New Polymorphs of $Ru^{III}P_3O_9$: *Cyclo*-Hexaphosphate $Ru_2P_6O_{18}$ and Metaphosphate $Ru(PO_3)_3$ with a Novel Structure

Hiroshi Fukuoka, Hideo Imoto, and Taro Saito

Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113, Japan

Two new polymorphs of ruthenium phosphate with RuP_3O_9 composition were prepared and their crystal structures were determined by single-crystal X-ray diffraction. They are *cyclo*-hexaphosphate $Ru_2P_6O_{18}$ and metaphosphate $Ru(PO_3)_3$. $Ru_2P_6O_{18}$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 6.292(2)$ Å, $b = 15.276(2)$ Å, $c = 8.365(2)$ Å, $\beta = 106.54(2)°$, $V = 770.6(3)$ Å^3, $Z = 2$, $R = 0.043$, $R_W = 0.035$. The structure contains *cyclo*-hexaphosphate rings stacking obliquely along the [100] direction and is isotypic with B-form *cyclo*-phosphates. $Ru(PO_3)_3$ has a novel structure and crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.957(1)$ Å, $b = 10.324(2)$ Å, $c = 5.030(1)$ Å, $\alpha = 92.45(2)°$, $\beta = 92.31(2)°$, $\gamma = 98.61(1)°$, $V = 356.5(1)$ Å^3, $Z = 2$, $R = 0.030$, $R_W = 0.027$. It is built up of a network of infinite $[PO_3^-]_\infty$ chains and RuO_6 octahedra. The configuration of the metaphosphate chains is different from that in the C-form $Ru(PO_3)_3$. While the chains in the C-form consisting of $PO_3–O–PO_3$ units are condensed in nearly staggered configurations, the units in the new phosphate are eclipsed. © 1995 Academic Press, Inc.

INTRODUCTION

The phosphates containing trivalent transition metal ions show many crystal structures. Especially, many types of polymorphs have been discovered in the ternary phases of the formula MP_3O_9. In these polymorphs, phosphate ions are condensed into many types of *cyclo*-phosphate or metaphosphate ions. For instance, the phases known as A–C forms are *cyclo*-tetraphosphate, *cyclo*-hexaphosphate, and metaphosphate, respectively, and many transition metals are known to form the structures (1–18). There are other polymorphs known as D–G forms in the Al, Cr, Fe, and V phosphate systems, but they have been identified only by the X-ray powder patterns (1–3, 5).

In the Ru–P–O system, only a C-form phosphate $Ru(PO_3)_3$ has been known (18). It has a monoclinic unit cell and contains $Ru^{III}O_6$ octahedra and infinite chains of metaphosphate ions. In the study of the reaction between ruthenium chloride hydrate and 85% phosphoric acid, two new polymorphs with RuP_3O_9 composition have been ob-

tained and their crystal structures have been determined by single-crystal X-ray diffraction. They are *cyclo*-hexaphosphate (B-form) and metaphosphate. The latter phosphate crystallizes in the triclinic system and has a novel structure. To distinguish it from the C-form $Ru(PO_3)_3$, we call the new phosphate triclinic form or triclinic $Ru(PO_3)_3$ and call the C-form $Ru(PO_3)_3$ monoclinic form. The present paper deals with preparations and crystal structures of the two new polymorphs.

EXPERIMENTAL AND RESULTS

Preparation and Characterization

(a) *Ruthenium cyclo-hexaphosphate.* Ruthenium chloride hydrate (Tanaka–Kikinzoku, Ru 40.37%) and 85% phosphoric acid (Koso-kagaku) were mixed in a mole ratio of $2.7 < P/Ru < 3.0$ and heated at about 200°C in air for 1 hr. Then the sample was put in an alumina boat and was heated in an inert atmosphere at 200°C for 1 week and at 350°C for 1 week to yield a brown precursor. The precursor is stable in air at room temperature and shows a little solubility in water. On the analogy of the Al, Cr, and Fe phosphate (19, 20), the precursor seems to be $H_2RuP_3O_{10}$ (FW = 356). From the weight change of the whole reactants, the empirical formula weight FW = 361 was obtained for the precursor (P/Ru = 3.03), and it supports the assumed formula. Ruthenium *cyclo*-hexaphosphate was obtained by heating the precursor at 650°C for 1 week. X-ray powder patterns revealed the existence of small amount of RuO_2. *Cyclo*-hexaphosphate decomposed at 720°C and changed into monoclinic metaphosphate.

The precursor $H_2RuP_3O_{10}$ was formed by the preheating process at 350°C. It crystallized into three kinds of phosphates by heating at higher temperatures on which the phases depended. The variations of the products are illustrated in Fig. 1. When the precursor was heated at higher than 750°C, triphosphate ions ($H_2P_3O_{10}^{5-}$) condensed in metaphosphate ions to form monoclinic $Ru(PO_3)_3$. Heated at 400–500°C, the precursor changed into triclinic
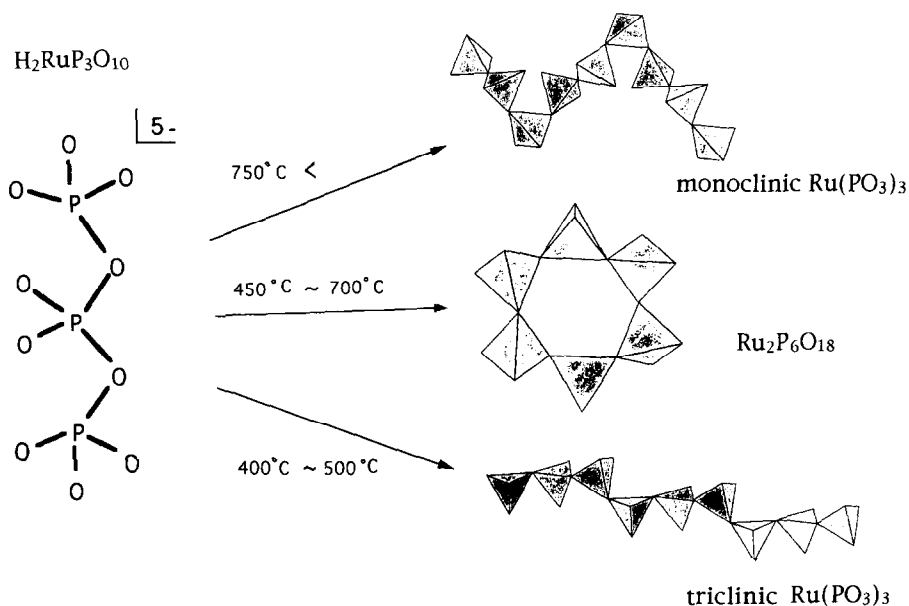
FIG. 1. The variations of the products obtained from the precursor $H_2RuP_3O_{10}$. Three types of phosphates were obtained from the precursor by heating it at different temperatures.

metaphosphate and *cyclo*-hexaphosphate. If it was rapidly heated up to 650–700°C, *cyclo*-hexaphosphate was yielded as the main product.

It was difficult to obtain a single phase of ruthenium *cyclo*-hexaphosphate from ruthenium chloride and phosphoric acid because a small amount of RuO_2 was also

formed by this method. An improved method, however, gave the single phase very easily.

Ruthenium chloride hydrate and 85% phosphoric acid in a mole ratio of 1 : 3.0 were reacted in HNO_3 solution (conc. $HNO_3 : H_2O = 3 : 1$ in volume) at 100°C for 1 week. The condensed precursor was heated slowly to 400°C and
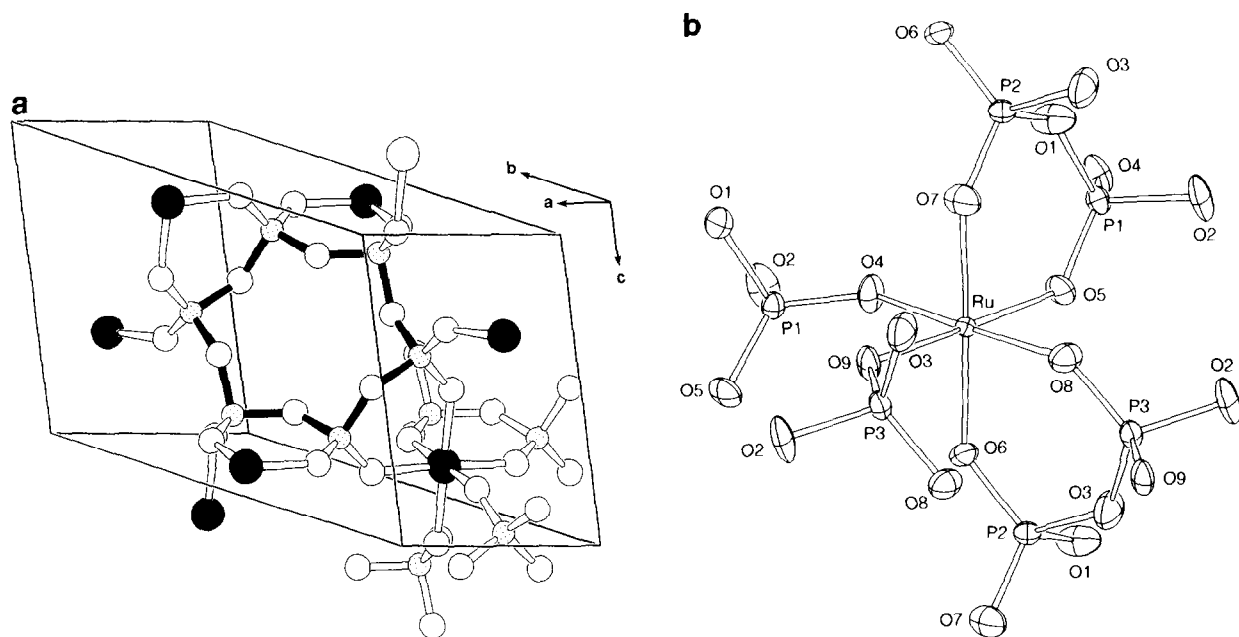

FIG. 2. (a) The crystal structure of the $Ru_2P_6O_{18}$. Filled circles show Ru atoms, open circles indicate O atoms, and dotted circles are P atoms. Black bonds show the *cyclo*-hexaphosphate ring. (b) The local structure around a Ru atom in $Ru_2P_6O_{18}$.

TABLE 1
Crystallographic Data for $Ru_2P_6O_{18}$ and $Ru(PO_3)_3$

	$Ru_2P_6O_{18}$	$Ru(PO_3)_3$
Formula weight	1351.94	675.97
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	6.292(2)	6.957(1)
b (Å)	15.276(2)	10.324(2)
c (Å)	8.365(2)	5.030(1)
α	—^{a}	92.45(2)°
β	106.54(2)°	92.31(2)°
γ	—^{a}	98.61(1)°
V (Å^3)	770.6(3)	356.5(1)
Z	2	2
F (000), electrons	644	322
D_{calc} (g·cm^{-3})	2.913	3.149
T(K) of data collection	300	300
Crystal size (mm)	0.10 × 0.10 × 0.07	0.25 × 0.10 × 0.05
Diffractometer		Rigaku AFC-6S	
Radiation (graphite monochromated)		Mo$K\alpha$ 0.7107 Å	
Scan mode		2θ-ω	
Scan speed (deg·min^{-1})		4.0	
Scan range (degree)	0.892 + 0.3 tan ω	1.500 + 0.3 tan ω
Collection region	$-8 \le h \le 8$	$-9 \le h \le 9$
	$0 \le k \le 20$	$-14 \le k \le 14$
	$0 \le l \le 11$	$0 \le l \le 7$
2θ limit		$4° \le 2\theta \le 60°$	
No. of measured reflections	2525	2240
No. of unique reflections	2253	2081
No. of observed reflections with $|F_o| > 3\sigma(|F_o|)$	1648	1755
Linear absorption coeff. (cm^{-1})	26.32	28.44
Absorption correction	ψ-scan with refl. 110	ψ-scan with refl. 002
Transmission factor	0.8734/0.9928	0.8847/1.0012
Extinction correction factor	1.5 × 10^{-7}	2.35 × 10^{-7}
No. of variable parameters	119	122
Weighting scheme		$w = 1/\sigma^2(|F_o|)$	
R, R_w^b	0.0431, 0.0347	0.0303, 0.0271
Goodness of fit, S^c	1.199	1.911
Residual density^d (eÅ^{-3})	1.12	1.03
Sift/esd(max)^e	0.00	0.00

^{a} The cell constant refinement is constrained in the monoclinic system.

^{b} $R = \Sigma(|\,|F_o| - |F_c|\,|)/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}(w = 1/\sigma(F_o)^2)$.

^{c} $S = [w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

^{d} The highest residual electrons of the final difference Fourier map.

^{e} The maximum shift/esd of the final cycle of the refinement.

resulted in a brown powder. Its IR spectrum showed a strong absorption peak of ν_{NO} at 1930 cm^{-1}. The single phase of ruthenium cyclo-hexaphosphate was obtained with the decomposition of this Ru–NO precursor between 600 and 700°C.

It was difficult to prepare single crystals suitable for the X-ray diffraction analysis. A large orange rhombic crystal was obtained by chance in a product made of P/Ru = 6.4 mixture at 470°C for 3 days.

(b) Triclinic $Ru(PO_3)_3$. The phosphate was obtained as an impure product, always contaminated with monoclinic metaphosphate or cyclo-hexaphosphate. Single crystals of it, however, were easily obtained. The mixture of ruthenium chloride hydrate and 85% phosphoric acid (Ru : P = 1 : 6.4) was heated in a platinum boat at 470°C for 3 days in N_2 gas. The product was washed by methanol and acetone to remove excess phosphoric acid, and yellow thin plate crystals of the triclinic $Ru(PO_3)_3$ were obtained with a small amount of crystals of cyclo-hexaphosphate. When triclinic $Ru(PO_3)_3$ was heated at 875°C, it

TABLE 2
Atomic Parameters for $Ru_2P_6O_{18}$ with Standard Deviations in Parentheses

Atom	x	y	z	U_{eq} (Å²)
Ru	0.12126(8)	0.13603(3)	0.37658(6)	0.0069(2)
P1	0.2096(3)	0.1600(1)	0.0165(2)	0.0093(6)
P2	0.5915(3)	0.1137(1)	0.2965(2)	0.0100(6)
P3	0.8477(3)	−0.0447(1)	0.2765(2)	0.0099(6)
O1	0.4622(8)	0.1533(3)	0.1195(5)	0.019(2)
O2	0.1735(9)	0.0730(3)	−0.0916(5)	0.019(2)
O3	0.6395(8)	0.0174(3)	0.2472(6)	0.021(2)
O4	0.1887(8)	0.2353(3)	−0.0979(5)	0.014(2)
O5	0.0631(7)	0.1528(3)	0.1270(5)	0.015(2)
O6	0.8024(7)	0.1629(3)	0.3594(5)	0.013(2)
O7	0.4446(7)	0.1100(3)	0.4060(5)	0.017(2)
O8	0.0555(7)	0.0063(3)	0.3408(5)	0.015(2)
O9	0.8183(8)	−0.1226(3)	0.3729(5)	0.014(2)

$U_{ij} \times 100$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	0.66(2)	0.81(2)	0.64(2)	−0.10(2)	0.259(15)	−0.07(2)
P1	1.16(7)	0.89(7)	0.75(6)	0.12(6)	0.27(6)	0.04(5)
P2	0.69(7)	1.15(7)	1.14(7)	0.14(6)	0.24(6)	−0.07(6)
P3	1.31(8)	0.92(7)	0.80(6)	−0.07(6)	0.43(6)	−0.14(5)
O1	1.2(2)	3.1(3)	1.4(2)	0.3(2)	0.3(2)	1.0(2)
O2	3.7(3)	0.9(2)	1.3(2)	−0.1(2)	1.2(2)	−0.4(2)
O3	1.7(2)	1.7(2)	2.6(3)	0.1(2)	0.1(2)	−1.0(2)
O4	2.4(3)	0.8(2)	1.2(2)	0.5(2)	0.7(2)	0.1(2)
O5	1.5(2)	2.3(3)	0.8(2)	−0.1(2)	0.5(2)	−0.1(2)
O6	0.9(2)	1.2(2)	2.0(2)	−0.3(2)	0.7(2)	−0.5(2)
O7	1.3(2)	2.6(3)	1.2(2)	0.3(2)	0.4(2)	0.3(2)
O8	1.2(2)	1.2(2)	2.2(2)	−0.0(2)	0.5(2)	−0.1(2)
O9	2.2(2)	1.3(2)	0.7(2)	−0.5(2)	0.7(2)	−0.2(2)

decomposed and monoclinic $Ru(PO_3)_3$ appeared. Below 430°C, mainly a black glassy material was yielded and no large crystals were obtained. On the other hand, above 500°C, the amount of the triclinic $Ru(PO_3)_3$ decreased and small single crystals of monoclinic $Ru(PO_3)_3$ were the main product.

Single-Crystal X-Ray Structure Determination

(a) *Ruthenium cyclo-hexaphosphate.* An orange rhombic crystal having the dimensions of $0.10 \times 0.10 \times 0.07$ mm was selected for intensity data collection. All measurements were made on a Rigaku AFC6S diffractometer with monochromatized $MoK\alpha$ radiation. The unit cell parameters determined by the least-squares fit of 21 reflections with 2θ ranging from 41° to 52° were $a = 6.292(2)$ Å, $b = 15.276(2)$ Å, $c = 8.365(2)$ Å, $\beta = 106.54(2)°$, $V = 770.6(3)$ Å³. Based on the Wissenberg photographs, the space group was determined to be $P2_1/c$ (No. 14).

The structure was solved by use of the initial parameters

of the isotypic compound $Cr_2P_6O_{18}$ (7) and refined by full-matrix least-squares refinement (ANYBLK) (21). The last cycle of the refinement converged at $R = 0.0431$ and $R_W = 0.0347$. The anisotropic thermal parameters were adopted for all atoms. A summary of the refinement of $Ru_2P_6O_{18}$ is listed in Table 1. Positional parameters and main interatomic distances and angles are given in Tables 2 and 3.

(b) *Ruthenium metaphosphate.* A yellow plate crystal having the dimensions of $0.25 \times 0.10 \times 0.05$ mm was selected for intensity data collection. The measurements were performed by the same procedure described above. The space group was determined to be $P\bar{1}$ with $a = 6.957(1)$ Å, $b = 10.324(2)$ Å, $c = 5.030(1)$ Å, $\alpha = 92.45(2)°$, $\beta = 92.31(2)°$, $\gamma = 98.61(1)°$, $V = 356.5(1)$ Å³. The positional parameters of the ruthenium and phosphorus atoms were determined by the Patterson method (SHELXS86) (22). The positions of oxygen atoms were determined by Fourier techniques (SHELXS76) (23). The structure was finally refined by full-matrix least-squares analysis (ANYBLK) (21) to $R = 0.0303$

TABLE 3
Bond Distances and Angles in $Ru_2P_6O_{18}$

Ru	O4	O5	O6	O7	O8	O9
O4	**2.010(4)**	2.794(6)	2.821(6)	2.856(6)	4.038(6)	2.881(6)
O5	87.5(2)	**2.031(4)**	2.882(6)	2.906(6)	2.873(6)	4.060(6)
O6	89.1(2)	90.9(2)	**2.012(4)**	4.029(6)	2.903(6)	2.836(6)
O7	90.3(2)	91.7(2)	177.2(2)	**2.018(5)**	2.835(6)	2.817(6)
O8	177.5(2)	90.1(2)	91.8(2)	88.9(2)	**2.029(4)**	2.905(6)
O9	91.0(2)	178.5(2)	89.1(2)	88.2(2)	91.4(2)	**2.030(4)**

P1	O1	O2	O4	O5
O1	**1.580(5)**	2.468(7)	2.461(6)	2.529(6)
O2	102.4(3)	**1.586(4)**	2.481(6)	2.456(6)
O4	107.1(3)	108.1(2)	**1.478(4)**	2.568(6)
O5	111.2(2)	106.3(3)	120.3(3)	**1.484(4)**

P2	O1	O3	O6	O7
O1	**1.592(4)**	2.452(6)	2.487(6)	2.518(6)
O3	101.3(3)	**1.580(5)**	2.515(6)	2.489(6)
O6	107.8(3)	110.2(3)	**1.485(4)**	2.525(6)
O7	110.3(3)	109.0(3)	117.0(3)	**1.476(5)**

P3	O2	O3	O8	O9
O2	**1.575(4)**	2.420(6)	2.486(6)	2.487(6)
O3	100.2(3)	**1.579(5)**	2.515(6)	2.505(6)
O8	108.6(3)	110.3(2)	**1.485(5)**	2.532(6)
O9	109.0(2)	110.0(3)	117.3(3)	**1.479(4)**

Note. Angle(P1–O1–P2) = 134.4(3)°, angle(P1–O2–P3) = 138.5(3)°, angle(P2–O3–P3) = 136.9(3)°.

TABLE 4
Atomic Parameters for Ru(PO$_3$)$_3$ with Standard Deviations in Parentheses

Atom	x	y	z	U (Å²)
Ru1	0.0	0.0	0.0	0.0071(2)
Ru2	0.5	0.5	0.0	0.0056(2)
P1	0.6723(2)	0.3611(1)	0.5015(2)	0.0096(5)
P2	0.9604(2)	0.1827(1)	0.5261(2)	0.0095(5)
P3	0.6848(2)	0.7715(1)	0.7593(2)	0.0104(5)
O1	0.1174(5)	0.9258(3)	0.6707(6)	0.014(2)
O2	0.1269(5)	0.6894(3)	0.5379(6)	0.011(1)
O3	−0.4768(5)	0.2370(3)	1.3839(6)	0.013(2)
O4	−0.6990(5)	0.3470(3)	1.0844(6)	0.016(2)
O5	−0.3333(5)	0.4766(3)	1.3366(6)	0.013(2)
O6	−0.1837(5)	0.7674(3)	0.5109(6)	0.014(1)
O7	0.2696(5)	1.0987(3)	1.0965(6)	0.015(2)
O8	0.0685(5)	0.8418(3)	1.1873(6)	0.014(2)
O9	0.3541(5)	1.6225(3)	1.2069(6)	0.015(2)

$U_{ij} \times 100$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru1	0.78(3)	0.72(2)	0.63(2)	0.10(2)	0.01(2)	0.08(2)
Ru2	0.69(3)	0.59(2)	0.43(2)	0.22(2)	−0.01(2)	0.11(2)
P1	1.02(6)	1.05(5)	0.89(5)	0.41(4)	−0.03(4)	0.02(4)
P2	0.98(6)	0.97(5)	1.00(5)	0.35(4)	0.10(4)	0.24(4)
P3	0.86(6)	1.02(5)	1.22(6)	0.07(4)	0.03(5)	0.12(4)
O1	1.8(2)	1.3(2)	1.2(2)	0.2(1)	0.1(1)	−0.4(1)
O2	0.9(2)	1.1(2)	1.4(2)	0.5(1)	0.1(1)	0.3(1)
O3	0.8(2)	1.3(2)	1.9(2)	0.2(1)	−0.2(1)	−0.1(1)
O4	1.4(2)	1.4(2)	2.0(2)	0.2(1)	−0.4(1)	0.6(1)
O5	1.5(2)	1.3(2)	1.1(2)	0.5(1)	−0.3(1)	0.3(1)
O6	1.0(2)	1.9(2)	1.3(2)	0.2(1)	0.4(1)	−0.1(1)
O7	1.4(2)	1.4(2)	1.5(2)	−0.2(1)	−0.1(1)	−0.4(1)
O8	2.0(2)	1.3(2)	1.0(2)	0.5(1)	0.2(1)	0.5(1)
O9	2.2(2)	1.9(2)	0.6(2)	1.1(2)	0.3(1)	−0.0(1)

and R_W = 0.0271. A summary of the refinement of Ru(PO$_3$)$_3$ is listed in Table 1. Positional parameters and main interatomic distances and angles are given in Tables 4 and 5.

IR and UV Spectroscopy

The IR spectra were measured by a Hitachi I-3000 spectrometer using KBr disks. The UV spectra were measured by a Hitachi U-3500 spectrometer. Measurements were performed using KBr disks similar to the ones used for the IR spectrum measurements.

DISCUSSION

Ruthenium Cyclo-Hexaphosphate

(a) *Structure.* The ruthenium *cyclo*-hexaphosphate is isotypic with $M_2P_6O_{18}$ (B-form) phosphates (M = Al, Fe, Cr) (7, 9). Its crystal structure is presented in Fig. 2a. A

12-membered ring of a *cyclo*-hexaphosphate ion can be seen at the center of the unit cell. The ring of diameter 4.04 Å (O3–O3 distance) is composed of six PO$_4$ tetrahedra sharing their corners. The center of the ring is an inversion center, and the six phosphorus atoms of the ring are located on a plane within the deviation of 0.05 Å. P–O$_{bridge}$ bond distances (1.575–1.592 Å) are longer than P–O$_{terminal}$ bond distances (1.476–1.485 Å) as in most of condensed phosphate ions.

Ru^{3+} ions are coordinated by four P$_6$O$_{18}$ ions as shown in Fig. 2b. Two of the P$_6$O$_{18}$ ions are bonded with the metal through two O atoms and compose P–O–Ru–O–P–O 6-membered rings. Six Ru–O bond distances are in the range of 2.010–2.031 Å, and the octahedron is almost regular.

Figure 3 shows the projection of the structure along the [100] direction. Black lines show the rings of the P$_6$O$_{18}^{6-}$ ions. The rings stack obliquely to form the tunnels running along the projected direction, and other tunnels consisting of

TABLE 5
Bond Distances and Angles in Ru(PO$_3$)$_3$

Ru1	O1	O7	O8
O1 × 2	**2.046(3)**	2.796(4)	2.792(4)
O7 × 2	86.75(13)	**2.026(3)**	2.871(4)
O8 × 2	86.55(12)	90.20(13)	**2.027(3)**

Ru2	O4	O5	O9
O4 × 2	**2.010(3)**	2.907(5)	2.850(4)
O5 × 2	91.23(12)	**2.057(3)**	2.894(5)
O9 × 2	90.08(14)	90.51(12)	**2.018(3)**

P1	O2	O3	O5	O9
O2	**1.579(3)**	2.450(4)	2.481(4)	2.487(4)
O3	100.9(2)	**1.598(3)**	2.550(4)	2.510(4)
O5	108.0(2)	111.5(2)	**1.487(3)**	2.554(4)
O9	108.2(2)	108.6(2)	118.2(2)	**1.491(3)**

P2	O1	O2	O6	O8
O1	**1.486(3)**	2.514(4)	2.537(4)	2.538(4)
O2	110.5(2)	**1.574(3)**	2.417(4)	2.474(4)
O6	111.4(2)	99.9(2)	**1.583(3)**	2.501(4)
O8	117.0(2)	107.7(2)	108.9(2)	**1.490(3)**

P3	O3	O4	O6	O7
O3	**1.579(3)**	2.536(4)	2.435(5)	2.471(4)
O4	111.1(2)	**1.496(3)**	2.501(4)	2.544(4)
O6	100.8(2)	108.8(2)	**1.580(3)**	2.505(4)
O7	107.7(2)	117.4(2)	109.8(2)	**1.482(3)**

Note. Angle(P1–O2–P2) = 135.7(2)°, angle(P1–O3–P3) = 130.6(2)°, angle(P2–O6–P3) = 132.3(2)°.
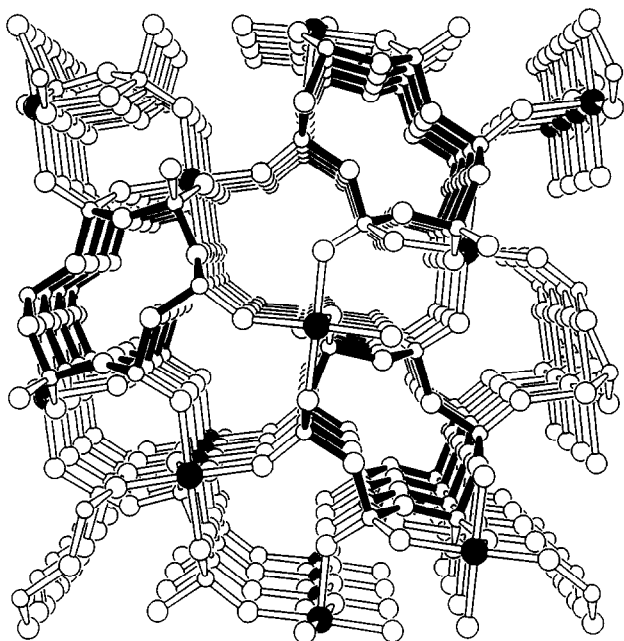
FIG. 3. The projection of the $Ru_2P_6O_{18}$ along the [111] direction. *Cyclo*-hexaphosphate ions are shown by the black bonds. Filled circles indicate ruthenium atoms. Large and small open circles indicate oxygen and phosphorus atoms, respectively.

Ru–O–P ten-membered rings also can be seen. The P_6O_{18} rings and RuO_6 octahedra are connected to form the three-dimensional network.

(b) *IR and UV spectra of $Ru_2P_6O_{18}$.* The IR spectrum is presented in Fig. 4. An absorption band at 794 cm^{-1} is assigned to ν_{P-O-P} symmetrical mode (24). In the UV spectrum, one peak and one shoulder peak are observed at 364 and 480–540 nm, respectively. Another peak was ob-

served around 220 nm, but due to the absorption of KBr, the peak top could not be well assigned. The UV spectrum of monoclinic $Ru(PO_3)_3$ shows peaks at 228 and 370–440 nm (shoulder). Both compounds contain Ru^{3+}, and the peaks were observed at close positions.
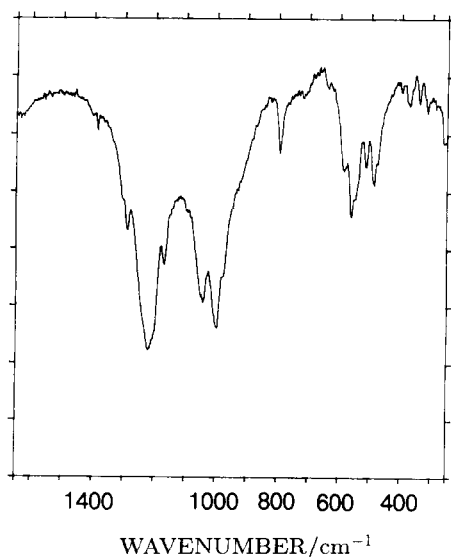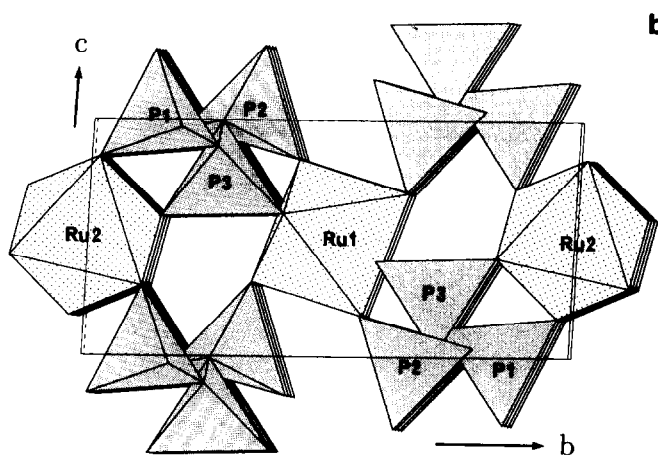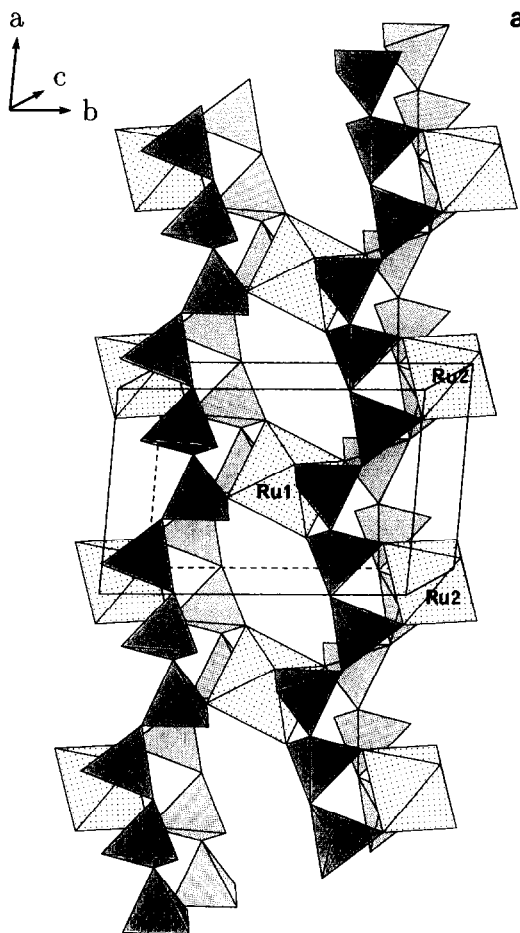

FIG. 4. The IR spectrum of the $Ru_2P_6O_{18}$.

FIG. 5. (a) The crystal structure of the triclinic $Ru(PO_3)_3$ projected on the *a–b* plane. Octahedra and tetrahedra show RuO_6 and PO_4 units. (b) Projection along the *a* axis (slightly tilted for the exposition of the stacking structure).

Ruthenium Metaphosphate

(a) *Structure.* The crystal structure of the triclinic $Ru(PO_3)_3$ projected on the *a–b* plane is given in Fig. 5a. It shows the linkage of Ru^{3+} ions and $[PO_3^-]_\infty$ linear chains. Four metaphosphate chains in a cell run parallel along the *a* axis. They are related to each other by the inversion or translation operation, and all chains are identical. Ruthenium atoms (Ru1, Ru2) are hexacoordinated and located at inversion centers (at origins and face centers of the triclinic unit cell). A ruthenium atom is connected with four metaphosphate chains to form the RuO_6 octahedron. Figure 5b shows the projection along the *a* axis. The $P_3O_9^{3-}$ units and two types of RuO_6 octahedra are stacking in this direction, and metaphosphate chains spiral along the *a* axis.

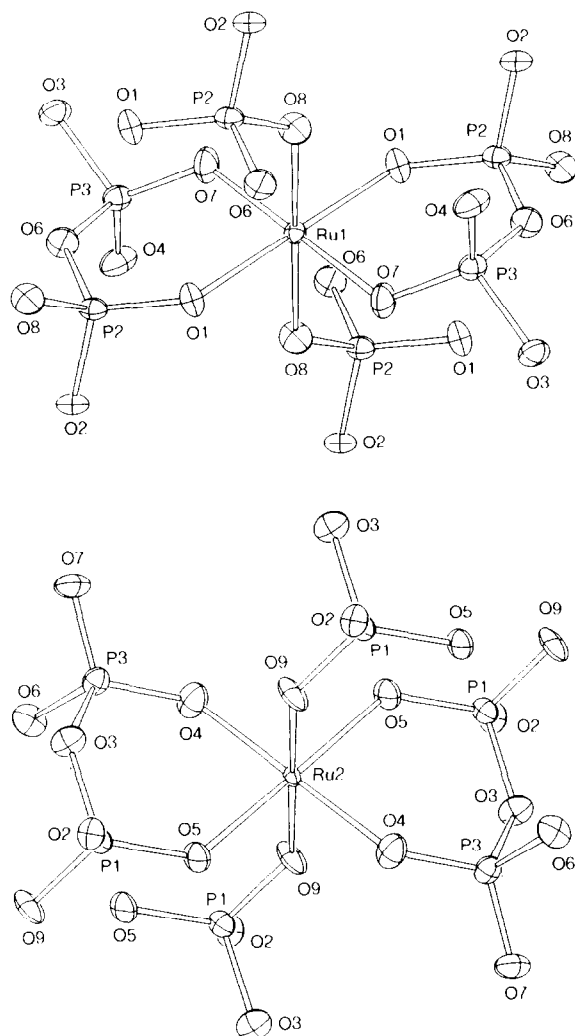The local structures around Ru1 and Ru2 are presented in Fig. 6. Both structures are almost the same. Ru–O
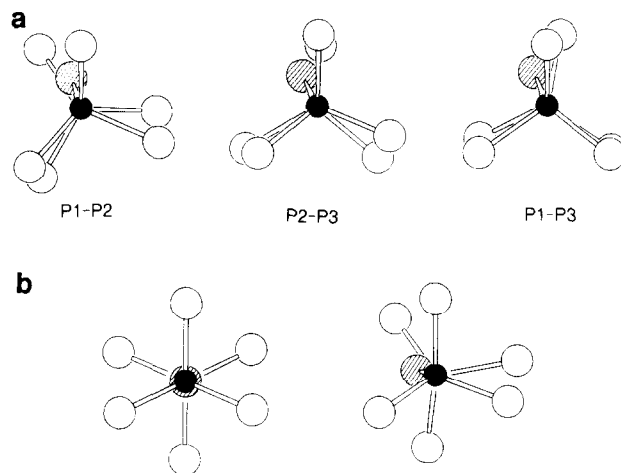
FIG. 7. The projections of the metaphosphate ions along the P–P vectors (a) in triclinic form and (b) in monoclinic form. Filled circles show phosphorus atoms. Hatched circles show bridging oxygen atoms.

bond distances are in the range of 2.01–2.06 Å, and RuO_6 are almost regular octahedra. In Fig. 6, equatorial coordination sites are connected with two metaphosphate ions as chelating ligands. Axial positions are occupied by two other chains, making the *trans* arrangement. In the $Ru_2P_6O_{18}$, the ruthenium atom also has two chelating *cyclo*-hexaphosphate ions, but it has the *cis* arrangement (Fig. 2b).

(b) *Comparison between polymorphs.* Monoclinic $Ru(PO_3)_3$ (C-form) is also a metaphosphate of trivalent ruthenium ions. Owing to an incommensurate superstructure, only the average structure has been solved by the single-crystal X-ray diffraction (18). The structure is complex but the important difference between triclinic and monoclinic phosphate is in the configuration of the metaphosphate ions. Metaphosphate ions are constructed with PO_4 tetrahedral units. Two PO_4 units can be condensed either in the eclipsed or staggered configuration. Figure 7 shows the projection of metaphosphate ions of the two polymorphs along all P–P vectors. It can be seen that the metaphosphate ion of the triclinic form has eclipsed configurations and the chain is almost linear (Fig. 5). On the other hand, in the monoclinic form the chain has almost staggered configurations and forms a complicated helix (5, 6, 12–16) (Fig. 8). The densities of three polymorphs are 2.91 $g \cdot cm^{-3}$ for $Ru_2P_6O_{18}$, 3.15 $g \cdot cm^{-3}$ for triclinic $Ru(PO_3)_3$, and 3.60 $g \cdot cm^{-3}$ for monoclinic $Ru(PO_3)_3$. The largest value of the monoclinic form can be ascribed to this helical structure. The two lighter phases decompose to change into the monoclinic form at high temperature as described above.

In oxides, the existence of Ru^{III} is rare (25). These phosphates therefore give good examples of Ru^{3+}–O distances. The average distances of the Ru–O bond are 2.022

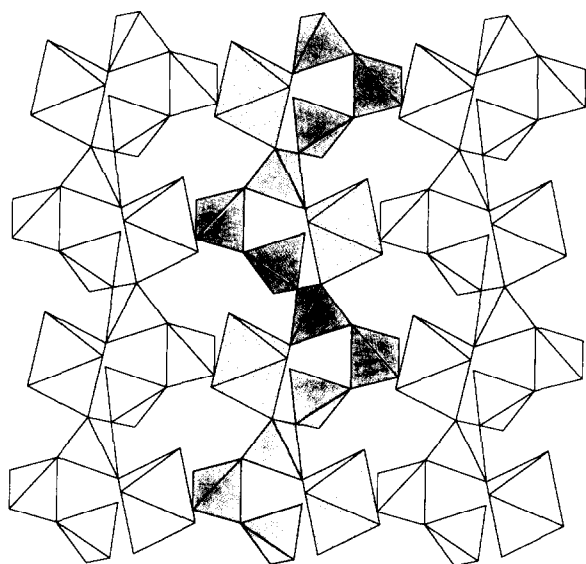FIG. 6. The local structures around Ru1 and Ru2 atoms in the triclinic $Ru(PO_3)_3$.

FIG. 8. The structure of the monoclinic $Ru(PO_3)_3$.

Å for $Ru_2P_6O_{18}$, 2.028 Å (for Ru1), and 2.033 Å (for Ru2) of triclinic form. These distances agree very well with the value expected from the effective ionic radii (1.21 Å (O^{2-}) + 0.82 Å (Ru^{3+}) = 2.03 Å) (26, 27).

REFERENCES

1. P. Rémi and A. Boullé, *Bull. Soc. Chim. Fr.* **1972**, (6)2213 (1972).
2. F. d'Yvoire, *Bull. Soc. Chim. Fr.* **1961**, 1762 (1961).
3. F. d'Yvoire, *Bull. Soc. Chim. Fr.* **1962**, 1237 (1962).
4. R. W. Douglass and E. Staritzky, *Anal. Chem.* **29**, 985 (1957).
5. K. Dostál, *Z. Chem.* **22**, 6,214 (1982).
6. H. van der Meer, *Acta Crystallogr. Sect. B* **32**, 2423 (1976).

7. M. Bagieu-Beucher and J. C. Guitel, *Acta Crystallogr. Sect. B* **33**, 2529 (1977).
8. M. Bagieu-Beucher and J. C. Guitel, *Acta Crystallogr. Sect. B* **34**, 1439 (1978).
9. M. Bagieu-Beucher, Thesis (1980).
10. L. Pauling and J. Sherman, *Z. Kristallogr.* **96**, 481 (1937).
11. G. Wappler, Diplom-Arbeit Miner. Petr. Instituts der Humboldt Univ. 1 1958; referred to in Ref. 8.
12. N. Middlemiss, F. Hawthorne, and C. Calvo, *Can. J. Chem.* **55**, 1673 (1977).
13. I. M. Watson, M. M. Borel, J. Chardon, and A. Leclaire, *J. Solid State Chem.* **111**, 253 (1994).
14. W. T. A. Harrison, T. E. Gier, and G. D. Stucky, *Acta Crystallogr. Sect. C* **50**, 1643 (1994).
15. P. Rittner and R. Glaum, *Z. Kristallogr.* **209**, 162 (1994).
16. A. I. Domanskii, Yu. F. Shepelev, Yu. I. Smolin, and B. N. Litvin, *Sov. Phys. Crystallogr.* **27**, (2)140 (1982).
17. K. K. Palkina, S. I. Maksimova, N. T. Chibiskova, N. N. Chudinova, and N. B. Karmanovskaya, *Russ. J. Inorg. Chem.* **38**, (8)1179 (1993).
18. H. Imoto, H. Horiuchi, T. Amamiya, S. Tsunesawa, H. Fukuoka, T. Saito, and N. Koga, submitted for publication.
19. P. Rémi, J. Fraissard, and A. Boullé, *Bull. Soc. Chim. Fr.* **1972**, 2222 (1972).
20. F. d'Yvoire, *Bull. Soc. Chim. Fr.* **1962**, 1224 (1962).
21. H. Imoto, S. Hayakawa, N. Morita, and T. Saito, *Inorg. Chem.* **29**, 2007 (1990).
22. G. M. Scheldrick, "SHELXS-86, Program for Crystal Structure Determination." University of Göttingen, Göttingen, Germany, 1986.
23. G. M. Scheldrick, "SHELXS-76, Program for Crystal Structure Determination." The University of Cambridge, Cambridge, UK, 1976.
24. M. Rzaigui, *J. Solid State Chem.* **89**, 340 (1990).
25. E. A. Seddon and K. R. Seddon, in "The Chemistry of Ruthenium" (R. J. H. Clark, Ed.), p. 173. Elsevier, New York, 1984.
26. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B* **25**, 925 (1969).
27. R. D. Shannon, *Acta Crystallogr. Sect. A* **32**, 751 (1976).