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SYNTHESIS AND STRUCTURE OF A SODIUM COMPLEX OF A HEXANUCLEAR COBALT(II) HYDROXYPYRIDINE DERIVATIVE

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Abstract—The reaction of the sodium derivative of 2-hydroxy-6-methylpyridine (Hmhp) with cobalt(II) acetate in methanol gives the heteropolynuclear complex $[Na\{Co(mhp)_2\}_6]^+(O_2CCH_3)^- \cdot 2CH_2Cl_2$, whose structure contains six-coordinated sodium and four-coordinated cobalt with adjacent cobalt atoms bridged by two hydroxymethylpyridine (mhp) ligands.

By now there are very many examples of crown ether complexes of alkali metals, in which a cyclic polyether with between four and eight oxygen atoms is suitably located round a cavity which can precisely accommodate one particular group 1 metal cation. Recently some more subtle variations on this theme have been reported. For example, in the complexes $[Mo(CO)_4\{Ph_2P(CH_2CH_2O)_n CH_2CH_2PPh_2\}M]^+$ (M = Li, Na; n = 4, 5) the ether oxygens of the 16- or 19-membered rings act as crown ligands for the alkali metal cations while the phosphorus atoms coordinate to the molybdenum.[1] Also, Pecoraco has coined the name "metallacrown" to describe dinuclear manganese(II) salicylhydroxamate complexes in which there is a cavity of radius 0.6 Å which can accommodate a sodium cation coordinated by four oxygen atoms from the complex and three other ligands. Lithium and magnesium analogues were also prepared.[2] This communication reports a new kind of metallacrown in which a sodium ion is coordinated by an octahedron of six oxygen atoms from anions of 2-hydroxy-6-methylpyridine (Hmhp) coordinated in a hexanuclear cobalt(II) complex.

Sodium methoxide/methanol solution (1.455 M, 13.75 cm^3, 0.02 mol) was added to a solution of Hmhp (2.18 g, 0.02 mol) in methanol (25 cm^3). This solution was added to anhydrous cobalt(II) acetate (1.77 g, 0.01 mol) in methanol. After 2 h stirring the solvent was removed, leaving a pink solid. This was dissolved in dry CH_2Cl_2, and crystals were obtained from the solution by concentration, filtering and the slow diffusion of hexane over several months. X-ray crystallographic analysis† shows that the crystals have the formula $C_{76}H_{79}Cl_4Co_6N_{12}NaO_{14}$, which represents a centrosymmetric hexanuclear $[Co_6(mhp)_{12}]$ molecule coordinated to an Na^+ ion with an acetate ion uncoordinated and two molecules of CH_2Cl_2 in the lattice. Because of disorder it has not been possible to locate the anion and solvent units precisely and the R factor cannot be reduced below 0.0830.

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† *Crystal data for* $C_{76}H_{79}Cl_4Co_6N_{12}NaO_{14}$: M = 1902.88, monoclinic, space group $C2/c$, a = 14.067(2), b = 24.508(3), c = 24.917(3) Å, β = 102.13(2)°, V = 8398(2) Å^3, Z = 4, D_c = 1.505 g cm^{-3}. Data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer with monochromated Mo-K_α radiation. Full-matrix least-squares refinement on F^2 of 534 parameters (with $I > 2\sigma(I)$) gave R_1 = 0.083, and for all unique reflections (5844) ωR_2 = 0.150. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

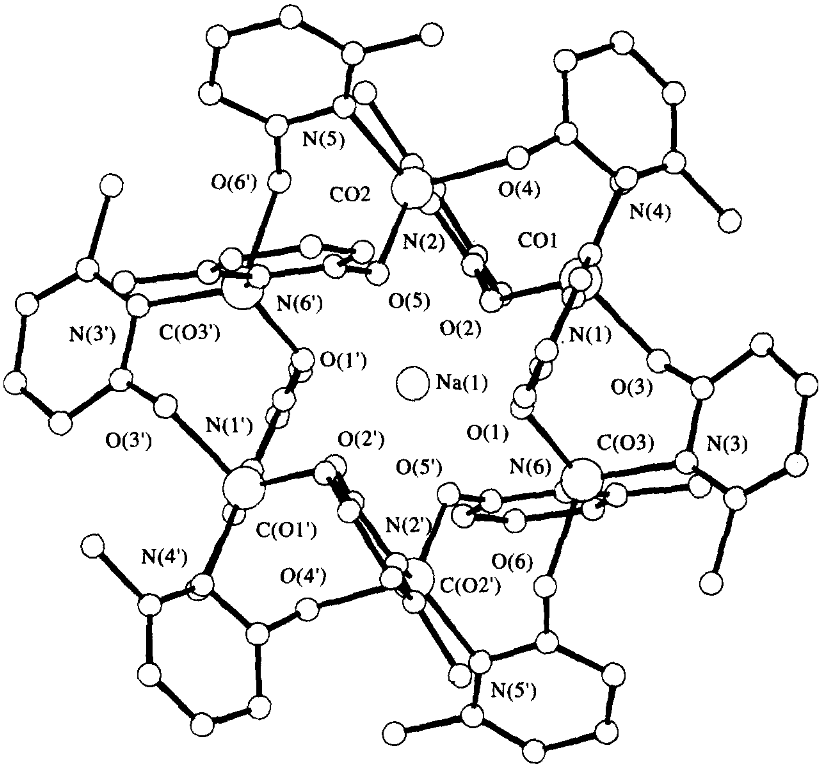

Fig. 1. X-Ray structure of $[Na\{Co(mhp)_2\}_6]^+$ cation showing the atomic numbering scheme

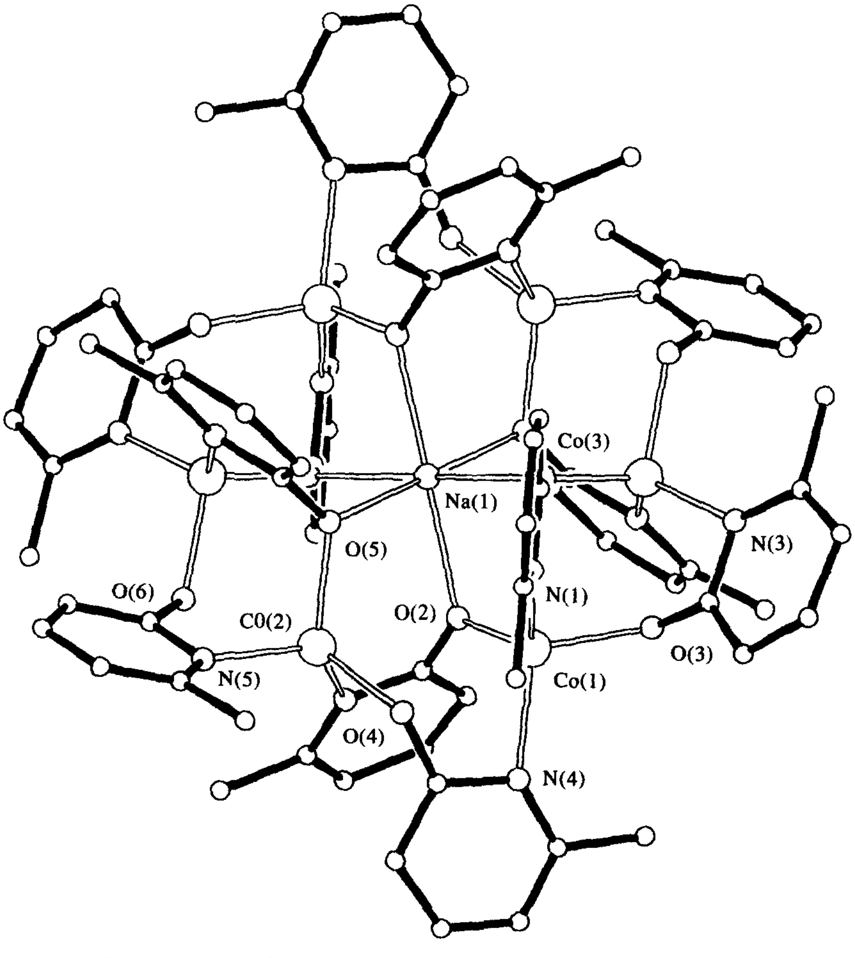

Fig. 2. X-Ray structure of the cation, showing octahedral coordination of sodium.

Table 1. Bond lengths (Å) and angles (°) involving cobalt or sodium

Bond lengths			
Co(1)—N(1)	2.037(10)	Co(1)—N(4)	2.081(10)
Co(1)—O(2)	1.989(8)	Co(1)—O(3)	1.977(9)
Co(2)—N(2)	2.052(10)	Co(2)—N(5)	2.047(10)
Co(2)—O(4)	1.997(9)	Co(2)—O(5)	1.992(8)
Co(3)—N(3)	2.037(11)	Co(3)—N(6)	2.039(10)
Co(3)—O(1)	1.983(8)	Co(3)—O(6)	2.005(8)
Na(1)—O(1)	2.306(8)	Na(1)—O(2)	2.261(8)
Na(1)—O(5)	2.278(8)		
Bond angles			
N(1)—Co(1)—N(4)	127.4(4)	N(1)—Co(1)—O(2)	119.3(4)
N(1)—Co(1)—O(3)	96.3(4)	N(4)—Co(1)—O(2)	97.8(4)
N(4)—Co(1)—O(3)	106.2(4)	O(2)—Co(1)—O(3)	108.5(4)
N(2)—Co(2)—N(5)	126.3(4)	N(2)—Co(2)—O(4)	96.8(4)
N(2)—Co(2)—O(5)	122.7(4)	N(5)—Co(2)—O(4)	104.1(4)
N(5)—Co(2)—O(5)	96.1(3)	O(4)—Co(2)—O(5)	109.0(4)
N(3)—Co(3)—N(6)	122.9(4)	N(3)—Co(3)—O(1)	99.9(4)
N(3)—Co(3)—O(6)	108.9(4)	N(6)—Co(3)—O(1)	121.3(3)
N(6)—Co(3)—O(6)	96.0(4)	O(1)—Co(3)—O(6)	106.7(4)
O(1)—Na(1)—O(2)	81.3(3)	O(1)—Na(1)—O(5)	97.7(3)
O(1)—Na(1)—O(2)[a]	98.7(3)	O(1)—Na(1)—O(5)[a]	82.3(3)

[a] Represents the symmetry transformation $-x+1/2,\ -y+1/2,\ -z$.

The detailed structure can be seen in Figs 1 and 2. Figure 1 emphasises the cavity accommodating the sodium atom; Fig. 2 shows the octahedral coordination of the alkali metal. The six cobalt atoms form a planar hexagonal ring. Each is coordinated tetrahedrally by two nitrogen and two oxygen atoms from four hydroxymethylpyridine (mhp) ligands. Six of the 12 mhp oxygen atoms are located at the corners of an octahedron and coordinate the sodium ion at the centre of the whole structure. Neither of the cations' coordination sphere is regular; bond angles for cobalt range from 127.4° [N(1)—Co(1)—N(4)] to 96.3° [N(1)—Co(1)—O(3)]; those for sodium from 81.3° [O(1)—Na—O(2)] to 98.7° [O(2)—Na—O(5)]. The metal–ligand bond lengths require no special comment. Bond lengths and angles involving the metal atoms are given in Table 1.

A very similar copper(II) analogue to our compound has been reported.[3] $[Na\{Cu(mhp)_2\}_6]^+$ NO_3^- is prepared from the reaction of copper(II) nitrate and 2-potassium-6-methylpyridine (Kmhp) prepared *in situ*, but the source of the central Na^+ ion was not identified. As with our compound, the R factor of 0.1019 ($R_w = 0.1274$) is rather high. A difference between the two compounds is that the copper atoms are approximately square planar, contrasting with our tetrahedral cobalts, but it is striking that a hexanuclear complex is formed in each case.

Our structure contrasts with three other classes of related compounds: (a) Garner's $[Co_{12}(OH)_6(O_2CCH_3)_6(mhp)_{12}]$ where a homometallic structure was isolated[4] from the reaction of $Co(O_2CCH_3)_2$ with Hmhp; (b) the 2-hydroxypyridine (Hhp) derivative $[Y_2Cu_8(hp)_{12}Cl_2O_2(NO_3)_2(H_2O)_2]^{2+}$ cation, in which the hp oxygens bridge a Y_2Cu_4 unit;[5] (c) the mixed copper–lanthanide complexes also prepared[3,6] from substituted hydroxypyridines. In none of these cases can the *d*-block complex be considered as acting as a ligand to another cation in the manner exhibited by our complex. We anticipate considerable interest in the question of whether other *s*-block cations are able to tailor the *d*-block complex to their own requirements and whether variations on the mhp ligand induce variations in the types of compound produced. It is noteworthy that the copper analogue[3] shows occupation of the central cation cavity by Na^+ rather than K^+, despite the latter's greater abundance in the preparative reaction, implying strong discrimination in favour of the less abundant smaller ion rather than forming a larger cavity to accommodate K^+.

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