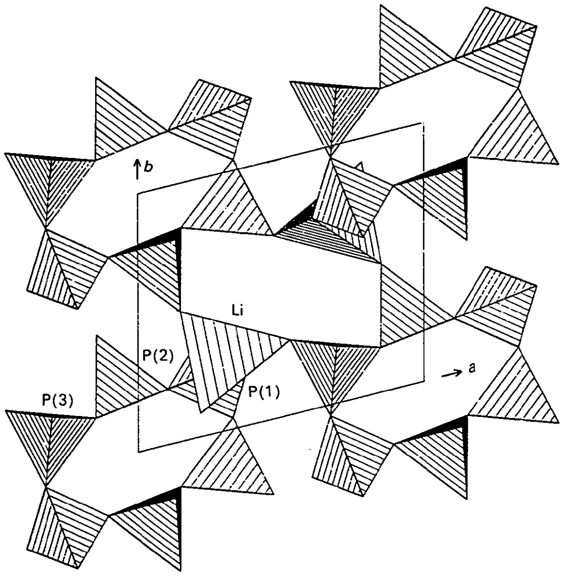

Fig. 1. Projection along the *c* axis of a layer of P_6O_{18} groups and LiO_4 tetrahedra. Ag atoms are not represented. Projection made for $-0{\cdot}45 < z < 0{\cdot}45$.

has five O-atom neighbours while Ag(2) has a sixfold coordination made by five O atoms and one water molecule. Inside the Ag-atom layer the shortest Ag—Ag distances are 3·140 for Ag(1)—Ag(1) and 3·304 Å for Ag(1)—Ag(2).

The main features of the hydrogen-bond scheme are described in Table 2. The drawings were prepared using the *STRUPLO* (Fischer, 1985) program.

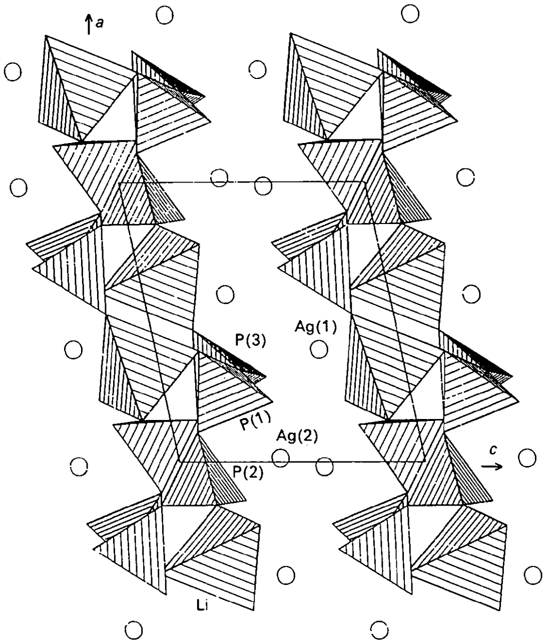

Fig. 2. Projection of the atomic arrangement of $Ag_4Li_2P_6O_{18}$.-$2H_2O$ along the *b* axis.

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Layer Structure of $[CoCl(H_2PO_2)].H_2O$

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Abstract. Chloro(phosphinato)cobalt(II) monohydrate, $M_r = 177{\cdot}39$, orthorhombic, *Pbca*, $a = 7{\cdot}416\,(4)$, $b = 13{\cdot}082\,(7)$, $c = 9{\cdot}483\,(5)$ Å, $V = 920\,(1)$ Å^3, $Z = 8$, $D_x = 2{\cdot}56$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 4{\cdot}48$ mm^{-1}, $F(000) = 696$, room temperature, $R = 0{\cdot}025$ for 1698 unique observed reflections; crystal growth by slow evaporation from an aqueous solution of $CoCl_2.6H_2O$ and H_3PO_2. Layers are built up from distorted $[CoO_3Cl_2(H_2O)]^{6-}$ octahedra, with Cl atoms in *cis* positions, sharing an edge of two O atoms, forming dimers connected together by corners (Cl atoms only). The $(H_2PO_2)^-$ tetrahedra connect two octahedra dimers and their O atoms are directed towards the next layer. The water

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molecule forms intralayer hydrogen bonds only. The sheets with formula $CoCl(H_2PO_2)(H_2O)$ are connected by weak (van der Waals) H—H, H—O and H—Cl bonds.

Introduction. The chemistry of transition metal derivatives of low oxidation oxophosphoric acids is complicated because redox reactions of these oxoanions have not been widely studied (Loub & Kratochvil, 1987; Durand, Loukili, Tijani, Rafiq & Cot, 1988; Brun & Dumail, 1971). On the other hand, the fact that $H_2PO_2^-$ contains only two donor O atoms (as opposed to four in PO_4^{3-}) makes it a good candidate for building low-dimensional solids containing transition metals.

We are currently undertaking a detailed synthetic, structural and magnetic study of the phosphites and hypophosphites of the first row transition metals (Marcos, Gómez-Romero, Amorós, Sapiña, Beltrán-Porter, Navarro, Rillo & Lera, 1990; Sapiña, Gómez-Romero, Marcos, Amorós, Ibáñez, Beltrán, Navarro, Rillo & Lera, 1989).

The present paper expands on our earlier work and describes the synthesis and structure of $CoCl(H_2PO_2).H_2O$.

Experimental. 5 ml of H_3PO_2 (30%) were added to an aqueous solution (5 ml) containing 11·268 g of $CoCl_2.6H_2O$, kept over sulfuric acid in a thermostated desiccator (298 K) for several days. Well formed purple crystals were separated by filtration from the blue mother liquor and washed with diluted hypophosphoric acid. Prismatic crystal 0·13 × 0·13 × 0·04 mm. Data collected on a Siemens AED-2 four-circle diffractometer, ω–2θ step-scan mode in 36 steps of $\Delta\omega = 0{\cdot}035°$. Time per step $T_{\min} = 1$ s and $T_{\max} = 4$ s. Lattice constants based on 30 reflections at $2\theta \approx 30°$. Absorption correction by the Gaussian method, $A_{\max} = 0{\cdot}71$ and $A_{\min} = 0{\cdot}34$. Intensity measurement of one independent set to $2\theta_{\max} = 75°$ within the range $0 \le h \le 12$, $0 \le k \le 22$, $0 \le l \le 16$. Standard reflections 010, 444 and $44\bar{4}$ had intensity variation 1·0%. 2773 reflections measured and 1698 independent reflections used for refinements $[|F| > 6\sigma(|F|)]$. Structure solved by direct methods with the *EEES* option of the *SHELX*76 program (Sheldrick, 1976). *F* magnitudes used in least-squares refinements. 70 parameters refined; max. $\Delta/\sigma = 0{\cdot}001$; secondary-extinction factor $x = 5\,(2) \times 10^{-8}$; atomic scattering factors for H, O, P, Cl, Co from *International Tables for X-ray Crystallography* (1974, Vol. IV); calculations with *SHELX*76 program (Sheldrick, 1976) on a MicroVAX II computer.

The automatic 'black-box' procedure of *SHELX*76 (Sheldrick, 1976) gives a solution with all non-H atoms. Then refinements of atomic coordinates and isotropic thermal motion led to $R = 0{\cdot}053$. The residual decreased to $R = 0{\cdot}028$ when the anisotropic thermal parameters were refined. Positions of all H atoms were found from a difference Fourier map calculated from data limited to $\sin\theta = 0{\cdot}4$. Geometrical constraints on angles or distances defining the H_2PO_2 tetrahedron or H_2O water molecule were not used for refining the H atomic positions. Only two isotropic thermal parameters were refined for the P-bonded and O-bonded H atoms because it was expected that the thermal motions of the P-bonded and the O-bonded H atoms would be different ($R = 0{\cdot}025$, $wR = 0{\cdot}029$). Max. and min. heights in final difference map: 0·96 and −0·56 e Å^{-3}. $w = 0{\cdot}61/[\sigma^2(|F_o|) + 0{\cdot}00109\,F_o^2]$.

Discussion. The final atomic coordinates and isotropic temperature factors are listed in Table 1.* Selected bond lengths and angles are given in Table 2. $CoCl(H_2PO_2).H_2O$ has a simple, open layer structure (Fig. 1) extending parallel to the *ac* plane. The layers are identically constituted, electrically neutral and bonded together by van der Waals and very weak hydrogen bonds. There are no close contacts between them. The shortest distances between layers involve the H(1) or (H2) atoms of the $(H_2PO_2)^-$ group; they are all larger than 2·6 Å (Table 2), in agreement with the sum of the intermolecular (van der Waals) standard radii for H 1·17, O 1·52 and Cl 1·78 Å. Similar behaviour is observed in other layer hypophosphite compounds $Ca(H_2PO_2)_2$ (Loopstra, 1958) and $Zn(H_2PO_2)_2$ (Weakley, 1979) where the sheets make contacts with each other through H—H interactions. Normally, the two H atoms of the hypophosphite ion $[H_2PO_2]^-$ are not acidic and not involved in strong hydrogen bonds. However, the favourable relative arrangement of P, O, H and Cl atoms could indicate the existence of hydrogen-bonding interactions P—H(1)···O(2) and a very weak unusual interlaminar hydrogen-bonding network between the H(2) and Cl atoms [P—H(2)···Cl].

In $CoCl(H_2PO_2).H_2O$, the layers are built from $[CoO_3Cl_2(H_2O)]^{6-}$ distorted octahedra, with Cl atoms in *cis* positions (Fig. 2), sharing an edge of two O atoms [di-μ-(O)H_2PO_2 bridges], forming dimer entities that could be considered as the basic units from which the layers are built up. Each dimer is surrounded by four identical units, and they are connected to each other by means of Cl and H_2PO_2 bridges. The layers can also be viewed, at this point,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53800 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and isotropic temperature factors with e.s.d.'s in parentheses*

	x	y	z	B(Å^2)
Co	0·11761 (3)	0·50057 (2)	0·14499 (2)	1·20 (1)*
P	0·22495 (5)	0·15392 (3)	0·38784 (4)	1·17 (1)*
Cl	0·87924 (5)	0·39750 (3)	0·26525 (4)	1·47 (1)*
O(1)	0·0858 (2)	0·0871 (1)	0·4626 (1)	1·31 (3)*
O(2)	0·6960 (2)	0·0943 (1)	0·4568 (1)	1·77 (4)*
O(3)	0·3775 (2)	0·0965 (1)	0·3168 (1)	1·56 (4)*
H(1)	0·285 (4)	0·211 (2)	0·478 (3)	2·2 (4)
H(2)	0·137 (4)	0·212 (2)	0·306 (3)	2·2 (4)
H(3)	0·577 (5)	0·089 (2)	0·432 (4)	3·3 (5)
H(4)	0·699 (5)	0·098 (2)	0·551 (4)	3·3 (5)

* $B_{eq} = \frac{4}{3}\sum_i\sum_j b_{ij}(a_i a_j)$ (Hamilton, 1959).

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Co octahedron, $\langle$Co—O,Cl$\rangle$ = 2·231

Co	O(3)	O(2)	O(1)	O(1)	Cl	Cl
O(3)	2·058 (1)	2·921 (1)	4·140 (1)	3·070 (1)	3·205 (1)	3·318 (1)
O(2)	89·7 (1)	2·084 (1)	2·976 (1)	2·893 (2)	4·580 (1)	3·200 (1)
O(1)	173·2 (1)	90·9 (1)	2·089 (1)	2·705 (2)	3·260 (1)	3·382 (1)
O(1)	93·9 (1)	86·3 (1)	79·4 (1)	2·144 (1)	3·299 (1)	4·641 (1)
Cl	88·8 (1)	176·2 (1)	90·1 (1)	90·2 (1)	2·499 (1)	3·719 (1)
Cl	92·6 (1)	87·7 (1)	94·2 (1)	171·2 (1)	95·9 (1)	2·511 (1)

P tetrahedron, $\langle$P—O,H$\rangle$ = 1·38

P	H(1)	H(2)	O(3)	O(1)
H(1)	1·22 (2)	1·97 (4)	2·25 (2)	2·20 (3)
H(2)	105 (3)	1·26 (3)	2·34 (3)	2·23 (2)
O(3)	110 (2)	114 (2)	1·515 (1)	2·569 (1)
O(1)	106 (2)	106 (2)	115·2 (1)	1·526 (1)

Water molecule

O(2)—H(3)	0·92 (3)	H(3)—H(4)	1·45 (5)
O(2)—H(4)	0·90 (4)	H(3)—O(2)—H(4)	106 (6)

Intralayer hydrogen bonding

A—H···*B*	H···*B*	*A*—*B*	*A*H*B*
O(2)—H(3)···O(3)	1·84 (3)	2·707 (2)	157 (3)
O(2)—H(4)···Cl	2·43 (4)	3·230 (1)	148 (4)

Shortest interlayer distances

H(1)—O(2)	2·70 (3)	H(2)—Cl	3·10 (3)
H(1)—H(4)	2·60 (4)	H(2)—Cl	3·12 (3)

as zigzag chains of Cl-sharing octahedra running along the *a* axis. The Cl atoms are mainly responsible for the significant distortion of the octahedra (Co—Cl ≈ 2·5 Å). Their H atoms of the $[H_2PO_2]^-$ tetrahedra connecting two octahedra dimers are directed towards the next layer. The coordination polyhedra of the P atoms is C_1 because the two O and the two H atoms are crystallographically different. However, taking into account the bond lengths and angles (Table 2) this symmetry could be viewed as a pseudo C_{2v} symmetry. The P—H bond lengths (1·22 to 1·26 Å) are significantly shorter than in the previously reported neutron study for $Ca(H_2PO_2)_2$ (≈ 1·4 Å) (Loopstra, 1958) or in a more recent X-ray study on $NaH_2PO_2.\frac{4}{5}H_2O$ (Catti, 1979).

The water molecule only forms intralayer hydrogen bonds (Table 2). These bonds link the coordinated water molecule [O(2)] of each Co octahedron to one O atom [O(3)] of a hypophosphite tetrahedron [O(2)—H(3)···O(3)] and to one Cl atom [O(2)—H(4)···Cl]. The O—H lengths (≈ 0·9 Å) are as expected (*i.e.* shorter by 0·1–0·2 Å with respect to neutron diffraction studies).

A magnetic study of $CoCl(H_2O)(H_2PO_2)$, which exhibits weak ferromagnetism, has been published (Sapiña *et al.*, 1989).

Owing to the open layer structure of this product, a variety of guest molecules and ions of different sizes can be accommodated in the interlayer space. Thus, a detailed study of the intercalation chemistry of this material is in progress.

The drawings were prepared using the *STRUPLO* program (Fischer, 1985).

The authors are grateful to Professor M. Leblanc (University of Maine) for the X-ray data collection. MDM thanks the Spanish Ministerio de Educación y Ciencia for an FPI fellowship.

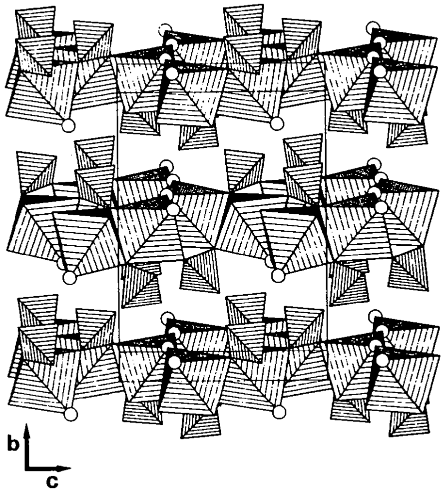

Fig. 1. Perspective view of the open crystal structure of $CoCl(H_2PO_2).H_2O$ (Cl, small open circles).

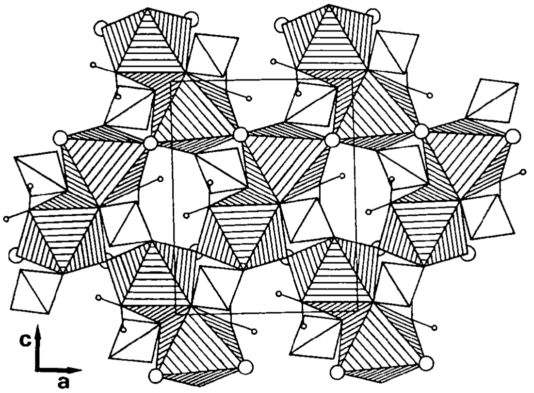

Fig. 2. The crystal structure of $CoCl(H_2PO_2).H_2O$ projected on (010) with x horizontal and z vertical (Cl, small open circles).

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Structure of Sodium 2-Keto-D-gluconate Monohydrate (Sodium D-*arabino*-2-Hexulosonate Monohydrate)

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Abstract. $Na(C_6H_9O_7).H_2O$, $M_r = 234{\cdot}13$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}269\,(4)$, $b = 8{\cdot}692\,(1)$, $c = 14{\cdot}251\,(2)$ Å, $V = 900{\cdot}4\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}72$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}710730$ Å, $\mu = 1{\cdot}88$ cm^{-1}, $F(000) = 488$, $T = 293$ K, final $R = 0{\cdot}034$ for 2045 reflections $[I > 2\sigma(I)]$. The sugar adopts the β-pyranose form. The sodium ion is surrounded by six O atoms originating from two molecules of 2-keto-D-gluconic acid and a water molecule. The compound forms infinite chains along a twofold screw axis parallel to **a**. One of the hydroxyl groups bridges between two sodium ions. The pyranose ketogluconic acid acts on one side as a tridentate ligand *via* O(11), O(61) and O(51), and as a bidentate ligand on the other side *via* O(41) and O(51). All available OH hydrogens participate in hydrogen bonding, further stabilizing the crystal lattice.

Introduction. As a part of a research program to examine the metal-ion-promoted reactions of 5-keto-D-gluconic and 2-keto-D-gluconic acid, for which compound-selective chemo- and biocatalytic preparative methods have recently become available (Smits, Kuster, van der Wiele & van der Baan, 1986), several complexes with monovalent cations have been prepared.

Crystals of the sodium, potassium, caesium and silver salts of 2-keto-D-gluconic acid have been obtained.

The formation of chelate ring systems in calcium 2-keto-D-gluconate trihydrate has been established crystallographically by Mazid, Palmer & Balchin (1976). The different overall stoichiometry resulting from the use of monovalent cations justifies the determination of the crystal structure of the sodium salt.

Experimental. A sample of sodium 2-keto-D-gluconate was supplied by AKZO Research BV (Arnhem, The Netherlands). The potassium, caesium and silver complexes were obtained by removal of sodium from the original sample with the use of acidic Dowex ion-exchange resin, followed by addition of an equivalent amount of the appropriate metal bicarbonate or metal nitrate. Crystalline material was obtained by precipitation from aqueous solution at room temperature by addition of ethanol until the solution became turbid (10 mmol dissolved in 5 ml water, about 4·5 ml ethanol added). A colourless needle of sodium 2-keto-D-gluconate monohydrate, grown from water/ethanol at room temperature, had approximate dimensions 0·25 × 0·3 × 0·6 mm. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell constants from setting angles of 24 reflections, $9 < \theta < 12°$. Corrections for Lorentz and polarization effects. Transmission coefficients 0·97 to 1·02; absorption correction was applied with *DIFABS*

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