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Structure of μ-*trans*-1,1,2,3,4,4-Hexacyanobutenediido-bis[(carbonyl)bis(triphenylphosphine)rhodium], a Product of the Reaction between the Radical Anion Tetracyanoethylenide and $RhCl(CO)[P(C_6H_5)_3]_2$

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The crystal and molecular structure of μ-*trans*-hexacyanobutenediido-bis[(carbonyl)bis(triphenylphosphine)rhodium], $[Rh(CO)[P(C_6H_5)_3]_2]_2$(HCBD) [HCBD = *trans*-1,1,2,3,4,4-hexacyanobutenediide] has been determined from three-dimensional X-ray diffraction data. The compound crystallizes with two molecules in space group C_i^1-$P\bar{1}$ of the triclinic system in a cell of dimensions $a = 16.483$ (2), $b = 18.580$ (3), $c = 12.813$ (2) Å; $\alpha = 105.02$ (1), $\beta = 103.83$ (1), $\gamma = 82.26$ (1)°. The structure was refined by least-squares techniques to a conventional R index on F of 0.058 based on 7028 reflections above background. The structure determination shows that the HCBD dianion is attached to the Rh atoms through Rh–N bonds forming a binuclear keteniminato complex. The geometry about the rhodium atoms is square planar with the phosphorus atoms trans to each other. Comparisons are made between the structural parameters of the bridging ligand *trans*-HCBD and those of K_2(*cis*-HCBD).

Introduction

By the reaction of *trans*-$RhCl(CO)[P(C_6H_5)_3]_2$ with the radical anion tetracyanoethylenide the binuclear complex $[Rh(CO)[P(C_6H_5)_3]_2]_2$(HCBD) [HCBD = *trans*-1,1,2,3,4,4-hexacyanobutenediide] is formed.[1] Infrared spectra are consistent with the *trans*-HCBD unit being coordinated by the nitrile nitrogen atoms forming a bridging keteniminato linkage.[1] We have undertaken the present study of this novel product in order to confirm this interpretation of the infrared data and to obtain metrical details on the *trans*-HCBD bridge. Although the existence of the general class of N-bound transition metal–keteniminato complexes has been established,[2-6] only a limited number of structures of this class are known[6,7] and none contains a bridging keteniminato group. In a previously reported structure of K_2(*cis*-HCBD), $K_2[(CN)_2CC(CN)C(CN)C(CN)_2]$,[8] it was found that the geometry of the dianion implies a high degree of delocalization of charge. By comparison of the present structure with the salt K_2(HCBD) we hoped to obtain information about the influence of the metal on the coordinated anion.

Experimental Section

Collection and Reduction of X-Ray Data. The binuclear complex $[Rh(CO)[P(C_6H_5)_3]_2]_2$(HCBD) was prepared from $RhCl(CO)[P(C_6H_5)_3]_2$ and potassium tetracyanoethylenide, as previously described.[1] The compound was recrystallized from CH_2Cl_2–CH_3CN. The air-stable crystals were orange-red with a wedge-shaped habit.

Weissenberg and precession photographs using Cu Kα radiation revealed no lattice symmetry nor did a cell reduction suggest any hidden symmetry. The crystal was thus assigned to the triclinic system and the subsequent successful refinement of the structure showed the space group to be C_i^1-$P\bar{1}$. A crystal of dimensions 0.15 × 0.5 × 0.5 mm was transferred to a Picker FACS-I automatic diffractometer. Lattice parameters were obtained as previously described[9] by hand centering of 14 reflections in the range $40° \leqslant 2\theta \leqslant 50°$. The constants of the reduced cell at 22° are $a = 16.483$ (2), $b = 18.580$ (3), $c = 12.813$ (2) Å; $\alpha = 105.02$ (1), $\beta = 103.83$ (1), $\gamma = 82.26$ (1)° (Cu Kα radiation, λ 1.540562 Å). A density of 1.37 g cm^{-3} calculated for 2 formula units of $[Rh(CO)[P(C_6H_5)_3]_2]_2$(HCBD) per unit cell agrees well with that of 1.39 (2) g cm^{-3} measured by flotation of the material in pentane–CCl_4.

Data were collected in shells of 2θ by the θ–2θ scan method using Cu Kα radiation prefiltered with Ni foil. The scan range in 2θ was from $-0.85°$ below the Kα_1 peak to $+0.75°$ above the Kα_2 peak. The takeoff angle was 3.3°, and the receiving aperture, 4.0 mm wide and 5.0 mm high, was positioned 32 cm from the crystal. The pulse height analyzer was set to admit about 85% of the Cu Kα peak. Initially stationary-crystal, stationary-counter background counts were taken for 10 sec at each end of the 2θ scan range. Beyond 2θ of 65° this was increased to 20 sec. A scan rate of 2°/min was used. Attenuators were automatically inserted if the intensity of the diffracted beam exceeded approximately 7000 counts/sec during a scan. The attenuators were of Ni foil and gave attenuator factors of about 2.3. Data were collected in the range $3.0° < 2\theta \leqslant 100°$. Beyond this point few reflections were above background. During the course of data collection six standard reflections from diverse regions of reciprocal space were measured every 100 reflections, and the intensities of these reflections remained constant within counting statistics. The data were processed as previously described[9,10] using a value of 0.04 for p. Of the 7983 reflections measured, 7441 obey the condition $F_o^2 > 3\sigma(F_o^2)$, and of these, 7028 are unique and were used in subsequent refinement.

Solution and Refinement of the Structure. A sharpened, origin-removed three-dimensional Patterson map was calculated[11] and interpreted to give the coordinates of the two rhodium and the four phosphorus atoms. The remaining nonhydrogen atoms were readily located by the usual combination of Fourier and least-squares techniques. Throughout the refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and where the weight, w, is $4F_o^2/\sigma^2(F_o^2)$. The agreement indices R_1 and R_2 are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. The atomic scattering factors for all nonhydrogen atoms were taken from

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(11) In addition to various local programs for the CDC6400, local modifications of the following programs were employed: Dewar's FAME program, Zalkin's FORDAP Fourier program, the AGNOST absorption program, Johnson's ORTEP II thermal ellipsoid plotting program, Busing's and Levy's ORFFE error function program. Our least-squares program, NUCLS, in its nongroup form, closely resembles the Busing and Levy ORFLS program. Final calculations were carried out by remote hook-up with the CDC7600 at Lawrence Berkeley Laboratories. The programs used of Professor K. N. Raymond were minor modifications of the above.

Table I. Positional, Thermal, and Group Parameters for $[Rh(CO)[P(C_6H_5)_3]_2]_2(HCBD)$

Atom	x	y	z	$10^4\beta_{11}$[a]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Rh(1)	0.25393 (3)[b]	−0.01121 (3)	0.25463 (4)	22.5 (3)	19.3 (2)	43.9 (5)	0.6 (2)	9.5 (2)	7.7 (2)
Rh(2)	0.20602 (3)	−0.56372 (3)	0.10162 (4)	33.4 (3)	21.8 (2)	44.9 (5)	−6.8 (2)	14.2 (3)	3.1 (2)
P(1)	0.3526 (1)	−0.00977 (9)	0.1516 (1)	23.7 (7)	19.5 (6)	43.2 (13)	−2.2 (5)	7.6 (8)	6.4 (7)
P(2)	0.1516 (1)	−0.0089 (1)	0.3536 (1)	23.3 (7)	24.0 (6)	46.8 (13)	−1.9 (5)	10.1 (8)	3.0 (7)
P(3)	0.3212 (1)	−0.5437 (1)	0.0398 (1)	32.1 (8)	22.5 (6)	49.7 (14)	−4.5 (6)	13.0 (8)	7.1 (8)
P(4)	0.1140 (1)	−0.5917 (1)	0.1945 (1)	30.6 (8)	22.8 (6)	53.0 (14)	−3.2 (6)	13.5 (8)	6.5 (8)
O(11)	0.1567 (4)	0.1193 (3)	0.1815 (5)	60 (3)	42 (2)	123 (6)	21 (2)	27 (3)	40 (3)
O(12)	0.1659 (3)	−0.6955 (3)	−0.0814 (4)	50 (3)	38 (2)	74 (4)	−8 (2)	18 (3)	−13 (3)
N(5)	0.3231 (3)	−0.0989 (3)	0.3101 (5)	27 (3)	26 (2)	58 (5)	1 (2)	16 (3)	16 (3)
N(6)	0.5748 (5)	−0.1722 (4)	0.4708 (6)	41 (4)	46 (3)	130 (8)	3 (3)	5 (4)	33 (4)
N(7)	0.4695 (6)	−0.2919 (5)	0.6027 (7)	106 (6)	73 (4)	114 (8)	−39 (4)	−36 (6)	54 (5)
N(8)	0.2751 (5)	−0.2782 (4)	0.1572 (6)	80 (5)	46 (3)	71 (6)	−24 (3)	−9 (4)	17 (4)
N(9)	0.2263 (4)	−0.4654 (4)	0.2180 (5)	56 (3)	28 (2)	78 (6)	−19 (2)	34 (4)	−2 (3)
N(10)	0.2829 (6)	−0.3637 (5)	0.5689 (6)	142 (8)	62 (4)	91 (7)	−22 (4)	35 (6)	35 (4)
C(1)	0.4193 (4)	−0.1950 (4)	0.4012 (5)	39 (4)	20 (2)	50 (5)	2 (2)	7 (4)	2 (3)
C(2)	0.3901 (4)	−0.2594 (4)	0.4219 (5)	36 (3)	22 (2)	56 (6)	−3 (2)	9 (4)	7 (3)
C(3)	0.3295 (4)	−0.3019 (4)	0.3515 (5)	39 (3)	21 (2)	50 (6)	−1 (3)	16 (4)	0 (3)
C(4)	0.2917 (5)	−0.3599 (4)	0.3753 (5)	50 (4)	22 (3)	50 (6)	−5 (3)	16 (4)	−1 (3)
C(5)	0.3661 (4)	−0.1429 (4)	0.3506 (5)	32 (3)	21 (3)	49 (5)	−5 (3)	13 (4)	4 (3)
C(6)	0.5052 (5)	−0.1810 (4)	0.4380 (6)	32 (4)	22 (3)	79 (7)	5 (3)	7 (4)	18 (3)
C(7)	0.4327 (6)	−0.2791 (4)	0.5228 (6)	67 (5)	34 (3)	57 (6)	−16 (3)	−15 (5)	22 (4)
C(8)	0.2981 (5)	−0.2875 (4)	0.2444 (6)	41 (4)	29 (3)	53 (7)	−12 (3)	1 (4)	12 (3)
C(9)	0.2555 (5)	−0.4176 (4)	0.2887 (7)	42 (4)	27 (3)	84 (7)	−3 (3)	33 (4)	10 (4)
C(10)	0.2885 (5)	−0.3616 (5)	0.4823 (6)	74 (5)	35 (3)	59 (7)	−11 (3)	18 (5)	14 (4)
C(11)	0.1948 (4)	0.0682 (4)	0.2075 (6)	37 (3)	26 (3)	55 (6)	6 (3)	17 (4)	15 (3)
C(12)	0.1833 (4)	−0.6449 (4)	−0.0081 (6)	31 (3)	28 (3)	68 (6)	−1 (2)	20 (4)	5 (4)

Group[c]	x_c	y_c	z_c	δ	ϵ	η
11	0.3463 (2)	0.1452 (2)	0.0812 (3)	−1.356 (3)	−2.588 (3)	−2.849 (3)
12	0.5429 (2)	−0.0317 (2)	0.2809 (2)	−2.408 (7)	1.984 (3)	2.268 (7)
13	0.3284 (2)	−0.1391 (2)	−0.0728 (2)	2.604 (4)	−2.564 (2)	−1.754 (4)
21	0.1699 (2)	0.1222 (2)	0.5762 (3)	2.650 (4)	−2.570 (3)	1.389 (4)
22	−0.0329 (2)	0.0251 (2)	0.2132 (3)	0.495 (6)	−2.101 (3)	−2.340 (6)
23	0.1425 (2)	−0.1570 (2)	0.4351 (3)	1.713 (3)	2.674 (3)	2.753 (4)
31	0.2714 (2)	−0.4359 (2)	−0.1278 (3)	−1.632 (3)	2.657 (3)	−2.367 (3)
32	0.4579 (2)	−0.4806 (2)	0.2572 (3)	−0.116 (3)	2.761 (3)	0.877 (3)
33	0.4208 (2)	−0.6827 (2)	−0.0987 (3)	1.580 (4)	2.505 (3)	−2.205 (4)
41	−0.0168 (2)	−0.4624 (2)	0.2908 (3)	2.865 (4)	−2.530 (4)	0.655 (4)
42	−0.0134 (2)	−0.7171 (2)	0.0621 (3)	−2.805 (5)	−2.358 (4)	−0.580 (5)
43	0.2425 (2)	−0.6413 (2)	0.3988 (3)	−2.864 (4)	2.405 (3)	2.148 (4)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant figures. [c] x_c, y_c, z_c are the fractional coordinates of the ring center; δ, ϵ, η (in radians) have been defined by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965). The groups 11–43 are phenyl rings.

a new tabulation,[12] while those for H were from the calculations of Stewart, *et al.*[13] The effects of anomalous dispersion were included in F_c.[14] An absorption correction was made. The crystal for data collection was measured and its faces were identified by optical means. The eight crystal faces were (010), ($\bar{1}\bar{1}0$), (001), (100), ($0\bar{1}\bar{1}$), ($\bar{1}00$), ($11\bar{1}$), and (1,14,3). The last face was used as an approximation to a broken face. Based on a calculated linear absorption coefficient of 49.55 cm^{-1}, *the transmission factors were found to vary between* 0.20 and 0.59.

The trial structure was refined by a least-squares procedure in which the phenyl rings were constrained to D_{6h} symmetry and treated as rigid groups (C–C = 1.390 Å) with each C atom being assigned an isotropic thermal parameter. The initial isotropic refinement, based on all 7028 data, converged to values of R_1 and R_2 of 0.077 and 0.116, respectively. Most of the 60 H atoms on the phenyl rings could be located on a subsequent difference Fourier map. This is good evidence that the correct space group $P\bar{1}$ has been used. The positions of the 60 phenyl hydrogen atoms were idealized on the assumption that C–H = 0.95 Å. Each hydrogen atom was assigned an isotropic temperature factor 1 Å^2 larger than that of the carbon atom to which it is attached. The contributions of the hydrogen atoms were included in subsequent structure factor calculations. Two cycles of full-matrix refinement (group atoms isotropic, nongroup atoms anisotropic) reduced the values of R_1 and R_2 to 0.058 and 0.086, respectively, for the 7028 observations and 379 variables. The final atomic parameters and their standard deviations, as estimated from the inverse matrix, are listed in Table I. The derived positions for the ring carbon atoms as well as the idealized positions of the phenyl hydrogen atoms are given in Table II.

An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices indicated no unusual trends and provided no evidence for extinction effects. The error in an observation of unit weight is 3.38 e. The maximum density on a final difference Fourier map is 0.89 e/Å^3, approximately 20% of the height of a carbon atom in this structure. The first ten peaks on this map are associated with the Rh atoms or with the phenyl rings. There is thus no evidence for solvent molecules. Association of residual density with phenyl rings is typical for this type of group refinement. Relaxation of the rigid-group approximation would undoubtedly improve the R index, but this is not really feasible because of the impossibly large number of variables that are involved. The final values of the structure amplitudes are tabulated as $10|F_o|$ and $10|F_c|$ (in electrons) for those reflections used in the refinement.[15]

Description and Discussion of the Structure

Figure 1 presents a drawing of the inner coordination sphere of the binuclear rhodium complex $[Rh(CO)[P(C_6H_5)_3]_2]_2(HCBD)$ and indicates the numbering scheme. The vibrational thermal ellipsoids at the 50% probability level are also displayed in this figure and the root-mean-square amplitudes of variation are presented in Table III.[15] These

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(12) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. 4, Kynoch Press, Birmingham, England, 1974, Table 2.2 A.

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(15) See paragraph at end of paper regarding supplementary material.

Table II. Derived Parameters for Ring Atoms

	Carbon				Hydrogen			
Ring atom[a]	x	y	z	B, Å^2	x	y	z	B, Å^2
111	0.3513 (3)[b]	0.0770 (2)	0.1103 (4)	2.4 (1)				
112	0.2858 (2)	0.0945 (2)	0.0266 (4)	3.9 (1)	0.245[c]	0.060	−0.010	5.3
113	0.2808 (3)	0.1627 (3)	−0.0025 (4)	4.7 (2)	0.236	0.175	−0.059	5.8
114	0.3414 (3)	0.2134 (2)	0.0521 (4)	5.3 (2)	0.338	0.260	0.032	6.4
115	0.4069 (3)	0.1959 (2)	0.1358 (4)	5.7 (2)	0.448	0.230	0.173	6.7
116	0.4118 (2)	0.1278 (3)	0.1648 (3)	4.2 (2)	0.456	0.116	0.222	5.6
121	0.4599 (2)	−0.0252 (2)	0.2229 (3)	2.4 (1)				
122	0.4810 (2)	0.0084 (2)	0.3357 (3)	3.6 (1)	0.439	0.036	0.373	4.1
123	0.5640 (3)	0.0020 (3)	0.3938 (3)	4.4 (2)	0.578	0.025	0.470	5.3
124	0.6258 (2)	−0.0381 (3)	0.3390 (4)	4.7 (2)	0.682	−0.042	0.378	5.5
125	0.6047 (2)	−0.0717 (3)	0.2261 (4)	4.4 (2)	0.647	−0.099	0.189	5.8
126	0.5218 (3)	−0.0653 (3)	0.1681 (3)	3.4 (1)	0.507	−0.088	0.091	4.4
131	0.3387 (3)	−0.0815 (2)	0.0231 (3)	2.4 (1)				
132	0.3661 (3)	−0.0752 (2)	−0.0691 (4)	3.8 (1)	0.392	−0.032	−0.066	4.5
133	0.3557 (3)	−0.1328 (3)	−0.1650 (3)	5.1 (2)	0.374	−0.129	−0.228	6.2
134	0.3180 (3)	−0.1967 (2)	−0.1687 (3)	5.2 (2)	0.311	−0.236	−0.234	6.1
135	0.2907 (3)	−0.2030 (2)	−0.0765 (4)	4.5 (2)	0.265	−0.246	−0.079	5.7
136	0.3010 (3)	−0.1454 (2)	0.0194 (3)	3.3 (1)	0.282	−0.150	0.082	4.4
211	0.1618 (3)	0.0644 (2)	0.4806 (3)	2.9 (1)				
212	0.1960 (3)	0.1301 (3)	0.4840 (3)	4.4 (2)	0.214	0.135	0.421	5.3
213	0.2040 (3)	0.1879 (2)	0.5796 (4)	6.0 (2)	0.227	0.233	0.582	6.7
214	0.1780 (4)	0.1800 (2)	0.6719 (3)	5.7 (2)	0.183	0.219	0.737	7.0
215	0.1439 (3)	0.1144 (3)	0.6685 (3)	5.0 (2)	0.126	0.109	0.731	6.0
216	0.1358 (3)	0.0566 (2)	0.5728 (4)	3.9 (1)	0.113	0.012	0.571	4.8
221	0.0465 (2)	0.0108 (3)	0.2766 (3)	2.9 (1)				
222	0.0250 (3)	−0.0274 (3)	0.1657 (4)	4.9 (2)	0.064	−0.063	0.133	6.7
223	−0.0544 (3)	−0.0130 (3)	0.1024 (3)	5.9 (2)	−0.069	−0.039	0.027	6.6
224	−0.1123 (2)	0.0394 (3)	0.1499 (4)	5.3 (2)	−0.166	0.049	0.107	6.2
225	−0.0908 (3)	0.0776 (3)	0.2608 (4)	5.2 (2)	−0.130	0.113	0.293	6.3
226	−0.0114 (3)	0.0633 (3)	0.3241 (3)	3.8 (1)	0.003	0.089	0.400	4.7
231	0.1458 (3)	−0.0933 (2)	0.3979 (4)	3.1 (1)				
232	0.2112 (2)	−0.1137 (3)	0.4794 (4)	4.0 (2)	0.258	−0.084	0.509	5.1
233	0.2079 (3)	−0.1773 (3)	0.5166 (4)	5.3 (2)	0.252	−0.191	0.572	6.6
234	0.1393 (4)	−0.2206 (3)	0.4724 (5)	6.6 (2)	0.137	−0.264	0.498	7.2
235	0.0739 (3)	−0.2003 (3)	0.3909 (5)	7.4 (2)	0.027	−0.230	0.361	8.5
236	0.0772 (3)	−0.1366 (3)	0.3536 (4)	5.6 (2)	0.033	−0.123	0.298	6.8
311	0.2960 (3)	−0.4802 (2)	−0.0510 (3)	2.9 (1)				
312	0.2167 (2)	−0.4418 (3)	−0.0627 (4)	3.9 (1)	0.180	−0.446	−0.018	4.6
313	0.1921 (2)	−0.3974 (3)	−0.1395 (4)	5.0 (2)	0.138	−0.371	−0.147	5.5
314	0.2467 (3)	−0.3915 (3)	−0.2046 (4)	4.4 (2)	0.230	−0.361	−0.257	5.4
315	0.3260 (3)	−0.4300 (3)	−0.1929 (4)	4.4 (2)	0.363	−0.426	−0.237	5.2
316	0.3507 (2)	−0.4744 (3)	−0.1162 (4)	4.0 (1)	0.405	−0.501	−0.108	5.4
321	0.3994 (2)	−0.5066 (2)	0.1602 (3)	2.9 (1)				
322	0.4205 (3)	−0.5466 (2)	0.2427 (4)	4.3 (2)	0.395	−0.592	0.233	5.6
323	0.4790 (3)	−0.5205 (3)	0.3397 (3)	5.0 (2)	0.493	−0.548	0.396	6.3
324	0.5164 (3)	−0.4545 (3)	0.3543 (3)	5.2 (2)	0.556	−0.437	0.420	6.4
325	0.4954 (3)	−0.4145 (2)	0.2717 (4)	4.6 (2)	0.521	−0.370	0.282	5.7
326	0.4369 (3)	−0.4406 (2)	0.1747 (3)	3.5 (1)	0.423	−0.413	0.119	4.3
331	0.3784 (3)	−0.6225 (2)	−0.0375 (3)	3.0 (1)				
332	0.4606 (3)	−0.6459 (3)	0.0072 (3)	4.0 (2)	0.488	−0.621	0.079	5.1
333	0.5030 (2)	−0.7061 (3)	−0.0540 (4)	5.0 (2)	0.559	−0.722	−0.024	6.1
334	0.4633 (3)	−0.7429 (2)	−0.1599 (4)	5.2 (2)	0.492	−0.784	−0.201	6.0
335	0.3811 (3)	−0.7194 (3)	−0.2046 (3)	4.6 (2)	0.354	−0.744	−0.277	5.6
336	0.3387 (2)	−0.6592 (3)	−0.1434 (3)	3.9 (2)	0.283	−0.643	−0.174	4.9
411	0.0416 (3)	−0.5181 (3)	0.2510 (4)	3.4 (1)				
412	0.0294 (3)	−0.4502 (3)	0.2196 (4)	5.3 (2)	0.061	−0.442	0.171	6.0
413	−0.0291 (4)	−0.3945 (3)	0.2594 (6)	7.6 (2)	−0.037	−0.348	0.238	7.8
414	−0.0753 (4)	−0.4067 (3)	0.3307 (6)	8.5 (3)	−0.115	−0.369	0.358	8.8
415	−0.0630 (4)	−0.4747 (4)	0.3621 (5)	7.7 (2)	−0.094	−0.483	0.411	7.9
416	−0.0046 (4)	−0.5304 (3)	0.3223 (5)	5.3 (2)	0.004	−0.577	0.344	6.4
421	0.0445 (3)	−0.6650 (3)	0.1223 (4)	3.8 (1)				
422	−0.0022 (4)	−0.6586 (3)	0.0182 (4)	5.0 (2)	0.005	−0.619	−0.012	5.6
423	−0.0601 (4)	−0.7107 (4)	−0.0419 (4)	7.2 (2)	−0.092	−0.706	−0.113	8.6
424	−0.0713 (4)	−0.7692 (3)	0.0020 (5)	8.0 (3)	−0.111	−0.805	−0.039	8.1
425	−0.0246 (4)	−0.7756 (3)	0.1061 (5)	7.7 (3)	−0.032	−0.815	0.136	8.6
426	0.0333 (4)	−0.7235 (3)	0.1662 (4)	6.3 (2)	0.065	−0.728	0.237	6.9
431	0.1831 (3)	−0.6203 (3)	0.3120 (3)	3.1 (1)				
432	0.1974 (3)	−0.5716 (2)	0.4168 (4)	4.6 (2)	0.167	−0.524	0.429	6.0
433	0.2569 (4)	−0.5927 (3)	0.5036 (3)	6.1 (2)	0.267	−0.560	0.575	7.6
434	0.3020 (3)	−0.6624 (3)	0.4857 (4)	6.2 (2)	0.342	−0.677	0.545	6.7
435	0.2876 (3)	−0.7111 (2)	0.3809 (5)	6.3 (2)	0.318	−0.758	0.369	8.0
436	0.2282 (3)	−0.6900 (2)	0.2941 (3)	4.8 (2)	0.216	−0.724	0.223	5.8

[a] The ring atoms are numbered sequentially with 111, 121, 131 attached to P(1), 211, 221, 231 attached to P(2), and so on. [b] The estimated standard deviations are derived from those of the group parameters. [c] The hydrogen atom 112 is attached to carbon atom 112, hydrogen 113 is attached to carbon 113, etc.

Table IV. Bond Distances (Å) and Angles (deg) in $[Rh(CO)[P(C_6H_5)_3]_2]_2(HCBD)$

Distances					
Rh(1)-P(1)	2.333 (2)	2.329 (6)[a]	C(1)-C(5)	1.40 (1)	1.413 (16)
Rh(1)-P(2)	2.330 (2)		C(1)-C(6)	1.42 (1)	
Rh(2)-P(3)	2.331 (2)		C(2)-C(7)	1.43 (1)	
Rh(2)-P(4)	2.320 (2)		C(3)-C(8)	1.43 (1)	
Rh(1)-C(11)	1.812 (8)	1.800 (12)	C(4)-C(9)	1.41 (1)	
Rh(2)-C(12)	1.788 (8)		C(4)-C(10)	1.39 (1)	
Rh(1)-N(5)	2.043 (6)	2.045 (7)	P(1)-C(111)	1.820 (5)	1.815 (7)
Rh(2)-N(9)	2.046 (7)		P(1)-C(121)	1.810 (3)	
C(11)-O(11)	1.144 (8)	1.150 (8)	P(1)-C(131)	1.818 (3)	
C(12)-O(12)	1.155 (8)		P(2)-C(211)	1.820 (4)	
N(5)-C(5)	1.152 (8)	1.153 (9)	P(2)-C(221)	1.820 (4)	
N(9)-C(9)	1.155 (9)		P(2)-C(231)	1.822 (5)	
N(6)-C(6)	1.142 (9)	1.14 (1)	P(3)-C(311)	1.808 (5)	
N(7)-C(7)	1.125 (9)		P(3)-C(321)	1.804 (4)	
N(8)-C(8)	1.141 (9)		P(3)-C(331)	1.826 (4)	
N(10)-C(10)	1.147 (9)		P(4)-C(411)	1.810 (5)	
C(1)-C(2)	1.455 (9)	1.449 (9)	P(4)-C(421)	1.813 (5)	
C(3)-C(4)	1.444 (9)		P(4)-C(431)	1.811 (5)	
C(2)-C(3)	1.359 (9)				

Angles					
P(1)-Rh(1)-P(2)	177.50 (6)		C(2)-C(3)-C(4)	126.2 (6)	
P(3)-Rh(2)-P(4)	167.19 (7)		C(8)-C(3)-C(4)	116.1 (6)	
N(5)-Rh(1)-C(11)	178.4 (3)		C(3)-C(4)-C(10)	122.8 (6)	
N(9)-Rh(2)-C(12)	175.1 (3)		C(3)-C(4)-C(9)	120.0 (6)	
P(1)-Rh(1)-N(5)	89.5 (1)		C(9)-C(4)-C(10)	117.1 (7)	
P(1)-Rh(1)-C(11)	89.9 (2)		C(111)-P(1)-C(121)	103.9 (2)	105 (2)
P(2)-Rh(1)-N(5)	93.0 (1)		C(111)-P(1)-C(131)	104.9 (2)	
P(2)-Rh(1)-C(11)	87.7 (2)		C(121)-P(1)-C(131)	105.8 (2)	
P(3)-Rh(2)-N(9)	87.2 (2)		C(211)-P(2)-C(221)	104.0 (2)	
P(3)-Rh(2)-C(12)	92.4 (2)		C(211)-P(2)-C(231)	104.1 (2)	
P(4)-Rh(2)-N(9)	89.9 (2)		C(221)-P(2)-C(231)	104.8 (2)	
P(4)-Rh(2)-C(12)	91.6 (2)		C(311)-P(3)-C(321)	109.8 (2)	
Rh(1)-C(11)-O(11)	177.4 (6)		C(311)-P(3)-C(331)	102.4 (2)	
Rh(2)-C(12)-O(12)	177.0 (6)		C(321)-P(3)-C(331)	103.5 (2)	
Rh(1)-N(5)-C(5)	172.9 (5)		C(411)-P(4)-C(421)	101.2 (2)	
Rh(2)-N(9)-C(9)	164.7 (6)		C(411)-P(4)-C(431)	106.0 (2)	
C(1)-C(5)-N(5)	178.7 (7)	178 (1)	C(421)-P(4)-C(431)	108.3 (2)	
C(1)-C(6)-N(6)	176.7 (8)		Rh(1)-P(1)-C(111)	115.3 (2)	114 (5)
C(2)-C(7)-N(7)	176.1 (9)		Rh(1)-P(1)-C(121)	113.9 (2)	
C(3)-C(8)-N(8)	177.3 (8)		Rh(1)-P(1)-C(131)	112.1 (2)	
C(4)-C(9)-N(9)	179.3 (8)		Rh(1)-P(2)-C(211)	113.2 (2)	
C(4)-C(10)-N(10)	177.6 (10)		Rh(1)-P(2)-C(221)	112.4 (2)	
C(5)-C(1)-C(6)	117.0 (6)		Rh(1)-P(2)-C(231)	117.2 (2)	
C(6)-C(1)-C(2)	119.6 (6)		Rh(2)-P(3)-C(311)	113.1 (2)	
C(5)-C(1)-C(2)	123.3 (6)		Rh(2)-P(3)-C(321)	107.4 (2)	
C(1)-C(2)-C(7)	115.2 (6)		Rh(2)-P(3)-C(331)	120.0 (2)	
C(1)-C(2)-C(3)	125.0 (6)		Rh(2)-P(4)-C(411)	119.1 (2)	
C(7)-C(2)-C(3)	119.8 (6)		Rh(2)-P(4)-C(421)	118.2 (2)	
C(2)-C(3)-C(8)	117.8 (6)		Rh(2)-P(4)-C(431)	103.2 (2)	

[a] These are average quantities. The estimated standard deviation of a single observation is the larger of that estimated from the inverse matrix or that from the agreement among values averaged.

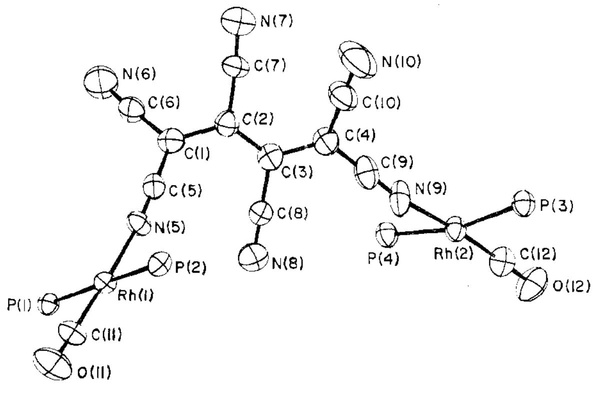

Figure 1. The inner coordination sphere and numbering scheme for $[Rh(CO)[P(C_6H_5)_3]_2]_2(HCBD)$ showing the vibrational ellipsoids at their 50% probability levels.

vibrational data appear to be reasonable; as expected, the greatest thermal motion is shown by the uncoordinated cyano nitrogen atoms. From the positional parameters in Table I and the correlation matrix the relevant interatomic distances and bond angles and their standard deviations were calculated and are presented in Table IV.

The crystal structure consists of individual monomeric molecules, each of which is one asymmetric unit. The stereodrawing of two complete molecules in a unit cell (Figure 2) represents a view along the x axis. All intermolecular contacts are normal, the shortest distance being 2.42 Å between H(213) and H(335) in adjacent molecules. The intermolecular distance between O(12) and H(214) of 2.51 Å is close to the sum of the van der Waals radii.

As was predicted on the basis of ir spectra, the simple Huckel MO calculations, and steric considerations concerning the uncoordinated dianion *trans*-HCBD,[1,8] in the present structure the two rhodium atoms are coordinated to the nitrogen atoms N(5) and N(9) to form a keteniminato linkage. Figure 3 represents a stereodrawing of one complete molecule. The view direction is the same as in Figure 1. Hydrogen atoms and atom labels have been omitted for the sake of clarity. The Rh-Rh distance is 10.043 (2) Å.

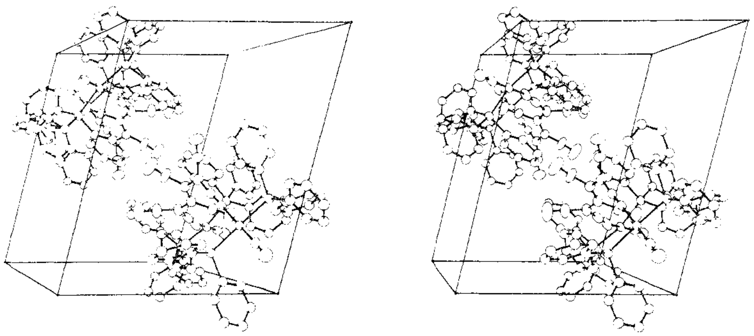

Figure 2. A stereoview of the unit cell of $[Rh(CO)[P(C_6H_5)_3]_2]_2(HCBD)$ along the x axis.

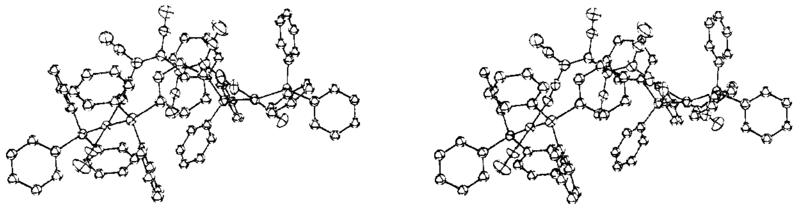

Figure 3. A stereoview of the $[Rh(CO)[P(C_6H_5)_3]_2]_2(HCBD)$ molecule, with hydrogen atoms omitted for the sake of clarity. The view is the same as for Figure 1.

Table V. Weighted Least-Squares Planes[a]

Plane Equation: $Ax + By + Cz - D = 0$ with x, y, z in Triclinic Coordinates

Plane	A	B	C	D
1	6.883	9.596	6.802	3.372
2	6.883	9.590	6.805	3.367
3	7.853	−11.943	6.846	9.077
4	8.029	−10.939	7.355	8.799
5	5.205	−5.461	−10.683	−1.054
6	12.169	−7.268	−6.345	3.970
7	11.777	−9.386	−4.613	5.085
8	13.347	−8.666	0.228	7.096
9	12.089	−8.498	−5.234	4.669
10	12.030	−8.475	−5.339	4.674

Deviations from Planes, Å

Atom	1	2	3	4
Rh(1)	0.0008 (5)			
P(1)	−0.007 (2)	−0.002 (2)		
P(2)	−0.008 (2)	−0.002 (2)		
N(5)	0.013 (5)	0.020 (5)		
C(11)	0.036 (7)	0.041 (7)		
Rh(2)			−0.0313 (5)	
P(3)			0.212 (2)	0.021 (2)
P(4)			0.216 (2)	0.019 (2)
N(9)			−0.250 (7)	−0.288 (7)
C(12)			0.009 (7)	−0.332 (7)

Atom	5	6	7	8	9	10
C(1)	0.015 (6)	0.005 (7)			−0.043 (7)	−0.120 (7)
C(2)	−0.006 (6)	−0.014 (7)	−0.003 (7)		0.043 (7)	−0.036 (7)
C(3)		0.005 (6)	0.008 (6)	−0.001 (7)	0.041 (6)	−0.028 (6)
C(4)			−0.003 (7)	0.003 (7)	−0.048 (7)	−0.118 (7)
C(5)	−0.005 (6)					
C(6)	−0.007 (7)					
C(7)		0.008 (9)				0.106 (9)
C(8)			−0.003 (7)			0.044 (7)
C(9)				−0.001 (7)		
C(10)				−0.002 (9)		
N(7)						0.230 (10)
N(8)						0.154 (8)

[a] By the method described by W. C. Hamilton, *Acta Crystallogr.*, **14**, 185 (1961).

Both rhodium atoms have their expected trans-phosphorus, square-planar coordination geometry formed by P(1), P(2), C(11), N(5) for Rh(1) and P(3), P(4), C(12), N(9) for Rh(2). Whereas Rh(1) lies nearly exactly in the plane of its ligands, the geometry about Rh(2) is severely distorted from a square-planar arrangement. The reasons for this distortion are not understood. Various weighted least-squares planes through the molecule are presented in Table V. These planes provide a measure of the nonplanarity of the coordination sphere around Rh(2). On the other hand those bonded distances expected to be chemically equivalent are approximately equal. The four independent Rh-P distances are in the expected range, the average length being 2.329 (6) Å. The two Rh-C bond lengths Rh(1)-C(11) and Rh(2)-C(12) are 1.812 (8) and 1.788 (8) Å, respectively. Similar rhodium-carbon bond distances are observed in other four-coordinated rhodium(I)-carbonyl complexes, such as the dimer *trans*-[RhCl(CO)-$[CH_2[As(C_6H_5)_2]_2]]_2$, Rh-C = 1.797 (10) Å,[16] and the dicarbonyl $Rh(CO)_2[(CH_3CO)_2CH]$, Rh-C = 1.76 (2) Å.[17] The mean value of the C-O bond is 1.150 (8) Å, slightly longer than the C-O bond distance of 1.10 (1) Å in the comparable Rh(I) complex *trans*-$[RhCl(CO)[CH_2[As(C_6H_5)_2]_2]]_2$.[16] This lengthening may indicate a stronger π-donor ability of a keteniminato-type ligand compared with a chlorine atom. On the basis of ir intensity measurements it was predicted that the keteniminato group is a good π donor.[18] The average value of the rhodium-nitrogen bonds Rh(1)-N(5) and Rh(2)-N(9) is 2.044 (7) Å. There appear to be no other Rh(I)-N bonds in four-coordinate complexes for comparison. The average C≡N and C-CN bond distances of the coordinated cyano groups CN(5) and CN(9) being 1.153 (9) and 1.41 (1) Å, respectively, are not significantly different from the CN and C-CN bond lengths of the uncoordinated cyano groups [mean value 1.14 (1) and 1.41 (2) Å, respectively] in the present complex. The Rh-N-C bond angles deviate from 180°, being 172.9 (5)° for Rh(1)-C(5)-N(5) and 164.7 (6)° for Rh(2)-C(9)-N(9). A similar arrangement of the keteniminato linkage is observed in the (cyano)(dicyanomethylketeniminato)carbonyl(tetracyanoethylene)bis(triphenylphosphine)iridium(I) complex[7] [Ir-N = 2.024 (8) Å, N-C = 1.158 (11) Å, C-C = 1.394 (13) Å, Ir-N-C = 161.9 (7)°].

Tables V and VI contain selected intramolecular bond distances, bond angles, torsion angles, and various least-squares planes that are useful in comparing the structural features of the *trans*-HCBD bridge in the present complex and the *cis*-HCBD dianion. The considerable deviation from planarity and the distortion of bond angles in both the *cis*- and *trans*-HCBD groups presumably arises in order to avoid short contacts between the cyano groups. The angles C(1)-C(2)-C(3) and C(2)-C(3)-C(4) in the *trans*-HCBD bridge are enlarged from the sp^2 angle of 120° to 125.0 (6) and 126.2 (6)°, respectively. The analogous angles in the *cis*-HCBD dianion are 127.6 and 125.8°. The nonplanarity of the four-carbon central chain is illustrated by the torsion angles and least-squares planes listed in Tables V and VI. The average unsigned, acute torsion angles about the C(1)-C(2), C(2)-C(3), and C(3)-C(4) bonds are 38, 8.5, and 25°, respectively, compared with 39, 12, and 18° for the *cis*-HCBD. Maverick, *et at.*,[8] have calculated the distortion of the dianion *trans*-HCBD by the extended Huckel method. They predicted angles C(1)-C(2)-C(3) = C(2)-C(3)-C(4) of 125.5° and torsion angles about C(1)-C(2), C(2)-C(3), and C(3)-C(4) of 21.3, 20.0, and 20.1°. It is interesting that in both the *cis*- and *trans*-HCBD structures the twisting of the molecules is unsymmetric, in that one end is more severely distorted than the other. There is no apparent steric reason for these distortions in the *trans*-HCBD structure. In the *trans*-HCBD structure each trigonal carbon atom is in the plane of its three immediate neighbors (Table V) whereas in the *cis*-HCBD structure the surrounding of the trigonal carbon atoms is slightly distorted from planarity.

Table VI. Comparison of Intramolecular Distances and Angles

	$[Rh(CO)[P(C_6H_5)_3]_2]_2$(*trans*-HCBD)	K_2(*cis*-HCBD)
Intramolecular Distances, Å		
C(1)-C(2)	1.455 (9)	1.442
C(2)-C(3)	1.359 (9)	1.399
C(3)-C(4)	1.444 (9)	1.434
C-CN[a]	1.413 (16)	1.42 (2)
C-N[a]	1.144 (10)	1.155 (9)
Bond Angles, Deg		
C(1)-C(2)-C(3)	125.0 (6)	127.6
C(2)-C(3)-C(4)	126.2 (6)	125.8
C-C-N[a]	178 (1)	178.1 (8)
Torsion Angles,[b] Deg		
C(6)-C(1)-C(2)-C(3)	−143.8 (7)	166.6
C(5)-C(1)-C(2)-C(3)	39.2 (10)	−22.3
C(1)-C(2)-C(3)-C(4)	−171.5 (6)	−12.1
C(2)-C(3)-C(4)-C(10)	25.0 (11)	−40.6
C(2)-C(3)-C(4)-C(9)	−155.6 (7)	142.8
Displacement of an Atom from a Plane, Å		
C(1) C(2)-C(6)-C(5)	−0.021 (7)	0.062
C(2) C(1)-C(3)-C(7)	0.020 (8)	0.0
C(3) C(2)-C(8)-C(4)	−0.011 (8)	−0.047
C(4) C(3)-C(9)-C(10)	−0.004 (8)	0.024

[a] These are average quantities. See footnote in Table IV. [b] The sense of these angles is defined by W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., March 1964. [c] Calculated from the data of ref 8.

The C(1)-C(2) and C(3)-C(4) distances of 1.455 (9) and 1.444 (9) Å, respectively, are not significantly longer than the analogous distances in the *cis*-HCBD (1.44 and 1.43 Å). They are somewhat shorter than the single bonds commonly observed in conjugated systems.[19] On the other hand, the C(2)-C(3) bond length of 1.359 (9) Å is not much longer than double bonds observed in related compounds, for example 1.339 (9) Å in monoclinic tetracyanoethylene,[20] 1.344 (3) Å in cubic tetracyanoethylene,[21] and 1.346 (3) Å in $(NC)_2C{=}CClCCl[C_6H_5]_2$.[22] In *cis*-HCBD the C(2)-C(3) bond length is 1.399 (9) Å.

It was stated that the geometry of the *cis*-hexacyanobutenediide dianion implies a high degree of delocalization of charge. This conclusion is also supported by extended Huckel calculations.[8] On the other hand, the coordination of the *trans*-HCBD dianion to a transition metal leads to only a slightly delocalized system as indicated by the relatively short central C=C bond distance and the small torsion angle around this bond. The theoretical calculations[8] on *trans*-HCBD predict a slightly longer central C=C distance and slightly shorter C(1)-C(2) and C(3)-C(4) distances than in *cis*-HCBD. That these predictions are not borne out for *trans*-HCBD bridging two $Rh(CO)[P(C_6H_5)_3]_2$ groups may indicate that the metals are altering the electronic nature of the HCBD ligand by acting as Lewis acids.

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Registry No. $[Rh(CO)[P(C_6H_5)_3]_2]_2(HCBD)$, 42063-67-2.

Supplementary Material Available. A listing of structure amplitudes and Table III, the root-mean-square amplitudes of vibration, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $7.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2870.

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Crystal Structure of Ferrous Phosphate, $Fe_3(PO_4)_2$

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The crystal structure of ferrous phosphate has been determined and refined by full-matrix least-squares procedures using automatic diffractometer data to a residual $R = 0.048$ ($R_w = 0.066$) with a data:parameter ratio of 15. The space group is $P2_1/c$ with $a = 8.881$ (2) Å, $b = 11.169$ (2) Å, $c = 6.145$ (1) Å, and $\beta = 99.36$ (3)°. $Fe_3(PO_4)_2$ is a pure end member of the series represented by the mineral graftonite–$(Fe,Mn,Ca,Mg)_3(PO_4)_2$–and is isotypic with it. Ferrous ions occupy three distinct coordination polyhedra; the variations in cation coordination among the compounds crystallizing in this structure type are discussed.

Introduction

The mineral graftonite, formulated as $(Fe,Mn,Ca,Mg)_3(PO_4)_2$,[1] crystallizes in the space group $P2_1/c$.[2] Several compounds which are isotypic with graftonite have been reported in recent years differing slightly in the coordination polyhedra surrounding the three crystallographically unique cation sites. Table I lists each of these compounds along with their unit cell parameters and cation coordination numbers. We have prepared single crystals of an end member of the graftonite solid solution series–ferrous phosphate–and wish to present the results of our crystal structure refinement.

Experimental Section

Preparation and Crystal Growth. Ferric phosphate, $FePO_4$, was synthesized by the thermal decomposition and reaction of a stoichiometric mixture of reagent grade ferric oxide and ammonium dihydrogen phosphate at 1000° in air. Then, in a sealed evacuated quartz tube, a stoichiometric mixture of ferric phosphate and iron metal was heated at 800° for 24 hr (the heat treatment repeated twice after regrinding) to produce ferrous phosphate.[3]

Attempts to heat ferrous phosphate to temperatures above 900° in sealed evacuated quartz tubes resulted in the quartz being attacked. Therefore, crystals were grown by sintering in the following manner. $Fe_3(PO_4)_2$ was packed into a gold tube (5 mm in diameter, 40 mm long) which had been welded shut at one end. This open capsule was then sealed under vacuum in a quartz tube and heated for 3 days at 1025°. Crystals up to a few tenths of 1 mm in size could be picked out of the sintered mass.

X-Ray Diffraction Data. A powder diffraction pattern was taken of a sample of ground single crystals on a Norelco diffractometer equipped with a graphite monochromator at a scan speed of $^1/_2$° 2θ/min using Cu Kα radiation. Table II presents the results of a least-squares refinement of these data indexed on the basis of a monoclinic unit cell.

A suitable crystal was ground to a sphere of radius 0.055 mm. Precession photographs revealed monoclinic symmetry with systematic absences confirming the space group $P2_1/c$.

The lattice parameters were determined in a PICK II least-squares refinement program using 48 reflections within the angular range $35° < 2\theta < 47°$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using Mo Kα_1 radiation. At 24° the lattice parameters are $a = 8.881$ (2) Å, $b = 11.169$ (2) Å, $c = 6.145$ (1) Å, and $\beta = 99.36$ (3)°, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated density, with $Z = 4$, is 3.948 g/cm^3.

Diffraction intensities were measured using Zr-filtered Mo Kα radiation at a takeoff angle of 2.5° with the diffractometer operating in the θ–2θ scan mode. Scans were made at 1°/min over 1.5° with allowance for dispersion and with 40-sec background counts taken at both ends of the scan. Of the 2150 independent data investigated in the angular range $2\theta < 65°$, 1766 were considered observable according to the criterion $|F_o| > 0.8\sigma_F$, where σ_F is defined as $0.02|F_o| + [C + k^2B]^{1/2}/2|F_o|Lp$; the total scan count is C, k is the ratio of scanning time to the total background time, and B is the total background count. Three reflections were systematically monitored and no random variations in intensity greater than 3% were observed over the data collection period; the mean variation was very much smaller.

The intensity data were corrected for Lorentz and polarization effects and absorption corrections[4] were applied for a spherical crystal with $\mu R = 0.43$; the maximum absorption correction applied was 5.0% of $|F_o|$.

Determination and Refinement of the Structure. The atomic positional parameters reported for graftonite[2] were used as the initial trial structure. Four cycles of least-squares refinement[5] of these positions using a $1/\sigma^2$ weighting scheme, zerovalent scattering factors for Fe, P and O,[6] isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion yielded a residual $R = 0.092$ ($R_w = 0.121$). The anisotropic refinement, based on a data to parameter ratio of 15:1 with 119 independently varied parameters, converged to a final $R = 0.048$ ($R_w = 0.066$) for the observed data. In the final refinement, the maximum extinction correction[7] was 3% of $|F_c|$ for the $10\bar{2}$ reflection.

Table III presents the final anisotropic coordinates and anisotropic thermal parameters.

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