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Bisulfite and Hydroxylamine Mutagenesis: Structures of Sodium N^4-Hydroxy-5,6-dihydrocytosine-6-sulfonate Monohydrate and Sodium N^4-Hydroxy-1-methyl-5,6-dihydrocytosine-6-sulfonate Tetrahydrate

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Abstract

The crystal structures of the sodium salts of N^4-hydroxy-5,6-dihydrocytosine-6-sulfonate and N^4-hydroxy-1-methyl-5,6-dihydrocytosine-6-sulfonate, products of the reaction of the mutagens hydroxylamine and bisulfite with cytosine or 1-methylcytosine, have been determined from X-ray data collected on an automated diffractometer. Both compounds are in the *imino* form, with the N^4-OH located *syn* to the ring N(3). This conformation would prevent such modified residues in a polynucleotide from participating in normal base pairing, a finding which has relevance to the assumed mechanism of mutations caused either by hydroxylamine alone or by the combination of both reagents. Sodium N^4-hydroxy-5,6-dihydrocytosine-6-sulfonate monohydrate: $C_4H_6N_3O_5S^-.Na^+.H_2O$, $P2_1/c$, $a = 12{\cdot}977\ (2)$, $b = 8{\cdot}384\ (2)$, $c = 8{\cdot}552\ (2)$ Å, $\beta = 106{\cdot}89\ (1)°$, $Z = 4$, $D_c = 1{\cdot}859$, $D_o = 1{\cdot}87$ Mg m^{-3}, $V = 890{\cdot}3$ Å^3, $M_r = 249{\cdot}2$, λ(Mo $K\alpha_1$) = 0·70926 Å, $T = 299 \pm 1$ K, $F(000) = 512$. Sodium N^4-hydroxy-1-methyl-5,6-dihydrocytosine-6-sulfonate tetrahydrate: $C_5H_8N_3O_5S^-.Na^+.4H_2O$, $P2_1/c$, $a = 6{\cdot}491\ (1)$, $b = 11{\cdot}129\ (2)$, $c = 17{\cdot}883\ (3)$ Å, $\beta = 93{\cdot}50\ (1)°$, $Z = 4$, $D_c = 1{\cdot}634$, $D_o = 1{\cdot}65$ Mg m^{-3}, $V = 1289{\cdot}4$ Å^3, $M_r = 317{\cdot}3$, λ(Mo $K\alpha_1$) = 0·70926 Å, $T = 299 \pm 1$ K, $F(000) = 664$. Both structures were solved by direct methods. Full-matrix least-squares refinement yielded an R of 0·036 for the 2325 significant data measured for the free-base derivative, and an R of 0·037 for the 2624 significant data measured for the blocked-base derivative. The methyl group and greater degree of hydration of the blocked-base derivative result in markedly different packing schemes.

Introduction

Bisulfite and hydroxylamine (and related nitrogen nucleophiles) have been widely employed for the modification of nucleic acids. Both reagents have been shown to be mutagenic in microbial systems, inducing primarily guanine–cytosine to adenine–thymine base-pair transitions (Hayatsu, 1976; Budowsky, 1976). Bisulfite is known to catalyze the deamination of cytosine, yielding uracil, under mildly alkaline conditions in aqueous media. The mechanism of hydroxylamine mutagenesis is less clear, but has been proposed to involve a modified cytosine residue resembling uracil or thymine in hydrogen-bonding and base-pairing capability. A problem arises in that hydroxylamine reacts with cytosine to yield more than one product (Budowsky, 1976).

Recently, Hayatsu (1977) has demonstrated a 'cooperativity' in the actions of bisulfite and hydroxylamine, both *in vitro* and *in vivo*. The *in vitro* modification of cytosine with a combination of bisulfite and hydroxylamine proceeds at a much higher rate than the reaction with either reagent alone, and yields a single major product. Hayatsu observed a concomitant increase in the mutagenicity of the combination of reagents, relative to that of either reagent alone, in a bacteriophage system.

We have determined the structure of sodium N^4-hydroxy-5,6-dihydrocytosine-6-sulfonate monohydrate (CYTOS), the product of the action of bisulfite and hydroxylamine on cytosine, and therefore the putative intermediate in the mutations caused by this combination of reagents. The structure of sodium N^4-hydroxy-1-methyl-5,6-dihydrocytosine-6-sulfonate tetrahydrate (MCYTOS) has also been determined and is compared with that of the derivative of the free base.

Experimental

CYTOS and MCYTOS were prepared essentially by the method of Hayatsu (1977). One mmol of cytosine or 1-methylcytosine was added to 15 ml of a solution 1·0 *M* with respect to both Na_2SO_3 and $H_2NOH.HCl$, adjusted to pH 6·2. The reaction mixture was refrigerated and, in the case of CYTOS, crystals formed

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after several days. MCYTOS did not crystallize after an extended period in the cold, but when the solution was warmed to room temperature crystals formed overnight. Both compounds were recrystallized from water by slow evaporation at room temperature.

The space groups and approximate cell dimensions were determined from precession and Weissenberg photographs. More accurate cell dimensions were obtained by least-squares refinement with the use of the observed setting angles for eight (CYTOS) and twelve (MCYTOS) Mo $K\alpha_1$ reflections, in the range $45 < 2\theta < 55°$, measured with an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). The density of the crystals was measured by flotation in mixtures of chloroform and dibromomethane. Crystal data are given in the *Abstract*.

Table 1. *Refinement parameters for CYTOS and MCYTOS*

	CYTOS	MCYTOS
Reflections measured	2589	2996
Reflections included in refinement $[\|F_o\| > 3\sigma(F_o)]$ (n)	2325	2624
Number of parameters (p)	169	237
$\sum \|F_o - \|F_c\|\| / \sum \|F_o\|$	0·036	0·037
$[\sum w(F_o - \|F_c\|)^2 / \sum wF_o^2]^{1/2}$	0·046	0·046
$[\sum w(F_o - \|F_c\|)^2/(n-p)]^{1/2}$	1·43	1·47
Average shift on the final round of refinement, as a percentage of the estimated standard deviation	7·1%	11·0%

Intensity data were collected on the diffractometer with Nb-filtered Mo $K\bar{a}$ radiation, using the θ–2θ step-scan technique. Of 2589 reflections measured for CYTOS and 2996 reflections measured for MCYTOS ($2\theta < 55°$), 2325 and 2624, respectively, met the criterion for observed data $[|F_o| > 3\sigma(F_o)]$. Each intensity was assigned a variance $\sigma^2(I)$ based on counting statistics plus a term $(0{\cdot}04I)^2$, empirically derived during refinement. Absorption corrections were not applied [μ(CYTOS) = 4·3 cm^{-1}, μ(MCYTOS) = 3·4 cm^{-1}]. No significant changes were observed in standard reflections during the course of either data collection.

The structures were solved by direct methods, MCYTOS with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), CYTOS with an earlier version of *MULTAN* (Germain, Main & Woolfson, 1971). H atoms were located from difference Fourier syntheses. The atomic parameters were refined by full-matrix least-squares methods, with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the H atoms. All refinements were performed with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The final agreement factors are given in Table 1. The final atomic parameters are given in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and H-atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36682 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional and isotropic thermal parameters* ($\times 10^4$) *for non-hydrogen atoms*

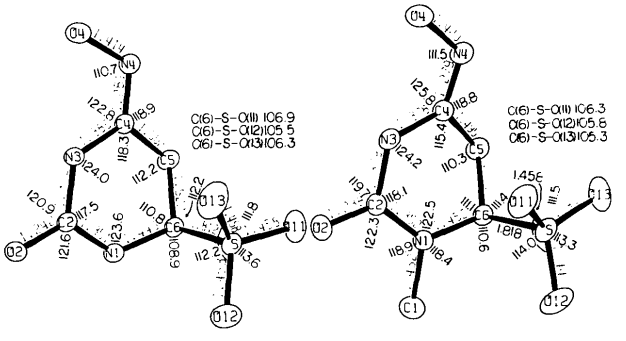
The isotropic temperature factor is $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$; the values given are the arithmetic averages of the principal components of the anisotropic temperature factors. Standard deviations in units of the last significant digits are given in parentheses.

	MCYTOS				CYTOS			
	x	y	z	U (Å^2)	x	y	z	U (Å^2)
C(1)	5809 (3)	4478 (2)	7387 (1)	308 (10)				
N(1)	7081 (2)	5008 (1)	6826 (1)	213 (7)	7535 (1)	−822 (2)	4266 (2)	234 (6)
C(2)	6414 (3)	4951 (1)	6096 (1)	188 (7)	8157 (1)	−1820 (2)	3691 (2)	190 (7)
O(2)	4804 (2)	4423 (1)	5883 (1)	259 (6)	8039 (1)	−3289 (2)	3703 (2)	288 (6)
N(3)	7571 (2)	5517 (1)	5579 (1)	206 (7)	8931 (1)	−1152 (2)	3096 (2)	216 (6)
C(4)	9488 (3)	6016 (2)	5745 (1)	250 (8)	9155 (1)	466 (2)	3142 (2)	198 (7)
N(4)	10465 (2)	6701 (2)	5314 (1)	247 (7)	9888 (1)	1059 (2)	2586 (2)	273 (7)
O(4)	9320 (2)	6902 (1)	4622 (1)	297 (7)	10413 (1)	−155 (2)	1958 (2)	374 (7)
C(5)	10497 (3)	5673 (2)	6488 (1)	240 (9)	8548 (1)	1553 (2)	3957 (2)	225 (7)
C(6)	8926 (3)	5663 (2)	7082 (1)	193 (7)	7457 (1)	871 (2)	3937 (2)	186 (6)
S	8276 (1)	7178 (1)	7365 (1)	214 (2)	6441 (1)	1214 (1)	2006 (1)	185 (2)
O(11)	7089 (2)	7710 (1)	6731 (1)	315 (7)	6252 (1)	2929 (2)	1870 (2)	297 (7)
O(12)	7132 (3)	7043 (1)	8027 (1)	405 (8)	5508 (1)	301 (2)	2092 (2)	390 (8)
O(13)	10249 (3)	7786 (1)	7509 (1)	388 (8)	6891 (1)	622 (2)	739 (2)	359 (8)
Na	4135 (1)	2269 (1)	5789 (1)	262 (4)	6344 (1)	−4606 (1)	3144 (1)	248 (3)
$W(1)$	4428 (2)	7890 (1)	5435 (1)	311 (7)	5864 (1)	−2943 (2)	680 (2)	317 (7)
$W(2)$	2836 (3)	254 (2)	5510 (1)	398 (9)				
$W(3)$	7707 (2)	2019 (2)	6178 (1)	326 (8)				
$W(4)$	8859 (3)	5331 (2)	981 (1)	450 (10)				

Results

Drawings of the CYTOS and MCYTOS anions, including bond distances and angles, are shown in Fig. 1. The bond distances and angles about the six-membered rings are comparable to those observed in several 5,6-dihydrouracil structures [dihydrouracil (Rohrer & Sundaralingam, 1970); dihydrouridine (Sundaralingam, Rao & Abola, 1971); 5,6-dihydro-2-thiouracil (Kojić-Prodić, Ružić-Toroš & Coffou, 1976); sodium 5,6-dihydro-2-thiouracil-6-sulfonate monohydrate (Jain, Lee, Mertes & Pitman, 1978); sodium 5,6-dihydrouracil-6-sulfonate monohydrate (Barnes & Hawkinson, 1980)]. In particular, the N(3)–C(4) bond lengths and the C(2)–N(3)–C(4) bond angles are consistent with a single-bond character for the N(3)–C(4) bonds, and these values differ significantly from the average values for several neutral cytosine structures [1·339 (7) Å and 120·5 (1·3)° (Voet & Rich, 1970)]. The C(4)–N(4) bond lengths are significantly shorter than in any of the above cytosine structures [average value, 1·324 (20) Å], and compare well with the C=N bond lengths in other oxime structures [1·288 Å, N^4-hydroxy-1,5-dimethylcytosine (Shugar, Huber & Birnbaum, 1976); 1·302 Å, N^4-hydroxy-1-methylcytosine (Birnbaum, Kulikowsky & Shugar, 1979); 1·285 Å, *anti*-4-pyrimidinecarboxaldehyde oxime (Martínez-Ripoll & Lorenz, 1974)].

Table 3 lists the torsion angles about the anions. The O(4) atoms are essentially *syn* to the ring N(3) atoms, as was also observed in the related structures, N^4-hydroxy-1,5-dimethylcytosine (Shugar *et al.*, 1976) and N^4-hydroxy-1-methylcytosine (Birnbaum *et al.*, 1979). The sulfonate groups are attached *axially* to the puckered rings, and the sulfonate O atoms are approximately staggered with respect to the substituents on C(6).

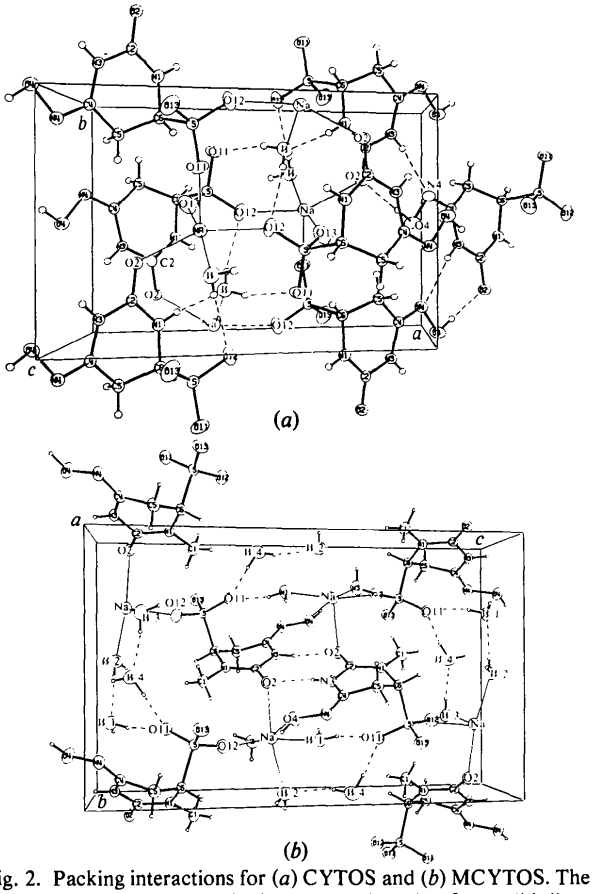


(*a*) (*b*)

Fig. 1. Bond distances (Å) and angles (°) for (*a*) CYTOS and (*b*) MCYTOS. The thermal ellipsoids are drawn at the 50% probability level. The average standard deviation in the bond lengths and bond angles is 0·002 Å and 0·2°. Illustrations were prepared with the aid of the computer program *ORTEP* (Johnson, 1965).

Table 3. *Torsion angles* (°)

	CYTOS	MCYTOS
Ring angles		
N(1)–C(2)–N(3)–C(4)	4·1 (2)	8·1 (2)
C(2)–N(3)–C(4)–C(5)	2·8 (2)	13·4 (2)
N(3)–C(4)–C(5)–C(6)	−25·9 (2)	−41·1 (2)
C(4)–C(5)–C(6)–N(1)	40·7 (1)	47·9 (2)
C(5)–C(6)–N(1)–C(2)	−38·3 (2)	−30·1 (2)
C(6)–N(1)–C(2)–N(3)	15·6 (2)	1·4 (2)
Exocyclic angles		
C(1)–N(1)–C(2)–O(2)		−2·9 (2)
C(1)–N(1)–C(2)–N(3)		176·2 (2)
O(2)–C(2)–N(3)–C(4)	−175·6 (1)	−172·7 (2)
C(2)–N(3)–C(4)–N(4)	179·6 (1)	−168·8 (2)
N(3)–C(4)–N(4)–O(4)	−0·4 (2)	0·2 (3)
O(4)–N(4)–C(4)–C(5)	176·3 (1)	177·9 (1)
N(4)–C(4)–C(5)–C(6)	157·2 (1)	141·0 (2)
C(4)–C(5)–C(6)–S	−81·3 (1)	−75·9 (2)
C(5)–C(6)–S–O(11)	−67·1 (1)	70·1 (1)
C(5)–C(6)–S–O(12)	171·7 (1)	−168·4 (1)
C(5)–C(6)–S–O(13)	52·4 (1)	−48·3 (1)
C(6)–N(1)–C(2)–O(2)	−164·8 (1)	−177·7 (2)
O(11)–S–C(6)–N(1)	169·9 (1)	−54·1 (1)
O(12)–S–C(6)–N(1)	48·7 (1)	67·4 (1)
O(13)–S–C(6)–N(1)	−70·6 (1)	−172·4 (1)
S–C(6)–N(1)–C(2)	85·6 (2)	94·2 (2)
S–C(6)–N(1)–C(1)		−80·6 (2)
C(5)–C(6)–N(1)–C(1)		155·1 (2)



(*a*) (*b*)

Fig. 2. Packing interactions for (*a*) CYTOS and (*b*) MCYTOS. The broken lines represent hydrogen bonds. The fine solid lines represent Na^+-ion coordination interactions.

Table 4. *Distances* (Å) *and angles* (°) *in the hydrogen bonds, D–H–A*

Donor (*D*)	Acceptor (*A*)	Symmetry operation*	*D–A*	H *A*	*D–H–A*
CYTOS					
N(1)	*W*(1)	$x, -\frac{1}{2}-y, \frac{1}{2}+z$	2·960 (3)	2·14 (3)	172 (3)
N(3)	N(4)	$2-x, -\frac{1}{2}+y, \frac{1}{2}-z$	2·946 (2)	2·16 (3)	159 (3)
O(4)	O(2)	$2-x, \frac{1}{2}+y, \frac{1}{2}-z$	2·731 (2)	1·88 (4)	171 (3)
W(1)	O(11)	$1-x, -y, -z$	2·970 (2)	2·15 (3)	165 (3)
W(1)	O(12)	x,y,z	3·065 (3)	2·40 (4)	170 (5)
MCYTOS					
N(3)	O(2)	$1-x, 1-y, 1-z$	2·953 (2)	2·13 (2)	170 (2)
O(4)	*W*(3)	$2-x, 1-y, 1-z$	2·748 (2)	1·81 (3)	167 (3)
W(1)	N(4)	$-1+x, y, z$	2·889 (2)	2·10 (3)	168 (3)
W(1)	O(11)	x,y,z	2·812 (2)	2·02 (3)	163 (3)
W(2)	*W*(1)	$x, -1+y, z$	2·834 (2)	2·09 (4)	168 (4)
W(2)	*W*(4)	$-1+x, \frac{1}{2}-y, \frac{1}{2}+z$	2·840 (3)	1·84 (4)	168 (3)
W(3)	*W*(4)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	2·749 (3)	1·96 (4)	167 (3)
W(3)	O(13)	$2-x, -\frac{1}{2}+y, \frac{3}{2}-z$	2·761 (2)	1·93 (3)	173 (3)
W(4)	O(11)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	2·839 (2)	2·02 (4)	158 (4)
W(4)	*W*(2)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	2·823 (3)	2·07 (5)	162 (5)

* The symmetry operation is applied to the acceptor-atom coordinates given in Table 2.

Table 5. Na^+*-ion coordination*

	Symmetry operation*	
CYTOS		
Na···O(2)	x,y,z	2·382 (2) Å
Na···O(11)	$x, -1+y, z$	2·323 (2)
Na···O(12)	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$	2·353 (2)
Na···O(13)	$x, -\frac{1}{2}-y, \frac{1}{2}+z$	2·289 (2)
Na···*W*(1)	x,y,z	2·451 (2)
MCYTOS		
Na···O(2)	x,y,z	2·440 (2)
Na···O(4)	$1-x, 1-y, 1-z$	2·494 (2)
Na···O(12)	$1-x, -\frac{1}{2}+y, \frac{3}{2}-z$	2·332 (2)
Na···*W*(1)	$1-x, 1-y, 1-z$	2·437 (2)
Na···*W*(2)	x,y,z	2·436 (2)
Na···*W*(3)	x,y,z	2·396 (2)

* Symmetry operation applied to atom in Table 2.

The ring pucker in CYTOS is consistent with the trend for ring puckering observed in a review of several dihydropyrimidine structures (Emerson & Sundaralingam, 1980), with C(5) and C(6) displaced to opposite sides of the least-squares plane of atoms N(1), C(2), N(3) and C(4), and with C(6) farther from the plane (0·338 Å) than C(5) (0·193 Å). However, in MCYTOS C(5) is farther from the plane (0·459 Å) than is C(6) (0·164 Å). In these structures, packing interactions with the sulfonate substituent at C(6) can be expected to exert considerable influence on the ring conformation.

Fig. 2 shows views of the packing interactions in CYTOS and MCYTOS. Hydrogen-bond and Na^+-ion-coordination parameters are given in Tables 4 and 5. The CYTOS anions are packed as ribbons of screw-related anions, along the **b** direction. Ribbons related by the **c** glide overlay in the **c** direction, resulting in layers of anions alternating with channels of solvent and Na^+ ions along the **a** direction.

The greater hydration of the MCYTOS crystal, and the 1-methyl substituent, result in markedly different packing interactions. The MCYTOS anions are packed as discrete hydrogen-bonded pairs, related by a center of symmetry. Adjacent pairs are bridged by a network of hydrogen bonds to the water molecules, and by coordination to the Na^+ ion.

Discussion

Hydroxylamine causes primarily guanine–cytosine to adenine–thymine base-pair transitions (Budowsky, 1976). Until recently, it has been assumed that a modified cytosine residue, resembling uracil in base pairing, was responsible for the nearly specific mutagenesis caused by this reagent. Such a molecule can be produced by substitution of hydroxylamine at position four of the cytosine ring, if the N(4)-hydroxyl group is located *anti* to the ring N(3). However, in both structures reported of such modified cytosine molecules, N^4-hydroxy-1,5-dimethylcytosine (Shugar *et al.*, 1976) and N^4-hydroxy-1-methylcytosine (Birnbaum *et al.*, 1979), the hydroxyl group has been found to be *syn* to N(3), as we have found in CYTOS and MCYTOS. Should the combination of bisulfite and hydroxylamine also be shown to cause specifically guanine–cytosine to adenine–thymine transitions, the mechanism of such mutations may be similar to that of hydroxylamine alone. It appears unlikely that either case may be explained entirely by a change in base pairing.

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Structural Characterization of a Substituted Derivative of $Ru_3(CO)_{12}$: 1,2;3,1-Bis{μ-[Bis(diphenylphosphino)methane]-*P*,*P'*}-1,1,2,2,2,3,3,3-octacarbonyl-*triangulo*-triruthenium(0) Acetone Solvate

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Abstract

$Ru_3(CO)_8\{(C_6H_5)_2PCH_2P(C_6H_5)_2\}_2.n(CH_3)_2CO$ ($n \simeq 2$), orthorhombic, $Pca2_1$, $a = 21{\cdot}371\ (5)$, $b = 15{\cdot}655\ (2)$, $c = 18{\cdot}242\ (4)$ Å, $V = 6103$ Å^3, $Z = 4$, $d_{calc} = 1{\cdot}537$, $d_{exp} = 1{\cdot}54$ g cm^{-3}, μ(Mo $K\alpha$) = 8·8 cm^{-1}. The structure was solved from a Patterson synthesis and refined to a final R of 0·051 for 3830 reflections. The complex is derived from $Ru_3(CO)_{12}$ by substitution of four equatorial carbonyl ligands by the P atoms of two edge-bridging bis(diphenylphosphino)-methane ligands. Metal–metal bonds within the metal framework are 2·826 (2), 2·833 (2) and 2·858 (2) Å.

Introduction

Several tridentate phosphine ligands have recently been designed to prevent cluster degradation under hard reaction conditions (de Boer, van Doorn & Masters, 1978; Arduini, Bahsoun, Osborn & Voelker, 1980). Such ligands were also found efficient in a template synthesis of clusters (Osborn & Stanley, 1980). However, the reaction of these tripod ligands with $Ru_3(CO)_{12}$ gave poor yields of the capped products; This was attributed to the fact that the capped product is derived from axial substitution, whereas equatorial substitutions are generally easier with phosphines (Arduini *et al.*, 1980).

We recently suggested an alternative way to retain the cluster frame by using an edge-bridging ligand such as bis(diphenylphosphino)methane (dppm): reaction of this ligand with $Ru_3(CO)_{12}$ gave good yields of the new complex $Ru_3(CO)_8(dppm)_2$ (Lavigne & Bonnet, 1981). We now report the X ray structural determination of this species.

Experimental

Suitable crystals for the complex were grown from a $\frac{1}{3}$ acetone/ethanol mixture as red, lozenge-based parallelepiped platelets: $Ru_3(CO)_8(dppm)_2.n(CH_3)_2CO$ ($n \simeq 2$).

Although the presence of acetone molecules in the lattice was unambiguously determined by mass spectrometry and ^{1}H NMR spectroscopy, the precise number of such molecules could not be accurately determined from analytical results.

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