

## Structure of *cis*-Diacetonitrile[ferrocenylbis(diphenylphosphine)]rhodium(I) Perchlorate Acetonitrile Solvate

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**Abstract.**  $[\text{Rh}(\text{C}_{34}\text{H}_{28}\text{FeP}_2)(\text{C}_2\text{H}_3\text{N})_2]\text{ClO}_4 \cdot \text{C}_2\text{H}_3\text{N}$ ,  $M_r = 879.9$ , triclinic,  $P\bar{1}$ ,  $a = 10.785$  (2),  $b = 13.301$  (2),  $c = 15.265$  (2) Å,  $\alpha = 65.73$  (1),  $\beta = 84.67$  (1),  $\gamma = 77.23$  (1)°,  $V = 1946.9$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.501$ ,  $D_m = 1.47$  (5) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha_1) = 0.70926$  Å,  $\mu = 9.86$  cm<sup>-1</sup>,  $F(000) = 852$ ,  $T = 292$  K, final  $R = 0.059$ ,  $wR = 0.036$  for 7885 reflections [ $I \geq 2\sigma(I)$ ]. The geometry about the central Rh atom is a distorted square-planar configuration. The C—N distances of the acetonitrile ligands clearly indicate a triple bond. The cyclopentadienyl rings of the ferrocenyl moiety show a staggered conformation and their planes are slightly tilted with respect to each other.

**Introduction.** *cis*-Diacetonitrile[ferrocenylbis(diphenylphosphine)]rhodium(I) perchlorate,  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Rh}(\text{MeCN})_2]\text{ClO}_4$ , is one of a series of tertiary ferrocenylphosphine rhodium complexes which are catalyst precursors for the hydrogenation of a range of olefins (Cullen, Kim, Einstein & Jones, 1983, 1985). The structures of  $[(\text{P}-\text{P})\text{Rh}(\text{nbnd})]\text{ClO}_4$ ,  $[(\text{P}-\text{P}) = (\eta^5\text{-}R^1R^2\text{PC}_5\text{H}_4)\text{Fe}(\eta^5\text{-}R^3R^4\text{PC}_5\text{H}_4)]$ ;  $R^1 = R^2 = R^3 = R^4 = \text{C}(\text{CH}_3)_3$ , or Ph;  $R^1 = R^2 = \text{Ph}$ ,  $R^3 = R^4 = \text{C}(\text{CH}_3)_3$ ;  $R^1 = R^3 = \text{Ph}$ ,  $R^2 = R^4 = \text{C}(\text{CH}_3)_3$ ; nbnd = norbornadiene] and some comparative rate studies have been reported by Cullen *et al.* (1983, 1985). Their results showed a correlation between the structures of the complexes and their catalytic activity for olefin hydrogenation. Further studies of the hydrogenation of tertiary alkyl and aryl phosphines showed that some of these rhodium complexes could react with hydrogen in the absence of substrates in various solutions to form bridging and/or terminal rhodium hydrides (Kim, 1984).

Crystal structures of some rhodium hydrides have been determined (Butler, Cullen, Mann & Nurse, 1985; Butler, Cullen, Kim, Einstein & Jones, 1984). A possible hydrogenation pathway has been proposed, which involves dissolution of the rhodium(I) complex followed by oxidative addition of a hydrogen molecule to rhodium(III) to form a dihydrido

tertiary phosphine rhodium complex (Butler *et al.*, 1984, 1985). However, the preparation of a hydride of an aryl phosphine complex  $[(\text{bppf})\text{Rh}(\text{nbnd})_2]^+$  {bppf =  $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2$ }, in  $\text{CH}_3\text{OH}$  or  $\text{CH}_3\text{CN}$  has not yet been achieved. The title complex was the product of an attempt to prepare the hydride of  $[(\text{bppf})\text{Rh}(\text{nbnd})_2]\text{ClO}_4$  in  $\text{CH}_3\text{CN}$  solution.

We have determined its structure, primarily to investigate the reason for the difficulty of hydride formation by the aryl phosphine complex and the mode of coordination of acetonitrile to rhodium.

**Experimental.** The compound  $[(\text{bppf})\text{Rh}(\text{CH}_3\text{CN})_2]\text{ClO}_4$  was obtained from  $[(\text{bppf})\text{Rh}(\text{nbnd})_2]\text{ClO}_4$  in  $\text{CH}_3\text{CN}$  solution at room temperature (Butler *et al.*, 1984). The density of the crystal was measured by flotation in a mixture of hexane and chloroform.

Crystal dimensions  $0.48 \times 0.24 \times 0.43$  mm, sealed in glass capillary, space group and approximate unit-cell parameters determined from precession photographs. Data collected on a modified Picker four-circle diffractometer, graphite-monochromated Mo  $K\alpha$  radiation,  $\omega$ - $2\theta$  scan, the NRCC diffractometer control system (Gabe, Larson, Lee & Wang, 1979), PDP8a computer. Final lattice constants determined from a refined orientation matrix with 25 reflections [ $51.0 < 2\theta < 55.0^\circ$ , Mo  $K\alpha_1$  radiation ( $\lambda = 0.70926$  Å), ranges of  $h$ ,  $k$  and  $l$ : 0 to 14, -16 to 17, -19 to 19 respectively]. Three reflections (207, 800, 366) measured after every 47 reflections, intensities decreased by 2%; 8935 reflections ( $3 \leq 2\theta \leq 60^\circ$ ) measured, 7885 with  $I \geq 2\sigma(I)$  used for refinements; Lorentz-polarization and absorption corrections (min. and max. transmission factors = 0.615 and 0.822) applied. Calculations performed by the XTAL system of crystallographic programs (Stewart, Hall, Alden, Olthof-Hazekamp & Doherty, 1983).

The values of  $\langle |E| \rangle$  and  $\langle |E^2 - 1| \rangle$  were 0.828 and 0.884 which are intermediate between the theoretical values for centric and noncentric distributions. Therefore, in the early stage of the structure determination, the space group of the crystal was assumed to be  $P1$ . Structure solved by a combination

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of direct methods and Patterson method. An analysis of the coordinates of the atoms in the two molecules showed that they were approximately related by a center of symmetry. The atomic coordinates were then transformed to place the center of symmetry at the origin and the structure was refined in both  $P1$  and  $P\bar{1}$  space groups. The Hamilton significance test, based on the weighted  $R$  factors, clearly indicated that the space group was  $P\bar{1}$ .

The positional parameters of all H atoms were constrained during the refinement to those of the C atoms to which they were bonded. The isotropic temperature factors of the H atoms were assigned and not refined. The least-squares weights were modified to remove dependence of the average value of  $w\Delta^2(F)$  on  $|F_o|$  and  $(\sin\theta)/\lambda$  (Wang & Robertson, 1985). Dispersion corrections were made for the Rh, Fe, Cl and P atoms; the dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 149). Difference synthesis showed the presence of a solvent molecule. The final refinement agreement factors with full-matrix least squares on  $F$ , using 7885 observed reflections and 584 least-squares variables, were  $R = 0.029$  and  $wR = 0.018$ . The average shift/e.s.d. and the maximum shift/e.s.d. for structural parameters were 0.004 and 0.4, respectively, at the termination of refinement, and the maximum residual electron density was  $0.8 e \text{ \AA}^{-3}$ .

**Discussion.** The atomic coordinates and equivalent isotropic thermal parameters, with their standard deviations in parentheses, are listed in Table 1\* and selected bond distances and bond angles are listed in Table 2. A view of the complex ion with atom numbering is shown in Fig. 1.

The coordination about the Rh atom involves a bidentate ferrocenylbis(diphenylphosphine) ligand and two acetonitrile ligands in a square-planar configuration. The P—Rh—P angle is greater than  $90^\circ$  whereas the N—Rh—N angle is less than  $90^\circ$ . The Rh—P bond distances are significantly shorter than those in similar complexes with the norbornadiene (nbd) ligand (Cullen *et al.*, 1985) replacing the two acetonitrile ligands. The P—Rh—P angle and the twist angle  $\gamma$  [defined as the dihedral angle between the P(1)—Rh—P(2) plane and the N(1)—Rh—N(2) plane] are both smaller in  $[(bppf)Rh(CH_3CN)_2]^+$ . The Rh—P bond distances, the P—Rh—P bond angles and the twist angles of the  $[(bppf)-$

Table 1. *Atom coordinates and temperature factors* ( $\text{\AA}^2 \times 100$ )

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U/U <sub>eq</sub>
Rh	0.01437 (1)	0.25185 (1)	0.23891 (1)	3.42 (1)
Fe	0.34026 (3)	0.10326 (3)	0.11691 (3)	4.76 (3)
P(1)	0.21228 (4)	0.17933 (4)	0.29558 (3)	3.51 (3)
P(2)	0.02103 (5)	0.15053 (4)	0.15101 (4)	3.64 (4)
N(1)	-0.0159 (2)	0.3602 (2)	0.3069 (2)	4.8 (2)
N(2)	-0.1691 (2)	0.3256 (2)	0.1888 (2)	5.0 (2)
C(1)	-0.0378 (3)	0.4291 (2)	0.3346 (2)	5.7 (2)
C(2)	-0.0613 (5)	0.5197 (4)	0.3681 (4)	9.7 (5)
C(3)	-0.2644 (2)	0.3695 (2)	0.1527 (2)	5.5 (2)
C(4)	-0.3846 (3)	0.4269 (4)	0.1006 (4)	8.9 (4)
C(11)	0.2376 (2)	0.0377 (2)	0.3916 (1)	4.0 (1)
C(12)	0.1391 (2)	-0.0202 (2)	0.4187 (2)	5.0 (1)
C(13)	0.1541 (3)	-0.1257 (2)	0.4951 (2)	6.4 (2)
C(14)	0.2665 (4)	-0.1736 (2)	0.5437 (2)	6.9 (3)
C(15)	0.3662 (3)	-0.1170 (2)	0.5174 (2)	6.7 (2)
C(16)	0.3520 (3)	-0.0115 (2)	0.4422 (2)	5.4 (2)
C(21)	0.2676 (2)	0.2561 (2)	0.3553 (2)	4.1 (2)
C(22)	0.2174 (3)	0.2493 (2)	0.4442 (2)	5.7 (2)
C(23)	0.2531 (4)	0.3109 (4)	0.4886 (2)	7.4 (3)
C(24)	0.3406 (4)	0.3776 (3)	0.4460 (3)	7.8 (3)
C(25)	0.3902 (4)	0.3851 (3)	0.3588 (3)	7.7 (3)
C(26)	0.3540 (3)	0.3253 (2)	0.3122 (2)	5.7 (2)
C(31)	-0.0721 (2)	0.0401 (2)	0.2025 (2)	4.5 (2)
C(32)	-0.1605 (2)	0.0435 (2)	0.2741 (2)	5.1 (2)
C(33)	-0.2381 (3)	-0.0354 (3)	0.3107 (2)	6.8 (3)
C(34)	-0.2282 (4)	-0.1169 (3)	0.2759 (2)	8.1 (3)
C(35)	-0.1400 (5)	-0.1230 (3)	0.2076 (3)	8.1 (3)
C(36)	-0.0602 (4)	-0.0453 (3)	0.1701 (2)	6.2 (2)
C(41)	-0.0555 (2)	0.2430 (2)	0.0348 (2)	4.4 (2)
C(42)	-0.1424 (3)	0.2131 (3)	-0.0068 (2)	6.3 (2)
C(43)	-0.1981 (5)	0.2874 (4)	-0.0937 (3)	9.0 (4)
C(44)	-0.1688 (5)	0.3921 (4)	-0.1396 (3)	9.3 (4)
C(45)	-0.0841 (5)	0.4233 (3)	-0.0992 (3)	8.7 (3)
C(46)	-0.0272 (3)	0.3494 (3)	-0.0120 (2)	6.4 (2)
C(51)	0.1635 (2)	0.0783 (2)	0.1128 (2)	4.7 (2)
C(52)	0.2173 (3)	0.1145 (3)	0.0180 (2)	6.0 (3)
C(53)	0.3296 (3)	0.0337 (4)	0.0208 (3)	7.6 (4)
C(54)	0.3455 (3)	-0.0506 (3)	0.1138 (3)	7.6 (4)
C(55)	0.2439 (3)	-0.0249 (2)	0.1728 (2)	6.0 (2)
C(61)	0.3365 (2)	0.1771 (2)	0.2084 (2)	4.4 (2)
C(62)	0.3302 (3)	0.2594 (2)	0.1114 (2)	5.2 (2)
C(63)	0.4421 (3)	0.2293 (3)	0.0624 (2)	6.8 (3)
C(64)	0.5180 (3)	0.1307 (4)	0.1285 (3)	7.0 (3)
C(65)	0.4545 (2)	0.0978 (3)	0.2185 (2)	5.9 (2)
Cl(1)	0.62654 (9)	0.62303 (8)	0.23222 (8)	8.17 (8)
O(1)	0.6426 (5)	0.5273 (6)	0.3149 (5)	20.9 (9)
O(2)	0.7310 (5)	0.6129 (6)	0.1700 (5)	16.9 (7)
O(3)	0.6227 (7)	0.7120 (8)	0.251 (1)	27. (2)
O(4)	0.5097 (3)	0.6333 (4)	0.1900 (3)	11.2 (4)
C(71)	0.213 (1)	0.6816 (5)	0.3937 (6)	13.1 (8)
C(72)	0.341 (1)	0.6845 (8)	0.383 (1)	18 (1)
N(71)	0.113 (1)	0.6789 (7)	0.4018 (9)	20 (1)

$Rh(CH_3CN)_2]^+$  complex and related complexes are listed in Table 3. In the alkyl and aryl ferrocenylphosphine rhodium(I) complexes containing the nbd ligand, the correlation between the decrease in  $\gamma$ , the shortening of the Rh—P bond length and the decrease in the P—Rh—P bond angle is assumed to result from the steric crowding caused by the substituents of the P atoms (Cullen *et al.*, 1985).

In the ferrocene moiety, the two cyclopentadienyl rings are slightly tilted with a dihedral angle of  $4.7 (2)^\circ$ . The average values of the C—C bond distance and C—C—C bond angles of the cyclopentadienyl rings are  $1.425 (10) \text{ \AA}$  and  $108.0 (4)^\circ$ , respectively, which are similar to values in related complexes and close to the ideal values. The two P atoms are bent inward so that they are  $0.023 (9)$  and  $0.058 (8) \text{ \AA}$  from the corresponding cyclopentadienyl

\* Lists of structure factors, anisotropic thermal parameters, complete bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53495 (52 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and bond angles (°)

Rh(1)—P(1)	2.2311 (8)	Rh(1)—P(2)	2.4767 (7)
Rh—N(1)	2.053 (3)	Rh—N(2)	2.067 (2)
Fe—C(51)	2.017 (3)	Fe—C(52)	2.039 (3)
Fe—C(53)	2.053 (6)	Fe—C(54)	2.056 (5)
Fe—C(55)	2.034 (3)	Fe—C(61)	2.005 (3)
Fe—C(62)	2.023 (3)	Fe—C(63)	2.052 (4)
Fe—C(64)	2.064 (4)	Fe—C(65)	2.038 (4)
P(1)—C(11)	1.830 (2)	P(1)—C(21)	1.835 (3)
P(1)—C(61)	1.803 (2)	P(2)—C(31)	1.829 (2)
P(2)—C(41)	1.836 (2)	P(2)—C(51)	1.807 (2)
N(1)—C(1)	1.131 (4)	N(2)—C(3)	1.130 (3)
C(1)—C(2)	1.458 (7)	C(3)—C(4)	1.466 (5)
P(1)—Rh—P(2)	96.48 (2)	C(11)—P(1)—C(61)	106.3 (1)
P(1)—Rh—N(1)	92.02 (6)	Rh—P(2)—C(31)	113.4 (1)
P(2)—Rh—N(1)	171.15 (6)	Rh—P(2)—C(51)	125.8 (1)
C(51)—Fe—C(52)	41.4 (1)	C(31)—P(2)—C(51)	101.7 (2)
C(52)—Fe—C(53)	40.6 (1)	Rh—N(2)—C(3)	173.4 (2)
C(54)—Fe—C(55)	40.8 (1)	N(1)—C(1)—C(2)	177.5 (3)
C(61)—Fe—C(65)	41.6 (1)	P(1)—C(11)—C(12)	119.4 (2)
C(63)—Fe—C(64)	40.2 (1)	P(1)—C(21)—C(22)	119.5 (2)
Rh—P(1)—C(11)	115.9 (1)	P(2)—C(31)—C(32)	119.0 (2)
Rh—P(1)—C(61)	116.5 (1)	P(2)—C(41)—C(42)	123.4 (2)
P(1)—Rh—N(2)	177.05 (8)	C(21)—P(1)—C(61)	101.8 (1)
P(2)—Rh—N(2)	86.38 (8)	Rh—P(2)—C(41)	108.7 (1)
N(2)—Rh—N(1)	85.1 (1)	C(31)—P(2)—C(41)	103.8 (1)
C(51)—Fe—C(55)	41.5 (1)	C(41)—P(2)—C(51)	100.9 (1)
C(53)—Fe—C(54)	39.8 (2)	Rh—N(1)—C(1)	172.2 (2)
C(61)—Fe—C(62)	41.6 (1)	N(2)—C(3)—C(4)	176.6 (4)
C(62)—Fe—C(63)	41.1 (1)	P(1)—C(11)—C(16)	121.8 (2)
C(64)—Fe—C(65)	40.4 (1)	P(1)—C(21)—C(26)	121.8 (2)
Rh—P(1)—C(21)	113.9 (1)	P(2)—C(31)—C(36)	120.0 (2)
C(11)—P(1)—C(21)	100.3 (1)	P(2)—C(41)—C(46)	117.9 (2)

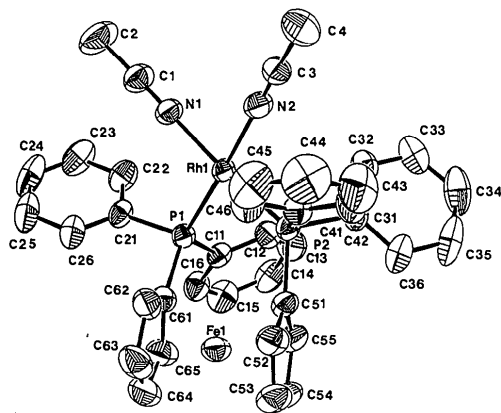


Fig. 1. The complex cation, with numbering scheme. The ellipsoids correspond to 50% probability.

planes. The staggered conformation of the cyclopentadienyl rings is similar to the conformation of ferrocene in [(bpf)Rh(nbd)]<sub>2</sub>ClO<sub>4</sub> and other related complexes. The cyclopentadienyl rings of the complex are planar, within the uncertainties in the coordinates of the atoms. The Fe—C bond distances are not identical, indicating that the position of the ferrocene is not at the center of the ferrocene moiety.

The N—C—C chains of the acetonitrile ligands are essentially linear and the C atoms deviate only slightly from the P(1)—P(2)—N(1)—N(2) mean plane. The C—N bond lengths [1.132 (7) and 1.133 (5) Å] of the acetonitrile ligands clearly indicate a triple bond equivalent to that (1.134 Å)

Table 3. Summary of important bond parameters of the title complex and related complexes

	(a)	(b)	(c)	(d)	(e)
Rh—P	2.466	2.391	2.416	2.335	2.2311
Rh—P'	2.458	2.356	2.388	2.317	2.2467
Rh—MP*	2.069	2.108	2.097	2.113	
Rh—N					2.053
Rh—MP*	2.048	2.077	2.050	2.083	
Rh—N'					2.067
P—Rh—P'	103.71	100.25	98.60	96.82	96.48
M—Rh—M'	68.4	68.0	69.1	68.2	
N—Rh—N'					85.1
γ	36.8	14.4	20.0	5.9	2.55 (6)

[(P—P)Rh(nbd)]ClO<sub>4</sub>, nbd = norbornadiene] [(P—P) = (η<sup>5</sup>-R<sup>1</sup>R<sup>2</sup>PC<sub>5</sub>H<sub>4</sub>)-Fe(η<sup>5</sup>-R<sup>3</sup>R<sup>4</sup>PC<sub>5</sub>H<sub>4</sub>)].

(a) R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = C(CH<sub>3</sub>)<sub>3</sub>.

(b) R<sup>1</sup> = R<sup>2</sup> = Ph, R<sup>3</sup> = R<sup>4</sup> = C(CH<sub>3</sub>)<sub>3</sub>.

(c) R<sup>1</sup> = R<sup>3</sup> = Ph, R<sup>2</sup> = R<sup>4</sup> = C(CH<sub>3</sub>)<sub>3</sub>.

(d) R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = C(CH<sub>3</sub>)<sub>3</sub>, or Ph.

(e) *cis*-Diacetonitrileferrocenylbis(diphenylphosphine)rhodium(I) perchlorate.

\*Midpoints of the double bonds of nbd.

Table 4. Selected torsional angles (°)

Rh(1)—P(1)—C(61)—Fe(1)	-56.4 (1)	Rh(1)—P(1)—C(11)—C(12)	5.1 (3)
P(1)—C(61)—Fe(1)—C(51)	17.0 (1)	Rh(1)—P(1)—C(21)—C(22)	71.5 (2)
C(61)—Fe(1)—C(51)—P(2)	18.9 (2)	Rh(1)—P(1)—C(61)—C(62)	30.6 (3)
Fe(1)—C(51)—P(2)—Rh(1)	-14.2 (2)	Rh(1)—P(2)—C(31)—C(32)	15.2 (2)
C(51)—P(2)—Rh(1)—P(1)	-18.5 (1)	Rh(1)—P(2)—C(41)—C(52)	-134.5 (2)
P(2)—Rh(1)—P(1)—C(61)	50.2 (1)	Rh(1)—P(2)—C(51)—C(52)	-145.0 (3)



Fig. 2. Stereoscopic view of the central ring of the cation.

in an acetonitrile tris(triphenylphosphine)rhodium complex (Pimblett, Garner & Clegg, 1985) but shorter than the C—N triple bond length (1.158 Å) [International Tables for X-ray Crystallography (1968, Vol. III)] in RCN molecules.

The phenyl rings of the complex are essentially planar with an average C—C bond distance of 1.384 (15) Å, and an average C—C—C bond angle of 120.0 (7)°. The two phenyl rings and the cyclopentadienyl ring bonded to each P atom form a propeller conformation, which minimizes intramolecular crowding. The torsional angles of the phenyl and cyclopentadienyl rings, referred to as the Rh—P bonds, are listed in Table 4.

The foregoing would be consistent with the molecules adopting a conformation which would show at least approximate local twofold symmetry through the Rh and Fe atoms. Yet they do not. The reasons presumably involve the compatibility of the coordination requirements of the Fe, Rh and P atoms and the steric requirements of the bulky outer groups. In

order to define the general conformation of the complex we will focus on the six-membered ring formed by atoms Rh(1), P(1), C(51), Fe(1), C(61) and P(2); we do not intend to imply that this ring is of significance in the usual chemical sense. The conformation of this central fragment of the complex is shown in Fig. 2. An analysis of the ring by the method of Cremer & Pople (1975) shows that the ring has a large puckering amplitude ( $Q = 0.567$ ), with angular deviations  $\theta_2 = 234.9$ ,  $\varphi_2 = 123.8^\circ$ . This corresponds to a half-boat conformation with the atom P(1) furthest from the mean plane of the ring. Bond angle Rh—P(2)—C(51) [ $125.8(1)^\circ$ ] is substantially larger than Rh—P(1)—C(61) [ $116.5(1)^\circ$ ].

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## Comparison of Two Hydrated Forms of Sodium Inosine 5'-Monophosphate

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**Abstract.** The crystal and molecular structure of a decahydrated form of the sodium salt of inosine 5'-monophosphate ( $C_{10}H_{12}N_4O_8P^- \cdot Na^+ \cdot 10H_2O$ ) was solved to study the effect of hydration on the conformation of nucleic acids. Monoclinic, space group  $P2_1$ ,  $a = 8.730(3)$ ,  $b = 22.349(7)$ ,  $c = 12.282(4)$  Å,  $\beta = 109.68(3)^\circ$ ,  $V = 2256.52$  Å<sup>3</sup>,  $M_r = 550.34$ ,  $Z = 4$ ,  $F(000) = 1196$ ,  $D_x = 1.62$  g cm<sup>-3</sup>,  $\mu = 21.7$  cm<sup>-1</sup>,  $\lambda(Cu K\alpha) = 1.54056$  Å,  $R = 0.070$ ,  $wR = 0.102$  for 3404 unique [ $I_{net} > 2\sigma(I_{net})$ ] observed reflections out of 3457 unique reflections. The two molecules (*A* and *B*) in the asymmetric unit differ in the arrangement of the first shell of hydration and in the torsion angles of the ribose and phosphate. The bond lengths and angles are similar to those of the structure of a less hydrated ('dry') form of the same nucleotide ( $C_{10}H_{12}N_4O_8P^- \cdot Na^+ \cdot 8H_2O$ ) determined previously in

space group  $C222_1$  [Rao & Sundaralingam (1969). *J. Am. Chem. Soc.* **91**, 1210–1217]. The twofold symmetry in the 'dry' form is destroyed in the present crystal structure due to the relative displacement of the two independent molecules and reorganization of the hydration shell. Molecule *A* is different from (r.m.s. = 0.190 Å) while molecule *B* is similar to (r.m.s. = 0.093 Å) that of the 'dry' form. The conformation adopted is influenced mainly by the differences in the endocyclic torsion angles of the ribose.

**Introduction.** The importance of the hydration shell in determining the conformation of the nucleic acids, and hence their function, has been widely recognized (Saenger, 1984). The crystal structure of sodium inosine 5'-monophosphate (5'-IMP;  $C_{10}N_4O_8H_{12}P^- \cdot Na^+ \cdot 8H_2O$ ),  $R = 0.10$ , has been reported (Rao & Sundaralingam, 1969). In this 'dry' form structure, only six of the water molecules

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