

Fig. 1. The molecular structure of $[\text{Os}(\text{CO})_2(\text{C}_6\text{H}_4\text{NNC}_6\text{H}_5)_2]$.

nigan, Knox & Pauson, 1969). Related Os complexes with $(\text{CH}_3\text{NCHC}_6\text{H}_4-)$ (Choo Yin & Deeming, 1977) and benzo[*h*]quinoline (Bruce, Goodall & Stone, 1973) as the ligands have also been prepared from $\text{Os}_3(\text{CO})_{12}$.

Two coordinated azobenzene ligands have also been observed in the structure of bis(azobenzene)-rhodium acetate (Craik, Knox, Pauson, Hoare & Mills, 1971). However, in the Rh complex the two *ortho*-metallated C bonds are *cis* to each other while the Rh–N bonds are *trans*. In the title compound the Os atom displays a slightly distorted octahedral coordination geometry, with the largest deviation caused by the bite requirement of the azobenzene ligand, but the two Os–N bonds are *cis* to each other as are the two Os–C bonds of the chelating ligand. The two carbonyl ligands are also *cis* to each other. The Os–C(carbonyl) bond *trans* to the coordinated N atom is significantly shorter than the Os–C bond *trans* to the *ortho*-

metallated C atom. This suggests that the azobenzene C atom is involved in π -bonding to the metal with competition between the two *trans* C atoms for the π -electron density on the Os, giving rise to the longer Os–C bond. Both Os–N bonds are longer than the terminal Os–N distance of 1.94 (3) Å in $[\text{HOs}_2(\text{CO})_{13}(\text{C}_6\text{H}_5\text{NC}_6\text{H}_4\text{N})]$ (Dawoodi, Mays & Raithby, 1980) where π -donation is considered to be present.

The N–N lengths in the title compound are similar to the value in $[\text{Rh}(\text{O}_2\text{CCH}_3)(\text{C}_6\text{H}_5\text{NNC}_6\text{H}_4)_2]$ (Craik, Knox, Pauson, Hoare & Mills, 1971), and indicate the presence of considerable multiple N–N bonding. The geometry of the remainder of the ligand corresponds closely to the expected values.

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Structure of the Flavone-3-monophosphate–Magnesium Complex

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Abstract. $\text{C}_{15}\text{H}_9\text{O}_6\text{P}^{2-} \cdot \text{Mg}^{2+} \cdot 5\text{H}_2\text{O}$, monoclinic, $C2/c$, $a = 40.877$ (3), $b = 6.296$ (1), $c = 14.139$ (1) Å, $\beta = 101.72$ (1)°, $Z = 8$, $D_m = 1.60$, $D_c = 1.604$ Mg m $^{-3}$ ($T = 295$ K). The structure was solved by direct methods and refined by the block-diagonal least-

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squares method to a final R value of 0.041 for 2721 reflections measured on a diffractometer. The crystal consists of hydrophobic layers, containing the aromatic portions of the flavone molecule, separated by hydrophilic layers which contain the phosphate group, the

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keto O, the Mg^{2+} ion and the water molecules. Coordination of Mg^{2+} by the keto O(4) and the phosphate O(1P) results in a seven-membered chelate ring. The P—O(3) ester bond is unusually long, 1.661 (2) Å.

Introduction. Flavone-3-monophosphate and flavone-3-diphosphate were synthesized for use as an ultra-sensitive assay for alkaline phosphatase (Land & Jackim, 1966). Our interest in the structure of the flavone phosphates arose both because of their ability to serve as substrates for the alkaline and acid phosphatases, and, more importantly, because of their ability to form complexes with divalent cations. In particular, we obtained the magnesium-flavone complex, a useful model for the chelation of Mg^{2+} ions by organic phosphates, important in the biochemistry of nucleotides and coenzymes, and rarely obtained in the crystalline state.

Flavone-3-diphosphate triammonium salt was purchased from the Chemical Dynamics Corporation, New Jersey, USA. Our X-ray investigation revealed that we received instead flavone-3-monophosphate. This was confirmed by NMR spectroscopy of the uncomplexed molecule in solution, which showed a peak for the organic monophosphate and a second peak for orthophosphate. Bright-yellow crystals were obtained by slow diffusion of the flavone into a $MgCl_2$ solution. Crystals were also obtained with $HgCl_2$, $CdCl_2$, $BaCl_2$, $PbCl_2$, $ZnCl_2$ and $CuCl_2$ in place of the $MgCl_2$.

A rectangular crystal of dimensions $0.4 \times 0.2 \times 0.05$ mm was selected for analysis. Preliminary Weissenberg photographs showed the systematic absences: $hkl: h + k = 2n + 1, h0l: l = 2n + 1$ ($h = 2n + 1$), and $0k0: k = 2n + 1$. The space group was, therefore, Cc or $C2/c$. Density was measured by flotation in a $CHCl_3$ – $CHBr_3$ solution, and is reported with other crystal parameters in the *Abstract*. The crystal was mounted on a Picker FACS-1 X-ray diffractometer with the b axis coincident with the ϕ axis of the goniostat. Cell constants were determined by a least-squares fit of 24 accurately centered reflections. Intensity data were collected with Ni-filtered Cu radiation ($\lambda = 1.5418$ Å) by the ω – 2θ scan method with a scan rate of 2° min^{-1} , scan range of 1.6° , and background counts of 10 s at each scan limit. A total of 2880 independent reflections were scanned to a limit of 127° on 2θ . 2721 reflections had $I > 1.5\sigma(I)$ and were used in the structure analysis after applying the usual Lorentz and polarization corrections. A crystal-decay correction of less than 2%, based on intensity standards collected at intervals of 75 reflections, and an empirical absorption correction based on a ϕ curve, with minimum and maximum corrections of less than 10%, were applied to the data. The value of $R = \sum |F_i - F_{av}| / \sum F_{av}$ for 903 pairs of equivalent reflections was

less than 1%. The space group was shown to be $C2/c$ from a statistical analysis (Howells, Phillips & Rogers, 1950) of the normalized intensities.

The structure was solved by direct methods using *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The positions of all non-hydrogen atoms in the structure except the solvent oxygens were revealed in the initial E map. A series of structure factor calculations followed by difference Fourier maps revealed all the other atoms.

The positions of the non-hydrogen atoms, with anisotropic temperature factors, and the H atoms, with isotropic temperature factors, were submitted to several cycles of block-diagonal least-squares refinement, minimizing $\sum w_i(|F_o| - |F_c|)^2$, where $w_i = 1/\sigma_i^2$, based on counting statistics (Stout & Jensen, 1968). The final unweighted value of $R = \sum |F_o| - |F_c| / \sum |F_o|$ for the observed reflections was 0.041. The R value was 0.043 including unobserved reflections.* The maximum ratio of the shift over estimated standard deviation for the atomic parameters in the final cycle of refinement was less than 0.3.

Scattering factors for Mg^{2+} were obtained from *International Tables for X-ray Crystallography* (1974). Those for P, O, and C were from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965).

Discussion. An *ORTEP* (Johnson, 1965) drawing of the flavone-3-monophosphate-magnesium complex is displayed in Fig. 1. Positional coordinates for the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35676 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

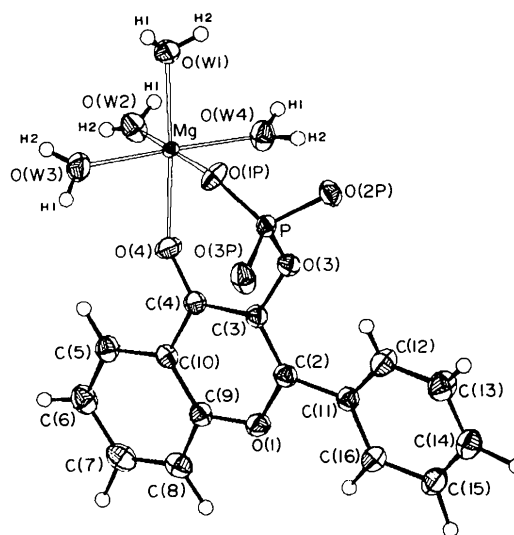


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the flavone-3-monophosphate- Mg^{2+} complex, showing the 50% probability surfaces for the non-hydrogen-atom thermal ellipsoids.

Table 1. *Positional coordinates and B_{eq} 's for non-hydrogen atoms and positional coordinates and isotropic temperature factors for hydrogen atoms*

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}/B (\AA^2)*
P	0.32229 (1)	0.0648 (1)	-0.0750 (0)	1.47 (2)
Mg	0.30771 (2)	0.3101 (1)	0.1170 (1)	0.88 (3)
O(1)	0.43974 (4)	0.3088 (3)	0.0056 (1)	2.23 (5)
O(3)	0.36009 (4)	0.0473 (2)	-0.0050 (1)	1.92 (5)
O(4)	0.35393 (4)	0.4154 (3)	0.0985 (1)	2.38 (5)
O(1P)	0.30062 (4)	0.1834 (3)	-0.0177 (1)	2.16 (4)
O(2P)	0.31299 (4)	-0.1678 (3)	-0.0879 (1)	2.14 (4)
O(3P)	0.32641 (4)	0.1759 (3)	-0.1656 (1)	2.67 (6)
O(W1)	0.25948 (4)	0.2229 (3)	0.1319 (1)	2.20 (5)
O(W2)	0.31972 (4)	0.4220 (3)	0.2582 (1)	2.53 (4)
O(W3)	0.29128 (4)	0.6049 (3)	0.0651 (1)	2.99 (5)
O(W4)	0.32677 (4)	0.0212 (3)	0.1730 (1)	2.60 (5)
O(W5)	0.25013 (4)	0.7988 (3)	0.1664 (1)	2.68 (5)
C(2)	0.41324 (6)	0.1703 (4)	-0.0213 (2)	1.83 (7)
C(3)	0.38409 (5)	0.2010 (4)	0.0084 (2)	1.71 (7)
C(4)	0.37945 (6)	0.3853 (4)	0.0666 (2)	1.77 (7)
C(5)	0.40574 (6)	0.7152 (4)	0.1442 (2)	2.21 (7)
C(6)	0.43359 (6)	0.8418 (4)	0.1705 (2)	2.55 (8)
C(7)	0.46379 (6)	0.7841 (4)	0.1441 (2)	2.64 (8)
C(8)	0.46559 (6)	0.6058 (4)	0.0891 (2)	2.28 (8)
C(9)	0.43702 (6)	0.4821 (4)	0.0613 (2)	1.94 (7)
C(10)	0.40741 (6)	0.5310 (4)	0.0890 (2)	1.84 (7)
C(11)	0.42326 (6)	-0.0071 (4)	-0.0782 (2)	1.91 (6)
C(12)	0.40072 (6)	-0.1604 (4)	-0.1239 (2)	2.56 (8)
C(13)	0.41155 (6)	-0.3251 (5)	-0.1738 (2)	2.92 (9)
C(14)	0.44480 (6)	-0.3461 (4)	-0.1786 (2)	2.60 (8)
C(15)	0.46734 (6)	-0.1943 (4)	-0.1350 (2)	2.51 (8)
C(16)	0.45684 (6)	-0.0257 (4)	-0.0853 (2)	2.22 (8)
H1(O/W1)	0.2402 (6)	0.261 (5)	0.089 (2)	6.1 (9)
H2(O/W1)	0.2575 (6)	0.102 (5)	0.140 (2)	5.3 (8)
H1(O/W2)	0.3186 (6)	0.342 (5)	0.302 (2)	6.2 (8)
H2(O/W2)	0.3212 (7)	0.514 (5)	0.281 (2)	6.3 (9)
H1(O/W3)	0.2989 (6)	0.671 (4)	0.031 (2)	4.0 (7)
H2(O/W3)	0.2822 (7)	0.689 (5)	0.090 (2)	6.7 (9)
H1(O/W4)	0.3254 (9)	-0.045 (5)	0.221 (2)	10.1 (11)
H2(O/W4)	0.3267 (7)	-0.089 (5)	0.139 (2)	8.3 (10)
H1(O/W5)	0.2553 (5)	0.799 (4)	0.211 (1)	2.5 (6)
H2(O/W5)	0.2287 (8)	0.765 (6)	0.144 (3)	10.2 (12)
H(C5)	0.3849 (5)	0.749 (3)	0.163 (2)	1.8 (5)
H(C6)	0.4331 (6)	0.969 (5)	0.199 (2)	5.1 (8)
H(C7)	0.4867 (6)	0.887 (4)	0.165 (2)	4.0 (7)
H(C8)	0.4883 (5)	0.564 (3)	0.075 (1)	1.1 (5)
H(C12)	0.3782 (6)	-0.147 (4)	-0.129 (2)	2.8 (6)
H(C13)	0.3969 (6)	-0.417 (4)	-0.211 (2)	5.0 (8)
H(C14)	0.4552 (6)	-0.475 (5)	-0.218 (2)	5.5 (8)
H(C15)	0.4928 (5)	-0.195 (3)	-0.142 (1)	1.7 (5)
H(C16)	0.4742 (6)	0.085 (4)	-0.052 (2)	3.4 (6)

$$* B_{eq} = \frac{4}{3} \sum_i \sum_j (a_i \cdot a_j) \beta_{ij}$$

atoms are given in Table 1, bond lengths and bond angles in Table 2.

The P—O(3) ester bond is unusually long, 1.661 (2) Å, compared with the average P—O ester bond length of 1.605 Å (Sundaralingam, 1973) in nucleoside mono- and diphosphates.

A P—O bond length of 1.621 (5) Å has been observed in disodium DL- α -glycerophosphate hexahydrate (McAlister & Sundaralingam, 1980), and phosphate P—O ester bonds to substituted aromatic rings have been found to be as long as 1.64 (2) Å (Caughlan & Mazhar-ul-Haque, 1967). The long P—O bond in the present structure may be related to the

Table 2. *Bond lengths (\AA) and bond angles ($^\circ$) for the flavone-3-monophosphate-magnesium complex*

Mg—O(W1)	2.098 (2)	C(11)—C(12)	1.399 (4)
Mg—O(W2)	2.080 (2)	C(11)—C(16)	1.401 (4)
Mg—O(W3)	2.058 (2)	C(12)—C(13)	1.377 (4)
Mg—O(W4)	2.072 (2)	C(13)—C(14)	1.381 (4)
Mg—O(1P)	2.031 (2)	C(14)—C(15)	1.383 (4)
Mg—O(4)	2.068 (2)	C(15)—C(16)	1.388 (4)
P—O(1P)	1.513 (2)	C(2)—C(11)	1.482 (4)
P—O(2P)	1.515 (2)	C(2)—C(3)	1.355 (3)
P—O(3P)	1.499 (2)	C(3)—C(4)	1.457 (4)
P—O(3)	1.661 (2)	C(4)—C(10)	1.449 (4)
		C(5)—C(6)	1.378 (4)
O(1)—C(9)	1.363 (3)	C(5)—C(10)	1.407 (4)
O(1)—C(2)	1.382 (3)	C(6)—C(7)	1.408 (4)
O(3)—C(3)	1.364 (3)	C(7)—C(8)	1.376 (4)
O(4)—C(4)	1.232 (3)	C(8)—C(9)	1.392 (4)
		C(9)—C(10)	1.380 (4)
O(W1)—Mg—O(W2)	92.1 (1)	O(1)—C(2)—C(3)	120.9 (3)
O(W1)—Mg—O(W3)	91.5 (1)	O(1)—C(2)—C(11)	109.7 (3)
O(W1)—Mg—O(W4)	91.1 (1)	C(3)—C(2)—C(11)	129.3 (3)
O(W1)—Mg—O(1P)	91.9 (1)	O(3)—C(3)—C(2)	120.6 (3)
O(W2)—Mg—O(W3)	91.9 (1)	O(3)—C(3)—C(4)	118.1 (2)
O(W2)—Mg—O(W4)	86.2 (1)	C(2)—C(3)—C(4)	120.8 (3)
O(W2)—Mg—O(4)	88.2 (1)	O(4)—C(4)—C(3)	123.1 (3)
O(W3)—Mg—O(1P)	92.7 (1)	O(4)—C(4)—C(10)	120.7 (3)
O(W3)—Mg—O(4)	84.6 (1)	C(3)—C(4)—C(10)	116.1 (3)
O(W4)—Mg—O(1P)	89.1 (1)	C(6)—C(5)—C(10)	119.8 (3)
O(W4)—Mg—O(4)	92.7 (1)	C(5)—C(6)—C(7)	120.0 (3)
O(1P)—Mg—O(4)	88.1 (1)	C(6)—C(7)—C(8)	120.7 (3)
		C(7)—C(8)—C(9)	118.6 (3)
O(1P)—P—O(2P)	112.5 (1)	O(1)—C(9)—C(8)	116.7 (3)
O(1P)—P—O(3P)	114.0 (1)	O(1)—C(9)—C(10)	121.4 (3)
O(1P)—P—O(3)	106.8 (1)	C(8)—C(9)—C(10)	121.9 (3)
O(2P)—P—O(3P)	114.7 (1)	C(4)—C(10)—C(5)	121.2 (3)
O(2P)—P—O(3)	100.8 (1)	C(4)—C(10)—C(9)	119.6 (3)
O(3P)—P—O(3)	106.7 (1)	C(5)—C(10)—C(9)	119.0 (3)
		C(2)—C(11)—C(12)	122.9 (3)
Mg—O(1P)—P	135.1 (1)	C(2)—C(11)—C(16)	119.0 (3)
C(2)—O(1)—C(9)	120.9 (2)	C(12)—C(11)—C(16)	118.2 (3)
P—O(3)—C(3)	126.3 (2)	C(11)—C(12)—C(13)	120.4 (3)
Mg—O(4)—C(4)	149.3 (2)	C(12)—C(13)—C(14)	121.3 (3)
		C(13)—C(14)—C(15)	119.0 (3)
		C(14)—C(15)—C(16)	120.5 (3)
		C(11)—C(16)—C(15)	120.5 (3)

repulsive interaction between the O(3P) and C(3) atoms, which are only 3.046 (3) Å apart, and to the short O(1P)—Mg bond [2.031 (2) Å].

The dihedral angle between the least-squares planes of the phenyl ring and the benzopyran ring is only 7.6 (1)°.

Of particular interest is the conformation of the seven-membered ring formed by chelation of the Mg²⁺ ion by O(4) and O(1P). The conformation of this ring and the endocyclic torsion angles are shown in Fig. 2. The atoms of the ring are arranged in two planes, one containing Mg, O(4), C(4), C(3), and O(3) [maximum deviation of 0.025 (3) Å by C(3)], and the other containing Mg, O(1P), P, and O(3) [maximum deviation of 0.006 (2) Å by O(1P)], with a dihedral angle between them of 128.1 (1)°. The six Mg—O bond

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