Table 4. Hydrogen-bonding contacts in $Cu(allopurinol)_2SO_4.4H_2O$

X—H···Y	X—H (Å)	X···Y (Å)	X—H···Y (°)
N(14)—H(14)···O(4)	0·83 (2)	2·726 (2)	169 (2)
N(94)—H(94)···N(3B)	0·83 (2)	2·858 (2)	155 (2)
N(1B)—H(1B)···O(12)	0·86 (2)	2·801 (2)	164 (2)
N(9B)—H(9B)···O(11)	0·93 (2)	2·908 (2)	142 (2)
O(1)—H(11)···O(13)	0·78 (2)	2·801 (2)	166 (2)
O(1)—H(12)···O(64)	0·73 (2)	2·694 (2)	174 (3)
O(2)—H(21)···O(14)	0·77 (2)	2·738 (2)	167 (2)
O(2)—H(22)···O(12)	0·77 (2)	2·781 (2)	150 (2)
O(3)—H(31)···O(13)	0·91 (2)	2·745 (2)	165 (2)
O(3)—H(32)···O(6B)	0·73 (2)	2·837 (3)	168 (2)
O(4)—H(41)···O(13)	0·77 (2)	2·802 (2)	173 (2)
O(4)—H(42)···O(6B)	0·74 (2)	2·826 (2)	165 (2)

bond with a donor—acceptor distance of 2·726 (2) Å is observed between the allopurinol ligand and the noncoordinating water molecule.

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Structure of an Organometallic Polymer, $[Na\{(\eta^5\text{-}C_5H_5)Co[P(O)(OMe)_2]_3\}]_n$

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Abstract. Sodium (η^5-cyclopentadienyl)tris(dimethyl phosphito)cobaltate(1−), $M_r = 474\cdot14$, orthorhombic, $Pna2_1$, $a = 18\cdot195(8)$, $b = 9\cdot436(3)$, $c = 11\cdot316(5)$Å, $V = 1943$Å^3, $Z = 4$, $D_x = 1\cdot621$ g cm^{-3}, $\lambda(\text{Mo}K\alpha) = 0\cdot71073$Å, $\mu = 11\cdot83$ cm^{-1}, $F(000) = 976$, room temperature, final $R = 0\cdot036$ for 1337 observed reflections with $I \geq 3\sigma(I)$. The title compound is polymeric. Each $[(C_5H_5)Co\{P(O)(OMe)_2\}_3]^-$ (L_{OMe}^-) fragment behaves as a bridging ligand between two Na atoms; one end of the bridge is constituted by three complexing P=O O atoms, the other by two O(Me) O atoms of two distinct $P(O)(OMe)_2$ groups. The coordination polyhedron around the Na ions is approximately square pyramidal.

Introduction. The coordination chemistry of ligands of the type $[(\eta^5\text{-}C_5H_5)Co\{P(O)(OR)_2\}_3]^-$ (L_R^-) has

been extensively studied (see, for example, Kläui, 1990, and references cited therein). Such systems have been shown to be very useful for the complexation of a wide range of metal ions, including transition metal ions, alkaline-earth metal ions and lanthanides. In most cases these half-sandwich complexes behave as tripod ligands using their three P=O oxygen ligands. This has allowed, for example, the build-up of polynuclear supersandwich complexes having C_{3v} symmetry. Recently we have been dealing (Kläui, Müller, Eberspach, Boese & Goldberg, 1987) with the structure of sodium salts of the type NaL_R and have shown that hydrated $Na[(C_5H_5)Co\{P(O)(OEt)_2\}_3]$ crystallizes in the form of a trimeric aggregate $[NaL_{OEt}]_3.2H_2O$ in which each Na atom is bonded to three O donor atoms of the tripod ligands; one of them bridging two Na atoms, the second standing axial and the third standing equatorial to the central sodium triangle. Furthermore the sodium triangle is asymmetrically bicapped by the O atoms of the two water molecules. In order to understand whether the presence of water molecules is crucial for the stabilization of such triangular Na-aggregates we envisaged the study of anhydrous complexes of the type NaL_R. Although many attempts to obtain single crystals of such a complex have led to powders, we have now been able to obtain single crystals of *anhydrous* $Na[(C_5H_5)-Co\{P(O)(OMe)_2\}_3]$. The polymeric structure of this complex is described in this report.

L_R^- $(NaL_{OEt})_3 \cdot 2H_2O$
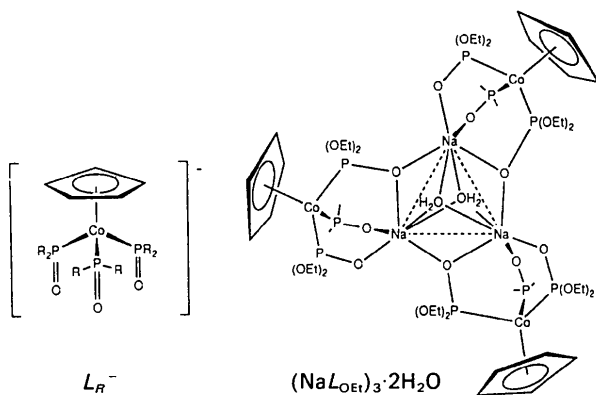
Experimental. The complex was prepared as described before (Kläui, Lenders, Hessner & Evertz, 1988). Yellow crystals were obtained by slow diffusion at room temperature of pentane into a *dry* CH_2Cl_2 solution of the complex. A single prismatic crystal ($0.21 \times 0.15 \times 0.12$ mm) was used to collect data at room temperature on an Enraf–Nonius CAD-4 four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained using angle data from 25 reflections with $15 \le 2\theta \le 24°$. Data collection details: ω–2θ collection mode, scan width = (1 +

$0.35\tan\theta)°$, variable scan rate with max. scan time 60 s per reflection, $2\theta_{max} = 50°$, collection range, h 0–11, k 0–13, l 0–21; 1986 unique reflections measured, 1337 considered as observed with $I \ge 3\sigma(I)$. Standards $\overline{1}28$, $\overline{2}2\overline{7}$, $\overline{1}2\overline{6}$, linear decay 5% in 28 h; intensity corrections for this decay were made. Intensities were corrected for Lorentz–polarization effect but not for absorption. Secondary extinction refined $[g = 2.1 (3) \times 10^{-7}]$ (Stout & Jensen, 1968). The crystal structure was solved by using the Patterson and Fourier difference methods and refined by full-matrix least squares with anisotropic thermal parameters for all non-H atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\{1/4[\sigma^2(I)/I + (0.05I)^2/I]\}^{-1}$. H atoms were introduced with their computed coordinates (distances C—H = 0.95 Å) in structure factor calculations and were assigned isotropic thermal parameters of $B = 5.0$ Å^2. The neutral-atom scattering factors used for all atoms and anomalous-scattering factors for all non-H atoms were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final $R = 0.036$, $wR = 0.049$, $\Delta\rho_{max} = 0.389$, $\Delta\rho_{min} = -0.374$ e Å^{-3} (last Fourier synthesis), $S = 1.552$; $(\Delta/\sigma)_{max} < 0.01$. The coordinates of Table 1 define the true absolute structure since, if they are inverted, refinement to convergence gives $R = 0.038$, $wR = 0.051$. For all computations the Enraf–Nonius *SDP* package was used (B. A. Frenz & Associates, Inc., 1982).

Discussion. Atomic coordinates and equivalent isotropic temperature factors are given in Table 1. Table 2† gives selected bond lengths and bond angles. Fig. 1 shows the atomic numbering of a single NaL_{OMe} moiety. The structure of the title compound is polymeric, the Na atoms playing the role of connecting ions between the monomeric L_{OMe}^- entities. The distance between two consecutive Na atoms is 5.823 (1) Å, that between two consecutive Co atoms is 7.533 (1) Å; the general aspect of the polymeric chains is shown in Fig. 2. The coordination polyhedron around each Na atom is a distorted *square pyramid* constituted by three P=O (tripod) O atoms and two O atoms of two distinct P—OMe groups of a neighbouring L_{OMe}^- ligand. The Na atom is displaced by 0.384 (3) Å from the O(2)—O(8)—O(3*)—O(9*) plane towards O(6*) (Table 2). Square pyramidal geometries have already been encountered for other five coordinate Na atoms

Table 1. *Positional parameters and equivalent isotropic temperature factors with their e.s.d.'s*

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^3B(3,3) + ab(\cos\gamma)B(1,2)$$
$$+ ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}(Å^2)
Co	0·59455 (5)	0·19026 (9)	0·694	2·21 (1)
P(1)	0·60490 (9)	−0·0298 (2)	0·7529 (2)	2·46 (3)
P(2)	0·6335 (1)	0·2749 (2)	0·8633 (2)	2·88 (4)
P(3)	0·4793 (1)	0·1976 (2)	0·7501 (2)	2·70 (4)
Na	0·4759 (2)	−0·0561 (3)	0·5085 (3)	3·11 (6)
O(1)	0·6879 (3)	−0·0810 (6)	0·7320 (6)	4·8 (1)
O(2)	0·5646 (4)	−0·1220 (5)	0·6517 (6)	4·0 (1)
O(3)	0·5802 (3)	−0·0800 (5)	0·8717 (6)	3·7 (1)
O(4)	0·6198 (4)	0·4427 (6)	0·8561 (6)	5·1 (2)
O(5)	0·7218 (3)	0·2662 (8)	0·8558 (7)	5·5 (2)
O(6)	0·6091 (3)	0·2216 (6)	0·9818 (6)	4·0 (1)
O(7)	0·4451 (4)	0·3485 (6)	0·7122 (7)	5·4 (1)
O(8)	0·4359 (3)	0·0976 (7)	0·6573 (6)	4·3 (1)
O(9)	0·4547 (3)	0·1634 (6)	0·8705 (6)	3·6 (1)
C(1)	0·7315 (6)	−0·139 (2)	0·822 (2)	9·0 (4)
C(2)	0·5615 (8)	−0·2738 (9)	0·662 (1)	6·5 (3)
C(4)	0·6162 (7)	0·528 (1)	0·953 (1)	7·2 (3)
C(5)	0·7651 (6)	0·263 (1)	0·965 (1)	7·5 (3)
C(7)	0·4216 (8)	0·449 (1)	0·791 (2)	9·2 (4)
C(8)	0·3580 (5)	0·080 (1)	0·670 (1)	8·0 (3)
C(9)	0·6636 (5)	0·3378 (8)	0·6102 (8)	3·7 (2)
C(10)	0·6857 (5)	0·200 (1)	0·5849 (8)	4·0 (2)
C(11)	0·6271 (5)	0·134 (1)	0·5199 (9)	4·2 (2)
C(12)	0·5678 (5)	0·2328 (9)	0·5179 (8)	3·8 (2)
C(13)	0·5912 (5)	0·3591 (9)	0·5736 (8)	3·6 (2)

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and distances* (Å) *of atoms to the plane* O(2)—O(8)— O(3*)—O(9*)

Co—P(1)	2·187 (2)	Na—O(2)	2·371 (6)
Co—P(2)	2·190 (2)	Na—O(8)	2·338 (6)
Co—P(3)	2·190 (2)	O(1)—C(1)	1·40 (1)
Co—C(9)	2·104 (7)	O(2)—C(2)	1·438 (9)
Co—C(10)	2·072 (7)	O(4)—C(4)	1·36 (1)
Co—C(11)	2·128 (9)	O(5)—C(5)	1·46 (1)
Co—C(12)	2·094 (8)	O(7)—C(7)	1·37 (1)
Co—C(13)	2·100 (7)	O(8)—C(8)	1·43 (1)
P(1)—O(1)	1·603 (5)	C(9)—C(10)	1·39 (1)
P(1)—O(2)	1·615 (5)	C(9)—C(13)	1·40 (1)
P(1)—O(3)	1·495 (6)	C(10)—C(11)	1·44 (1)
P(2)—O(4)	1·605 (5)	C(11)—C(12)	1·42 (1)
P(2)—O(5)	1·610 (5)	C(12)—C(13)	1·41 (1)
P(2)—O(6)	1·499 (6)	Na—Na*	5·823 (1)
P(3)—O(7)	1·613 (5)	Co—Na	3·807 (3)
P(3)—O(8)	1·617 (5)	Co—Na*	3·985 (3)
P(3)—O(9)	1·471 (6)	Co—Co	7·533 (1)
Na—O(3*)	2·256 (6)	Na—O(9*)	2·250 (6)
Na—O(6*)	2·219 (5)		

P(1)—Co—P(2)	93·11 (8)	O(2)—Na—O(8)	83·3 (2)
P(1)—Co—P(3)	91·45 (7)	P(1)—O(2)—Na	130·7 (3)
P(2)—Co—P(3)	92·71 (8)	P(3)—O(8)—Na	132·7 (3)
Co—P(1)—O(1)	108·8 (2)	O(3*)—Na—O(6*)	89·5 (2)
Co—P(1)—O(2)	105·0 (2)	O(3*)—Na—O(9*)	91·9 (2)
Co—P(1)—O(3)	123·2 (2)	O(6*)—Na—O(9*)	88·8 (2)
Co—P(2)—O(4)	105·4 (3)	O(2)—Na—O(9*)	88·5 (2)
Co—P(2)—O(5)	104·9 (3)	O(2)—Na—O(6*)	112·5 (2)
Co—P(2)—O(6)	124·2 (2)	O(2)—Na—O(3*)	157·9 (2)
Co—P(3)—O(7)	108·7 (2)	O(3*)—Na—O(8)	90·0 (2)
Co—P(3)—O(8)	105·2 (2)	O(8)—Na—O(9*)	162·5 (2)
Co—P(3)—O(9)	123·4 (2)	O(6*)—Na—O(8)	108·6 (2)
P(1)—O(3)—Na*	124·9 (3)	P(3)—O(9)—Na*	124·8 (3)
P(2)—O(6)—Na*	124·4 (3)		

O(2)	0·053 (6)	O(9*)	−0·051 (6)
O(8)	−0·053 (6)	Na	−0·384 (3)
O(3*)	0·051 (6)	O(6*)	−2·523 (6)

The equation of this plane is: $0·6801x + 0·7213y − 0·1308z − 5·1387 = 0$

Symmetry code: (*) $1 - x$, $-y$, $-\frac{1}{2} + z$.
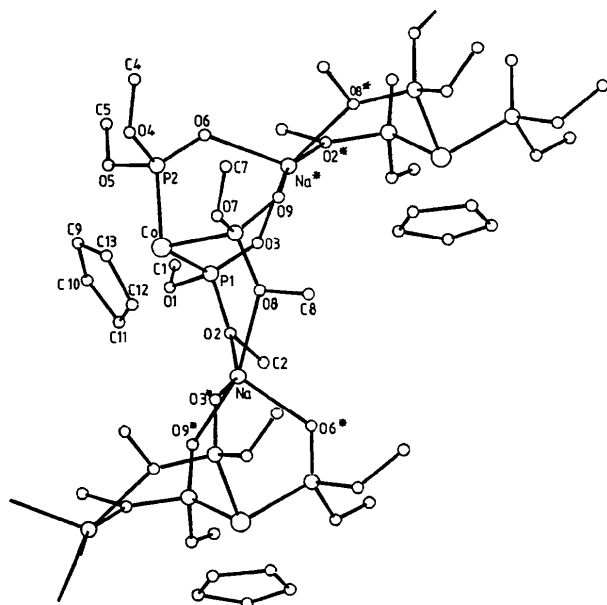
Fig. 1. Molecular configuration and atom-labelling scheme for Na[(η^5-C$_5$H$_5$)Co{P(O)(OMe)$_2$}$_3$].

in an O-atom environment (Karle, 1974). Two of the three P=O atoms appear to be rather more weakly bonded to the Na atom than the third one [Na— O(9*) 2·250 (6), Na—O(3*) 2·256 (6), Na—O(6*) 2·219 (5) Å] indicating that some electron density is withdrawn from the two corresponding P=O bonds [P(3)=O(9) and P(1)=O(3)] toward the methoxy
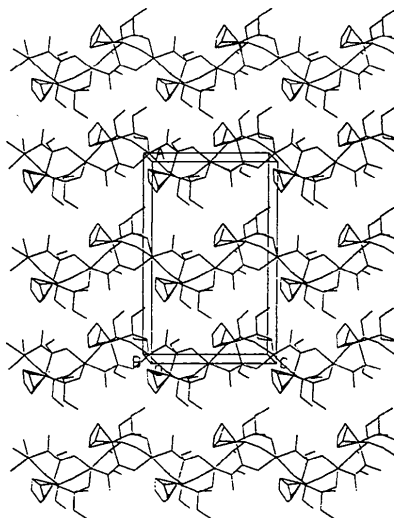
Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) drawing showing polymeric chains of [Na{(η^5-C$_5$H$_5$)Co[P(O)(OMe)$_2$]$_3$}]$_n$.

groups [O(2)—Me and O(8)—Me, respectively] used to form the link with the next monomer. The greater length of the Na—O(2) [2·371 (6) Å] and Na—O(8) [2·338 (6) Å] bonds compared with the other Na—O distances (see Table 2) reflects the poorer donor properties of methoxy groups vs P=O groups. The non-bonding O···O distances (P=O oxygen atoms) vary from 3·127 (7) to 3·239 (6) Å and demonstrate the flexibility of the tripod part of the ligand. This study indicates that L ligands alone (i.e. not combined with other donor molecules) do not favour the formation of small Na-aggregates, as found in $(NaL_{OEt})_3.2H_2O$. This obviously can be ascribed to the marked tendency of Na ions to have coordination number six or, to a lesser degree, five, a condition which can hardly be satisfied when a triangular array of Na atoms is surrounded only by ligands of the L type.

In conclusion the structure described here constitutes the first example in which a ligand of the type $[(\eta^5\text{-}C_5H_5)Co\{P(O)(OR)_2\}_3]^-$ acts as a pentapodal ligand. This property leads to the formation of an organometallic polymer.

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Structures of [Nb₂Cl₆(C₄H₈S)(PEt₃)₂], [Nb₂Cl₆(C₄H₈S)(C₄H₈O)₂] and [Ta₂Cl₆(C₄H₈S)(PMe₃)₂]

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Abstract. Di-μ-chloro-tetrachlorobis(tetrahydrothiophenato)(triethylphosphino)diniobium(III), [Nb₂Cl₆(C₄H₈S)(PEt₃)₂], di-μ-chloro-tetrachlorobis(tetrahydrofuranato)tetrahydrothiophenatodiniobium(III), [Nb₂Cl₆(C₄H₈S)(C₄H₈O)₂] and di-μ-chloro-tetrachlorobistetrahydrothiophenato(trimethylphosphino)ditantalum(III), [Ta₂Cl₆(C₄H₈S)(PMe₃)₂] crystallized in two crystal phases. These molecules are confacial bioctahedra with two bridging Cl atoms and one C₄H₈S molecule. (I) [Nb₂Cl₆(C₄H₈S)(PEt₃)₂], $M_r = 723.02$, orthorhombic, $P2_12_12_1$, $a = 9.512$ (2), $b = 14.171$ (3), $c = 21.948$ (5) Å, $V = 2958$ (1) Å³, $Z = 4$, $D_x = 1.623$ g cm⁻³, $\lambda(\text{Mo }K\alpha) = 0.71069$ Å, $\mu = 14.7$ cm⁻¹, $F(000) = 1456$, $T = 294$ K, $R = 0.0471$, 2153 unique observed reflections with $I > 3\sigma(I)$. The Nb—Nb distance is 2·718 (1) Å. The Nb—Cl_bridge distances range from 2·496 (3) to 2·530 (3) Å and Nb—S distances are 2·456 (3) and 2·461 (3) Å. The range of Nb—Cl_terminal distances is 2·392 (4) to

2·406 (3) Å. The Nb—P distances are 2·678 (4) and 2·675 (3) Å. (II) [Nb₂Cl₆(C₄H₈S)(C₄H₈O)₂], $M_r = 630.91$, monoclinic, $C2/c$, $a = 13.367$ (4), $b = 10.642$ (4), $c = 15.317$ (5) Å, $\beta = 93.71°$, $V = 2174$ (1) Å³, $Z = 4$, $D_x = 1.927$ g cm⁻³, $\lambda(\text{Mo }K\alpha) = 0.71069$ Å, $\mu = 18.5$ cm⁻¹, $F(000) = 1248$, $T = 294$ K, $R = 0.0557$, 1026 unique observed reflections with $I > 3\sigma(I)$. The Nb—Nb distance is 2·684 (2) Å. The Nb—Cl_bridge distances are 2·495 (4) and 2·497 (4) Å and the Nb—S distance is 2·401 (1) Å. The Nb—Cl_terminal distances are 2·372 (4) and 2·406 (3) Å. The Nb—O distance is 2·401 (4) Å. (IIIa) [Ta₂Cl₆(C₄H₈S)(PMe₃)₂], $M_r = 814.94$, triclinic, $P\bar{1}$, $a = 10.615$ (4), $b = 12.189$ (2), $c = 10.529$ (2) Å, $\alpha = 102.35$ (2), $\beta = 117.91$ (3), $\gamma = 87.86$ (2)°, $V = 1173$ (1) Å³, $Z = 2$, $D_x = 2.307$ g cm⁻³, $\lambda(\text{Mo }K\alpha) = 0.71069$ Å, $\mu = 101$ cm⁻¹, $F(000) = 760$, $T = 294$ K, $R = 0.0692$, 3263 unique reflections with $I > 3\sigma(I)$, (IIIb) [Ta₂Cl₆(C₄H₈S)(PMe₃)₂], triclinic, $P\bar{1}$, $a = 10.412$ (1), $b = 10.569$ (2), $c = 23.763$ (6) Å, $\alpha = 88.04$ (2), $\beta = 87.17$ (2), $\gamma = 64.52$ (1)°, $V =$

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