equivalent] from tri-nucleating chp ligands (Table 5). The nickel site therefore has

		2.3	
	2	Molecule 1 (≡**3**)*	Molecule 2 (≡**2**)
Ni–N(1R)	2.086(3)	2.078(4)	2.046(4)
Ni–N(2R)	2.062(3)	2.069(4)	2.059(4)
Ni–N(3R)	2.038(4)	2.057(4)	2.066(4)
Ni–O(1R)	2.115(3)	2.100(4)	2.139(4)
Ni–O(2R)	2.107(3)	2.121(3)	2.123(4)
Ni–O(3R)	2.144(3)	2.144(4)	2.108(3)
Na–N(1E)	2.434(5)	2.631(7)	2.438(6)
Na–N(1F)	2.473(6)	2.428(6)	2.468(6)
Na–O(2R)	2.334(3)	2.294(4)	2.479(4)
Na–O(3RA)	2.425(3)	2.414(4)	2.347(4)
Na–O(W)	2.342(4)	2.425(4)	2.328(4)
Na–O(WA)		2.404(5)	
N(3R)–Ni–N(2R)	102.20(13)	101.3(2)	105.3(2)
N(3R)–Ni–N(1R)	105.42(14)	108.8(2)	102.6(2)
N(2R)–Ni–N(1R)	106.17(13)	103.2(2)	106.5(2)
N(3R)–Ni–O(2R)	92.28(14)	93.18(15)	98.8(2)
N(2R)–Ni–O(2R)	63.95(12)	63.44(15)	64.17(15)
N(1R)–Ni–O(2R)	161.52(14)	156.6(2)	158.4(2)
N(3R)–Ni–O(1R)	157.89(12)	158.79(15)	153.7(2)
N(2R)–Ni–O(1R)	99.46(13)	99.8(2)	100.4(2)
N(1R)–Ni–O(1R)	63.80(13)	64.27(15)	63.8(2)
O(2R)–Ni–O(1R)	101.20(12)	97.77(14)	97.65(14)
N(3R)–Ni–O(3R)	63.99(12)	63.60(15)	64.23(15)
N(2R)–Ni–O(3R)	151.75(13)	155.4(2)	160.8(2)
N(1R)–Ni–O(3R)	101.42(13)	100.3(2)	91.8(2)
O(2R)–Ni–O(3R)	90.98(13)	96.56(2)	100.33(14)
O(1R)–Ni–O(3R)	98.02(11)	97.00(14)	92.65(15)
O(2R)–Na–O(W)	81.78(10)	94.74(14)	79.66(12)
O(2R)–Na–O(3RA)	161.77(13)	169.21(15)	161.9(2)
O(W)–Na–O(3RA)	80.52(10)	74.75(14)	82.68(12)
O(2R)–Na–N(1E)	92.08(14)	91.1(2)	97.3(2)
O(W)–Na–N(1E)	109.9(2)	84.5(2)	112.8(2)
O(3RA)–Na–N(1E)	98.02(15)	90.3(2)	93.2(2)
O(2R)–Na–N(1F)	106.03(14)	99.0(2)	88.1(2)
O(W)–Na–N(1F)	149.2(2)	166.3(2)	148.6(2)
O(3RA)–Na–N(1F)	87.27(14)	91.5(2)	105.2(2)
N(1E)–Na–N(1F)	99.6(2)	95.4(2)	97.4(2)
O(2R)–Na–O(WA)		81.9(2)	
O(W)–Na–O(WA)		84.8(2)	
O(3RA)–Na–O(WA)		74.75(14)	
N(1E)–Na–O(WA)		166.7(2)	
N(1F)–Na–O(WA)		96.8(2)	

Symmetry transformation used to generate equivalent atoms: A for **2** $-x$, y, $-z$; for **2.3** (molecule 1) $-x - 1$, $-y - 2$, $-z - 1$; for **2.3** (molecule 2) $-x$, y, $-z - \frac{3}{2}$. * To match atom labels to those in Fig. 3 add 3 to the label for N or O in column 1, *i.e.* N(1R) ≡ N(4R).

	4	**5**
	M = Ni	Co
M(1)–O(21)	2.117(4)	2.152(7)
M(1)–O(22)	2.182(4)	2.197(6)
M(1)–O(23)	2.052(4)	2.057(7)
M(1)–O(23A)	2.035(5)	2.084(7)
M(1)–N(11)	2.118(5)	2.180(8)
M(1)–N(12)	2.052(5)	2.119(8)
Na(1)–O(1)	2.365(6)	2.372(8)
Na(1)–O(22)	2.380(5)	2.371(7)
Na(1)–O(21B)	2.366(5)	2.377(8)
Na(1)–O(22C)	2.407(5)	2.439(8)
Na(1)–N(13C)	2.491(6)	2.513(8)
Na(1A)–O(1)	2.365(6)	2.372(8)
O(23)–M(1)–O(23A)	78.7(2)	79.9(3)
O(23)–M(1)–N(12)	96.8(2)	96.4(3)
O(23A)–M(1)–N(12)	165.5(2)	165.1(3)
O(21)–M(1)–O(23)	98.4(2)	98.9(3)
O(21)–M(1)–O(23A)	93.6(2)	93.1(3)
O(21)–M(1)–N(12)	100.6(2)	101.7(3)
N(11)–M(1)–O(23)	161.3(2)	160.9(3)
N(11)–M(1)–O(23A)	97.7(2)	98.3(3)
N(11)–M(1)–N(12)	90.9(2)	89.8(3)
N(11)–M(1)–O(21)	63.4(2)	62.1(2)
O(22)–M(1)–O(23)	101.6(2)	101.7(3)
O(22)–M(1)–O(23A)	103.9(2)	104.2(3)
O(22)–M(1)–N(12)	63.4(2)	62.2(2)
O(22)–M(1)–O(21)	155.7(2)	155.1(2)
O(22)–M(1)–N(11)	97.1(2)	97.1(3)
O(22)–Na(1)–O(1)	79.4(2)	79.33(15)
O(22)–Na(1)–O(21B)	137.6(3)	137.5(2)
O(1)–Na(1)–O(21B)	72.4(2)	72.1(2)
O(22)–Na(1)–O(22C)	86.0(3)	86.5(2)
O(1)–Na(1)–O(22C)	78.0(2)	78.80(15)
O(21B)–Na(1)–O(22C)	117.2(3)	116.9(2)
O(22)–Na(1)–N(13C)	136.7(3)	135.7(2)
O(1)–Na(1)–N(13C)	139.8(2)	141.1(2)
O(21B)–Na(1)–N(13C)	82.7(3)	83.5(2)
O(22C)–Na(1)–N(13C)	86.4(3)	86.2(2)

Symmetry transformations used to generate equivalent atoms: A $-x + 1$, $-y$, $-z + 2$; B x, $-y$, $z - \frac{1}{2}$; C $-x + 1$, y, $-z + \frac{3}{2}$.

Fig. 4 The tetranuclear Co₂Na₂ building-block from which the polymer **5** is constructed. Complex **4** is isostructural and the numbering scheme shown is common to both
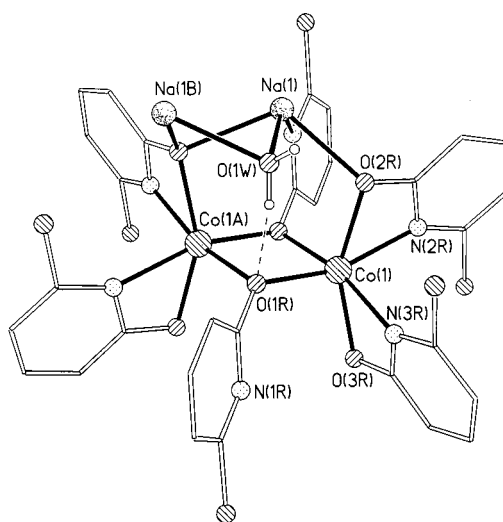
2 N- and 4 O-donors co-ordinated, rather than 3 N- and 3 O-donors as in complexes **1**–**3**.

The crystallographically unique sodium site is quite different to those found in complexes **1**–**3**. It is five-co-ordinate, involving one nitrogen and four oxygen atoms. The N-donor [N(13)] is derived from the chp ligand which provides the oxygen donor [O(23)] which bridges Ni(1) and Ni(1A), while the four oxygen donors are derived from a variety of ligands. Atom O(1) is from a μ-bridging water molecule, similar to those found in **1** to **3**, and bonds to two sodium centres. A further oxygen [O(21)] is μ bridging between a Ni and Na, and is derived from a chelating chp. The final two oxygen donors are derived from chelating chp ligands, but also bridge between two sodium sites and are hence μ₃ bridging. The result is that two neighbouring sodium sites are bridged by three O atoms, and within the polymer there are alternating dinuclear nickel and dinuclear sodium fragments (Fig. 5). Extending the concept of nickel complexes acting as ligands for sodium centres, the polymer **4** could be regarded as consisting of [Ni₂(chp)₆]²⁻ units ligating [Na₂-(H₂O)]²⁺ units, where in **2** there are two [Ni(xhp)₃]⁻ complex ligands binding to the [Na₂(H₂O)(MeCN)₄]²⁺ core.

A similar reaction, but using cobalt in place of nickel, leads to the complex [{Co₂Na₂(chp)₆(H₂O)}ₙ] **5**, which is isostructural with **4**. The metal–ligand bonds in **5** are slightly longer than in **4**, *e.g.* Co–O bonds average 2.123 Å in **5**, while Ni–O bonds
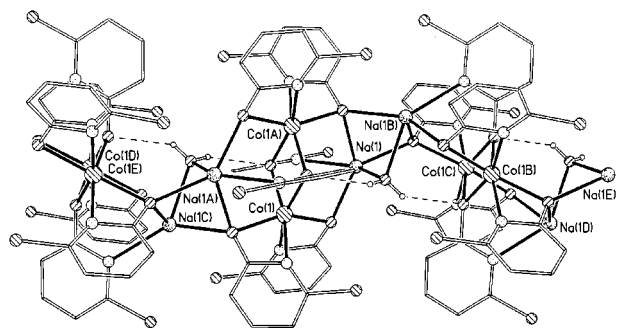
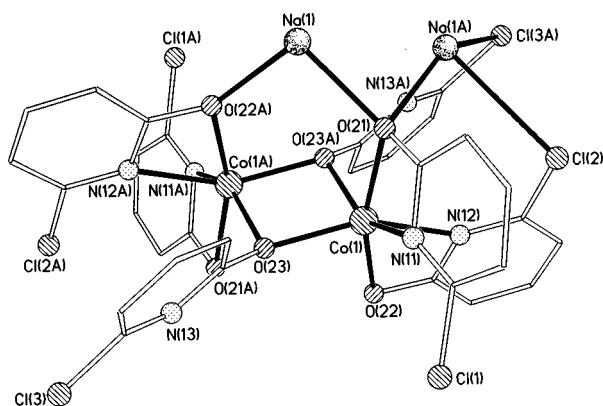**Fig. 5** A fragment of the one-dimensional polymer **5**; **4** is isostructural

Fig. 6 The tetranuclear Co_2Na_2 building-block from which the polymer **6** is constructed, also showing the atom-numbering scheme

Table 6 Selected bond lengths (Å) and angles (°) for compound **6**

Co(1)–O(23)	2.045(4)	Co(1)–O(21)	2.195(4)
Co(1)–O(23A)	2.083(4)	Co(1)–N(11)	2.131(4)
Co(1)–O(22)	2.168(4)	Co(1)–N(12)	2.152(5)
Na(1)–O(22A)	2.289(4)	Na(1)–O(21)	2.327(4)
Na(1)–O(22B)	2.409(4)	Na(1)–N(13C)	2.539(5)
Na(1)–Cl(2B)	3.073(3)	Na(1)–Cl(3C)	3.298(3)
O(23)–Co(1)–O(23A)	83.4(2)	O(23)–Co(1)–N(11)	104.1(2)
O(23A)–Co(1)–N(11)	150.1(2)	O(23)–Co(1)–N(12)	152.1(2)
N(11)–Co(1)–N(12)	88.0(2)	O(23A)–Co(1)–N(12)	98.7(2)
O(23)–Co(1)–O(22)	90.6(2)	O(23A)–Co(1)–O(22)	88.7(2)
N(11)–Co(1)–O(22)	119.7(2)	N(12)–Co(1)–O(22)	61.7(2)
O(23)–Co(1)–O(21)	107.4(2)	O(23A)–Co(1)–O(21)	88.52(14)
N(11)–Co(1)–O(21)	61.5(2)	N(12)–Co(1)–O(21)	100.5(2)
O(22)–Co(1)–O(21)	161.36(14)	O(22A)–Na(1)–O(21)	99.1(2)
O(22A)–Na(1)–O(21B)	119.2(2)	O(21)–Na(1)–O(21B)	95.37(14)
O(22A)–Na(1)–N(13C)	140.6(2)	O(21)–Na(1)–N(13C)	96.6(2)
O(21B)–Na(1)–N(13C)	94.8(2)	O(22a)–Na(1)–Cl(2B)	78.30(12)
O(21)–Na(1)–Cl(2B)	173.07(14)	O(21B)–Na(1)–Cl(2B)	80.54(11)
N(13C)–Na(1)–Cl(2B)	89.34(13)	O(22A)–Na(1)–Cl(3C)	90.21(12)
O(21)–Na(1)–Cl(3C)	103.04(13)	O(21B)–Na(1)–Cl(3C)	142.29(12)
N(13C)–Na(1)–Cl(3C)	50.96(12)	Cl(2B)–Na(1)–Cl(3C)	83.47(8)

Symmetry transformations used to generate equivalent atoms: A $-x + 1$, $-y + 1$, $-z + 1$; B $-x$, $-y + 1$, $-z + 1$; C $x - 1$, y, z; D $x + 1$, y, z.

Fig. 8 One of the two crystallographically independent Co_2Na_2 building-blocks from which the polymer **7** is constructed, showing the atom-numbering scheme

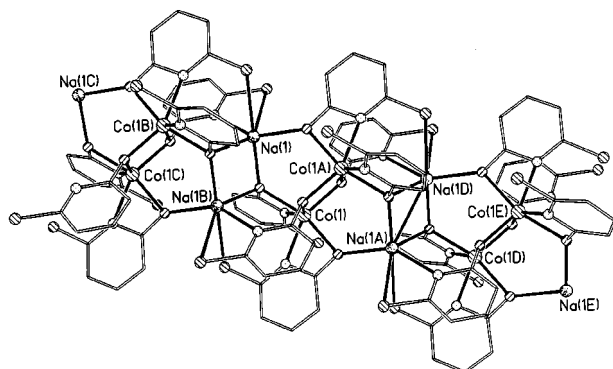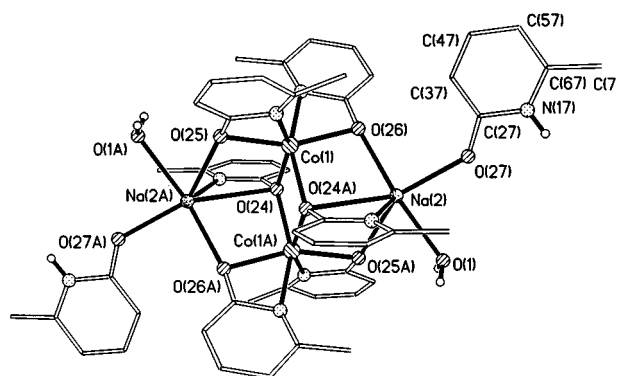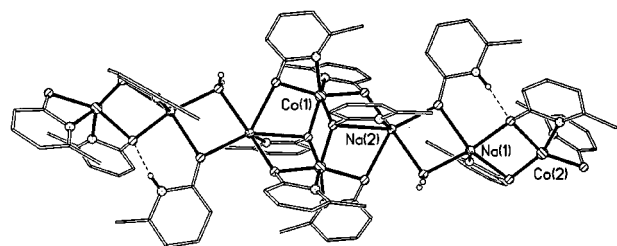**Fig. 7** A fragment of the one-dimensional polymer **6**

Fig. 9 A fragment of the one-dimensional polymer **7**

average 2.096 Å in **4** (Table 5). There are no further significant differences between the structures.

If the reaction mixture contains sodium formate, crystallisation of the paste from ethyl acetate leads to a further polymer, $[\{Co_2Na_2(chp)_6\}_n]$ **6** in low yield, which does not contain co-ordinated solvent or water (Figs. 6 and 7). The $[M_2(chp)_6]^{2-}$ complex ligand is similar to this fragment in **3** and **4**, with each Co bound to two chelating chp ligands and two μ-oxygen donors from further pyridonates. The sodium site is quite different from that in **3** and **4**, although it is probably best described as five-co-ordinate, involving one Cl-, one N- and three O-donors (Table 6). The N atom [N(13)] is again derived from the pyridonate which also provides the μ-oxygen atom which bridges Co(1) and Co(1A), and the oxygen atoms are again two μ₃ donors [O(21) and symmetry equivalents] which bridge two Na and one Co, and one oxygen [O(22)] which bridges to a Co. The fifth site in **3** and **4** is provided by a bridging water molecule, however as this group is absent in **6** a chlorine atom from chp [Cl(2) or symmetry equivalents] occupies the fifth site with a contact of 3.07 Å. This appears to be a new binding mode for the chp ligand: chelating to one metal through the O- and

N-donors, bridging to a second metal through the oxygen atom and contacting a third metal through the chlorine.

We have thus far been unable to isolate the cobalt equivalents for the molecular species **1**–**3**, however we have isolated a further polymeric complex $[\{Co_2Na_2(mhp)_6(Hmhp)(H_2O)\}_n]$ **7** which was prepared in very low yield from a reaction involving cobalt acetate and Na(mhp) (Fig. 8). The structure is extremely disordered, with two positions observed for one cobalt and four mhp ligands in the asymmetric unit. This disorder renders bond lengths and angles of dubious significance (Table 7), however the connectivity of the structure is clearly established. It is related to that of **4** and **5**. The cobalt sites in **7** are co-ordinated to two chelating mhp ligands, and two μ-oxygen atoms which bridged to a symmetry equivalent cobalt site. Thus

Table 7 Selected bond lengths (Å) for compound **7**

Ordered cobalt site

Co(1)–O(24)	2.053(4)	Co(1)–O(26)	2.137(5)
Co(1)–O(24A)	2.061(4)	Co(1)–N(15)	2.145(4)
Co(1)–O(25)	2.124(4)	Co(1)–N(16)	2.147(5)

Disordered cobalt site

Co(2)–O(21)	2.042(7)	Co(2′)–O(21′)	2.056(7)
Co(2)–O(21B)	2.049(10)	Co(2′)–N(12′)	2.101(7)
Co(2)–O(22)	2.128(7)	Co(2′)–O(23′)	2.140(10)
Co(2)–O(23)	2.125(10)	Co(2′)–O(21′A)	1.821(7)
Co(2)–N(12)	2.177(7)	Co(2′)–N(13′)	2.132(7)
Co(2)–N(13)	2.148(7)	Co(2′)–O(22′)	2.159(7)

Sodium

Na(1)–O(1)	2.325(6)	Na(2)–O(1)	2.424(6)
Na(1)–O(21)	2.628(7)	Na(2)–O(26)	2.309(5)
Na(1)–O(22)	2.182(7)	Na(2)–O(27)	2.401(11)
Na(1)–O(27)	2.461(10)	Na(2)–O(24B)	2.817(5)
Na(1)–N(11)	2.640(8)	Na(2)–O(25B)	2.424(6)
Na(1)–O(23A)	2.646(8)	Na(2)–N(14B)	2.421(5)
Na(1)–O(22′)	2.470(8)	Na(2)–O(27′)	2.299(11)
Na(1)–O(27′)	2.266(10)	Na(1)–O(23′A)	2.360(10)
Na(1)–N(11′)	2.290(7)		

Symmetry transformations used to generate equivalent atoms: A −x + 1, −y + 1, −z + 1; B −x, −y + 2, −z + 2.

$[Co_2(mhp)_6]^{2-}$ can be recognised as a structural feature similar to $[M_2(chp)_6]^{2-}$ in **4** and **5**. The sodium unit in **7** is different, in that each five-co-ordinate Na is bound to two μ-O-donors from mhp ligands chelating to cobalt, the N-donor of a mhp ligand which provides the O atom which bridges between cobalt centres, a μ-oxygen from water and finally a μ-oxygen from an Hmhp ligand. This final ligand represents the main difference between **7** and **4** and **5** with $[Na_2(Hmhp)(H_2O)]$ units each bound by two chelating 'complex ligands' of formula $[Co_2-(mhp)_6]^{2-}$. As each complex ligand binds to two Na-containing fragments, a polymer results (Fig. 9).

Discussion

The structures described illustrate how Na atoms can become involved in linking complexes of other metals into more complicated frameworks. The ability of the sodium to adopt many different co-ordination geometries is important in this role. Within the seven structures discussed here several different co-ordination geometries are adopted which are all more or less distorted.

In compound **2** there is one crystallographically unique sodium site, and it has a five-co-ordinate square-based pyramidal environment. A similar five-co-ordinate site [Na(2)] is found in **1**. The five bond lengths in these sites fall in the range from 2.269 to 2.542 Å, and bond angles involving the atom at the vertex of the pyramidal are between 82.1 and 109.9° while those within the square base are between 78.3 and 106.0° when *cis* and between 149.2 and 176.7° for *trans*.

In compound **1** the Na(1) site can be regarded as somewhat between five- and six-co-ordinate. Five bonds between 2.230 and 2.487 Å are found, plus one further contact of 3.008 Å. The angles are consistent with a distorted octahedron, with *trans* angles between 162.9 and 178.0° and *cis* angles between 68.5 and 109.6°. In compound **3** the sodium is six-co-ordinate, with no markedly longer bonds and angles close to that required for an octahedron.

In complexes **4** and **5** the question of co-ordination number becomes more debatable. The sodium site in both compounds has five contacts to O- or N-donors between 2.365 and 2.491 Å, however the angles at Na bear no relation to those of either a square-based pyramid or a trigonal bipyramid. In particular there is no angle near 180°, with the largest angle found 141.1°.
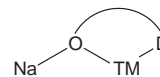
Scheme 1 The bridging mode found in many heterometallic compounds featuring Na. D = N, O or S, and O and D belong to a chelating ligand; TM = a transition metal

There is a much longer contact to a Cl atom [Na(1)···Cl(1) 3.360 Å] and inclusion of this atom within the sodium co-ordination sphere reveals a geometry close to that of a trigonal prism. The three O-donors which bridge between sodium sites [O(1), O(22) and O(22A)] form one trigonal plane which eclipses a plane described by O(21C), N(13A) and Cl(1). Whether the Na(1)···Cl(1) contact is sufficiently short to be regarded as a bond is debatable, however in any case the co-ordination geometry appears to be based on a trigonal prism.

In complex **6** there is again a question of co-ordination number. There are four bonds to O- or N-donors between 2.289 and 2.539 Å. The shortest contact to a Cl atom is 3.073 Å, and inclusion of this atom within the sodium co-ordination sphere leads to a geometry closer to trigonal bipyramidal than square pyramidal, with the *trans* angle between the axial atoms [Cl(2B) and O(21)] 173.1°. The angles between the axial and equatorial atoms fall between 78.3 and 99.1° while those within the equatorial plane are between 94.8 and 140.6°. The next nearest contact to a Cl is 3.298 Å but the geometry which results if this atom is regarded as bound to the Na is extremely irregular, and therefore it is probably simplest to regard this Na as five-co-ordinate.

In complex **7** the sodium geometries are still more distorted. The Na(1) site is disordered, however both models have very similar geometries as has the Na(2) site. The best description of the sites, which are six-co-ordinate, is as a plane of five oxygen donors capped with an additional N-donor at one apical site of a pentagonal bipyramid. The degree of distortion is considerable, mainly caused by the N- and one O-donor being derived from a chelating mhp ligand in every case. This has a concomitant effect of increasing all other angles involving these atoms. The angles found in the structures fall within the following ranges: between the two donors of the chelating mhp 50.3–50.8°, other angles to the apical N-donor 91.1–115.6° and the *cis* angles within the pentagonal plane 64.2–91.4°.

The degree of distortion in each of these sites makes the description chosen debatable but the important point is that Na adopts a variety of five- and six-co-ordinate geometries readily and therefore imposes no constraints on the overall structure of the co-ordination framework. This geometric flexibility, which reflects the non-directional electrostatic nature of the interaction between Na and donor atoms, seems complementary to those of transition metals. For these reasons sodium can play a primary role in mixed-metal complex formation, producing an array of structural motifs. Those relevant to the new compounds described here are discussed below.

In many of these structures, and certainly in compounds **1**–**7**, the motif shown in Scheme 1 is important, where a chelating ligand is attached to the 3d metal, and the oxygen donor of the chelator is shared with the sodium site. This motif is common for Schiff-base ligands, and examples are found where Na is surrounded by one,[13] two[14] or three[15] Schiff-base complexes of 3d metals. Several other 'sodium-centred' mixed-metal complexes have the core shown in Scheme 2. This common core can be described as a raft of six face-sharing 'broken cubes', and has been found with nuclearities {NaCu₆}**8**,[1] {NaCo₆}**9**,[16] {NaFe₆}**10**[17] and {Na₃Co₄}**11**.[18] Sodium occupies the M1 site in all these structures, as well as M2 and M3 in **11**. Only six molecular structures are known which contain this core,[19] but which do not contain sodium.

Other structures contain sub- or super-sets of Scheme 2. Examples are a {Na₂V₂}[20] **12** structure with M1 and M2 as Na and M4 and M6 as V. Changing the ligand from 2-sulfenyl-
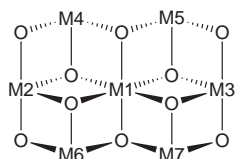
Scheme 2 A heptanuclear metal–oxygen core (M = Na or a transition metal)

phenol to catechol leads to an 'isomeric' $\{Na_2V_2\}$ structure **13**[21] with the metal positions exchanged. An expanded version of the core in **12** exists for $\{Na_2Fe_4\}$,[22] with the additional two metals bound at M7 and at a vertex related to M7 through an inversion centre. The $\{Na_4Ni_4\}$ core in **1** can be understood in a similar way with Na at M1, M2, M4 and M6 while Ni is found at M5 and M7 and their inverse relations. The Na_2M_2 cores of **12** and **13** can be combined in a third variant, a chain-polymer based around a $\{Na_2M_2\}$ repeat.[23] Most of the structures reported here belong to this category, with some variation in the exact propagation mode involved in the formation of each polymer.

The range of structural types reported here is therefore quite limited, and all can be related to Scheme 2. Previous work indicates an apparently limitless range of structural arrangements are possible from such mixed-metal inorganic syntheses. Examples include: a triangular structure with a $\{Na_3Co_3\}$ nuclearity[24] where at the centre of the molecule a pair of μ_3-oxides bridge three sodiums, which are surrounded by three peripheral cobalt atoms; a tetrahedral pattern of Mn^{II} surrounding a μ_4-oxo at the centre of a $\{Na_2Mn_4\}$ structure[25] which has sodium sites capping two opposite edges of the tetrahedron; an octahedral $\{Na_4Cr_2\}$ O-bridged core,[26] where the sodium sites are mutually *trans*; and perhaps the most beautiful architecture which is an $\{Na_4Cu_4\}$ complex[27] with four parallel $O–Cu^I–O$ linear units which are capped by three-co-ordinate sodiums, resulting in a pair of edge-sharing (Cu_3Na_2) trigonal bipyramids.

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