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Refinement of the Superstructure of C-Type Chromium(III) Tris(metaphosphate), $Cr(PO_3)_3$

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Abstract

Single crystals of $Cr(PO_3)_3$ suitable for X-ray investigations were obtained under various experimental conditions that favour volatilization of the phosphate and its recrystallization from the gas phase. The compound belongs to the series of phosphates $M(PO_3)_3$ (M^{3+} = Al, In, Sc, Ti, V, Fe, Mo, Rh, Ru) which adopt the C-type structure, characterized by one-dimensional infi-

nite metaphosphate chains and isolated MO_6 octahedra. Associated with the superstructure generally found for this structure type, in which the monoclinic b axis is tripled, three crystallographically different CrO_6 octahedra of almost ideal geometry [d_{ave}(Cr—O) = 1.96 (2) Å] were observed. Within the two independent metaphosphate chains distinctly different bond distances from P to bridging and terminal O atoms were found [d_{ave}(P—O_b) = 1.58 (1), d_{ave}(P—O_t) = 1.49 (1) Å].

Comment

C-Type $Cr(PO_3)_3$ is one of the six polymorphic modifications of this compound that have been reported in the literature (Rémy & Boullé, 1972). Up to now only the B-type structure (described as $Cr_2P_6O_{18}$; Bagieu-Beucher & Guitel, 1977) and the atomic arrangement of the sub-cell of C-$Cr(PO_3)_3$ (Yakubovich, Dimitrova & Savina, 1991) have been refined using X-ray single crystal data. In the paper by Yakubovich et al. (1991), anomalously high displacement coefficients for some atoms together with unreasonable P—O distances indicate the necessity of a refinement of the complete structure to obtain reliable information on interatomic distances and bond angles. The unit cell of the substructure of C-$Cr(PO_3)_3$ given by Yakubovich et al. (1991) [Ia, Z = 4, a = 9.367 (6), b = 6.344 (8), c = 10.544 (8) Å, β = 98.00 (6)°] is related by the transformation matrix T = (-1 0 -1, 0 3 0, 1 0 0) to the cell of the superstructure reported here.

Additional motivation for a detailed structure investigation of C-$Cr(PO_3)_3$ was drawn from polarized single-crystal UV/visible spectra of C-$Ti(PO_3)_3$ (Glaum & Hitchman, 1996). These measurements revealed the existence of three slightly differently distorted TiO_6 octahedra in agreement with a structure refinement published recently (Harrison, Gier & Stucky, 1994). This observation convincingly demonstrates once more that understanding of structure–property relationships can be reached only on the basis of complete structural information.

C-$Cr(PO_3)_3$ is a member of a series of isotypical tris(metaphosphates) $M(PO_3)_3$ [M = Al (van der Meer, 1976), In (Bentama, Durand & Cot, 1988), Sc (Domanskii, Shepelev, Smolin & Litvin, 1982), Ti (Harrison, Gier & Stucky, 1994), V (Middlemiss, Hawthorne & Calvo, 1977), Mo (Watson, Borel, Chardon & Leclaire, 1994), Ru (Fukuoka, Imoto & Saito, 1995), Rh (Rittner & Glaum, 1994)] for which the structures have been refined from single crystal data. C-$Fe(PO_3)_3$ also belongs to this series, but has been characterized so far from powder data only (Rémy & Boullé, 1972). The general aspects of the structure type have been described and discussed extensively in the references above, so apart from the specific crystallographic parameters found in this work, only a short discussion of the structure is appropriate.

Compared to the subcell refinement by Yakubovich *et al.* (1991), the distortion of the CrO$_6$ octahedra in the superstructure is significantly smaller with d_{max}(Cr—O) = 1.980 (2) and d_{min}(Cr—O) = 1.927 (2) Å (see Table 2). The maximum angular distortion from the ideal octahedral geometry is about 5°. Although the average Cr—O distances in *B*- and *C*-type Cr(PO$_3$)$_3$ are almost identical [d_{ave}(Cr—O) = 1.965 Å], the first shows a lower density by *ca.* 20%. This can be attributed to a less dense packing of the *cyclo*-hexaphosphate rings compared to the packing of the metaphosphate chains. The mean Cr—O distance in *C*-Cr(PO$_3$)$_3$ is 0.12 and 0.04 Å shorter than d_{ave}(*M*—O) in *C*-Mo(PO$_3$)$_3$ and *C*-Rh(PO$_3$)$_3$, respectively. From the structural information available on *C*-type *M*(PO$_3$)$_3$ phosphates no systematic influence of the *d*-electron configuration on the particular coordination geometry around M^{3+} can be derived.

Bond lengths [d_{ave}(P—O$_t$) = 1.49 (1), d_{ave}(P—O$_b$) = 1.58 (1) Å] and angles [bridging angles P—O—P 137.8 (2)–148.4 (2)°, bridging angles O—P—O 99.2 (2)–106.8 (2)°] within the two crystallographically independent metaphosphate chains (see Fig. 3) agree with those observed for other metaphosphates. The differences in length between terminal and bridging P—O bonds are thus smaller than claimed for the substructure [d_{ave}(P—O$_t$) = 1.42 (1), d_{ave}(P—O$_b$) = 1.66 (1) Å].

Fig. 2. Projection of the CrO$_6$ octahedra along the *c* axis to show the tilting of the octahedra around their average position in the subcell.
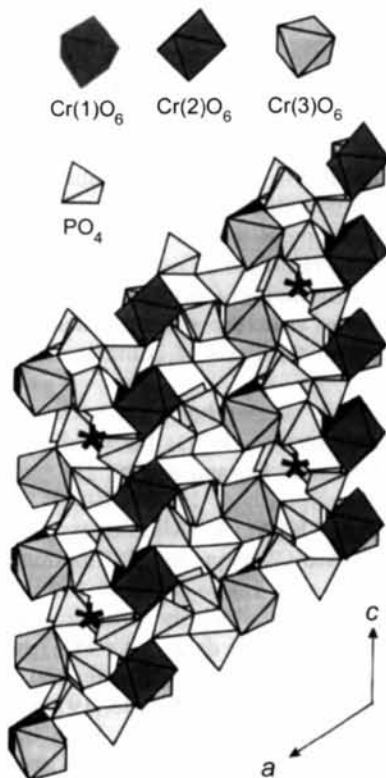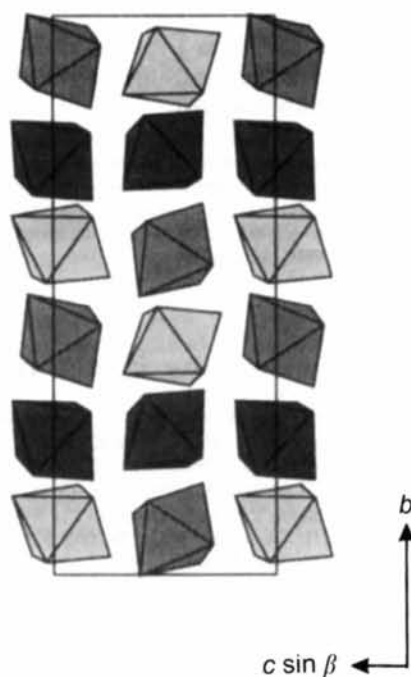

Fig. 1. *ATOMS* (Dowty, 1995) plot of the projection of one-third of the structure (0 < *z* < 0.33) on the *ac* plane with schematic coordination polyhedra. Corners of the unit cell are marked by '*'.
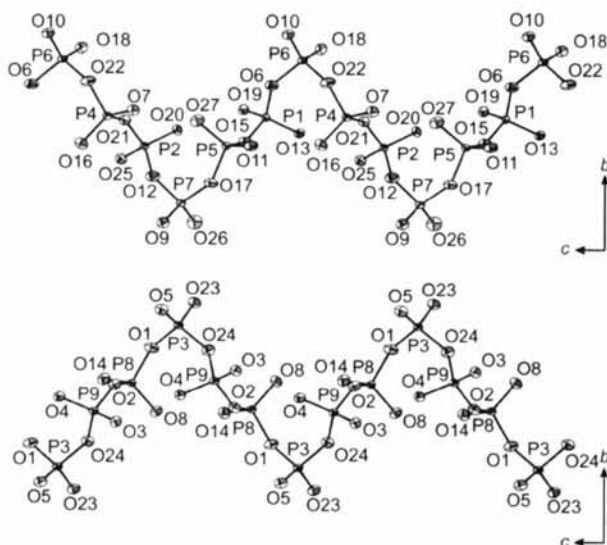

Fig. 3. *ORTEP* (Johnson, 1965) plot of the two crystallographically different metaphosphate chains. Ellipsoids are plotted at the 74% probability level.

Experimental

Solutions of chromium(III) nitrate and (NH$_4$)$_2$HPO$_4$ with the stoichiometric ratio Cr:P = 1:3.1 were mixed with nitric acid and evaporated to dryness. After the formation of nitric oxides had stopped (573 K, 3 h) the residue was transferred to a silica crucible and heated in air (1073 K) for 3 d. The resulting amorphous grey powder was turned into light-green

microcrystalline $Cr(PO_3)_3$ (C-type) by prolonged heating in air (1173 K, 4 d).

Attempts were made to crystallize $Cr(PO_3)_3$ by the use of reversible chemical vapour transport reactions (transport agent iodine, addition of a few mg of CrP or P as reducing agents, temperature gradient 1323–1223 K) in a way similar to that used for $Ti(PO_3)_3$ (Glaum & Gruehn, 1990). These experiments proved to be unsuccessful. Our investigations at 1173 K provide evidence for chromium(III) metaphosphate being in thermal equilibrium with gaseous phosphorus, CrP, $Cr_2P_2O_7$ (Glaum, Walter-Peter, Özalp & Gruehn, 1991), and $Cr_6(P_2O_7)_4$ (Glaum, 1992). Although the deposition of $Cr(PO_3)_3$ from the gas phase was never achieved under equilibrium conditions, the compound can be obtained reproducibly as well shaped crystals during irreversible transport experiments, starting with $CrPO_4$ and phosphorus (e.g. 287.6 mg $CrPO_4$, 24.6 mg P, 385.9 mg I, temperature gradient 1323–1223 K, silica ampoule, volume 17 cm³). To obtain $Cr(PO_3)_3$ at the lower temperature of the gradient it is essential to avoid equilibration of the system prior to application of the gradient, in contrast to the usual procedure in transport experiments.

The actual crystal used for data collection was grown by isothermal heating of mixtures of $Cr_4(P_2O_7)_3$ and $Zn_2P_2O_7$ under the influence of chlorine as mineralizer (1273 K, 3 d) in experiments aimed at the mixed diphosphate $Zn_2Cr_4(P_2O_7)_4$ (Gruss, 1995).

Crystal data

$Cr(PO_3)_3$
$M_r = 288.91$
Monoclinic
Cc
$a = 13.0610\,(10)$ Å
$b = 18.9771\,(15)$ Å
$c = 9.3473\,(9)$ Å
$\beta = 127.004\,(6)°$
$V = 1850.2\,(3)$ Å³
$Z = 12$
$D_x = 3.112$ Mg m⁻³
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 76 reflections
$\theta = 9.05–14.90°$
$\mu = 2.661$ mm⁻¹
$T = 293\,(2)$ K
Irregular, isometric
0.13 mm (radius)
Light green

Data collection

AED-2 (Fa. Stoe) diffractometer
$\theta/2\theta$ scans (Clegg, 1981)
Absorption correction:
ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.657$, $T_{max} = 0.742$
10 612 measured reflections
5386 independent reflections

4609 observed reflections
$[I > 2\sigma(I)]$
$R_{int} = 0.0219$
$\theta_{max} = 30°$
$h = -18 \rightarrow 18$
$k = -26 \rightarrow 26$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0208$
$wR(F^2) = 0.0602$
$S = 1.093$
5386 reflections

Extinction correction:
SHELXL93 (Sheldrick, 1993)
Extinction coefficient:
0.00178 (9)

354 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 0.4405P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.445$ e Å⁻³
$\Delta\rho_{min} = -0.498$ e Å⁻³

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: (Flack, 1983)
Flack parameter = 0.41 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}
Cr1	0.24998 (4)	0.24475 (3)	0.00003 (6)	0.00447 (12)
Cr2	0.23003 (6)	0.07967 (3)	0.46761 (8)	0.00481 (9)
Cr3	0.72756 (6)	0.91164 (3)	0.46394 (7)	0.00492 (10)
P1	0.60461 (8)	0.69618 (5)	0.16465 (11)	0.0051 (2)
P2	0.60225 (8)	0.63610 (4)	0.65772 (11)	0.0044 (2)
P3	0.50509 (8)	0.85378 (5)	0.75697 (11)	0.0054 (2)
P4	0.87662 (8)	0.80234 (4)	0.81174 (11)	0.0054 (2)
P5	0.88118 (8)	0.86267 (5)	0.31210 (11)	0.0050 (2)
P6	−0.02126 (8)	0.31502 (5)	0.21267 (10)	0.0054 (2)
P7	0.96438 (7)	0.01852 (5)	0.69345 (10)	0.0053 (2)
P8	0.58603 (8)	0.02654 (5)	0.13036 (10)	0.0050 (2)
P9	0.36325 (8)	1.03181 (4)	0.28674 (11)	0.0057 (2)
O1	0.5774 (3)	0.09855 (14)	0.2054 (3)	0.0105 (5)
O2	0.9472 (2)	0.47685 (13)	0.4436 (3)	0.0101 (5)
O3	0.2534 (2)	−0.05340 (14)	−0.2148 (3)	0.0086 (5)
O4	0.3286 (2)	−0.00220 (13)	−0.3850 (3)	0.0090 (4)
O5	0.3922 (2)	0.17804 (13)	0.0910 (3)	0.0113 (5)
O6	0.0166 (2)	0.26333 (13)	0.1157 (3)	0.0105 (4)
O7	0.7754 (2)	0.79012 (13)	0.8346 (3)	0.0096 (5)
O8	0.6032 (2)	−0.03210 (12)	0.2474 (3)	0.0096 (5)
O9	−0.1391 (2)	−0.02142 (13)	−0.4673 (3)	0.0098 (5)
O10	−0.1087 (2)	0.36848 (12)	0.0792 (3)	0.0087 (5)
O11	−0.2260 (2)	0.13806 (12)	−0.1740 (3)	0.0096 (5)
O12	0.0060 (2)	0.07454 (13)	0.6111 (3)	0.0115 (4)
O13	0.1332 (2)	0.16409 (12)	0.3306 (3)	0.0072 (4)
O14	0.6842 (2)	0.03427 (13)	0.0984 (3)	0.0100 (5)
O15	0.0130 (2)	0.14539 (12)	0.0028 (3)	0.0114 (4)
O16	−0.1463 (2)	0.14090 (12)	0.1861 (3)	0.0109 (5)
O17	−0.1004 (2)	0.06098 (12)	−0.2355 (3)	0.0095 (4)
O18	0.0963 (2)	0.33882 (13)	0.3890 (3)	0.0099 (5)
O19	0.2175 (2)	0.21191 (13)	0.1674 (3)	0.0079 (4)
O20	0.1421 (2)	0.16971 (12)	0.8270 (3)	0.0077 (4)
O21	0.0125 (2)	0.18908 (12)	0.4988 (3)	0.0092 (4)
O22	−0.1044 (2)	0.27008 (12)	0.2484 (3)	0.0110 (4)
O23	0.6029 (3)	0.19288 (13)	0.4055 (3)	0.0095 (5)
O24	0.4624 (2)	0.09438 (15)	0.3451 (3)	0.0106 (5)
O25	0.2046 (2)	−0.10933 (13)	0.1456 (3)	0.0081 (4)
O26	0.0751 (2)	−0.02022 (14)	−0.1544 (3)	0.0136 (5)
O27	−0.1280 (2)	0.18838 (12)	−0.3166 (3)	0.0112 (4)

Table 2. *Selected geometric parameters (Å)*

Cr1—O27^i	1.949 (2)	P3—O23^{viii}	1.486 (3)
Cr1—O19	1.953 (3)	P3—O1^{viii}	1.578 (3)
Cr1—O23^{ii}	1.957 (3)	P3—O24^{viii}	1.584 (3)
Cr1—O7^{iii}	1.965 (3)	P4—O7	1.479 (3)
Cr1—O5	1.969 (3)	P4—O16^{ix}	1.485 (2)
Cr1—O20^{iv}	1.971 (2)	P4—O22^{ix}	1.574 (2)
Cr2—O4^v	1.958 (2)	P4—O21^{ix}	1.580 (2)
Cr2—O10^i	1.961 (2)	P5—O11^{ix}	1.481 (3)
Cr2—O13	1.964 (2)	P5—O27^{ix}	1.492 (2)
Cr2—O25^{vi}	1.965 (3)	P5—O15^{ix}	1.572 (2)
Cr2—O3^{vi}	1.968 (3)	P5—O17^{ix}	1.576 (2)
Cr2—O26^{vi}	1.973 (3)	P6—O10	1.475 (2)
Cr3—O9^{viii}	1.927 (2)	P6—O18	1.494 (2)
Cr3—O14^{viii}	1.952 (3)	P6—O22	1.567 (3)
Cr3—O11^{ix}	1.965 (3)	P6—O6	1.602 (3)
Cr3—O18^x	1.973 (2)	P7—O26^{xiii}	1.476 (2)
Cr3—O16^{ix}	1.975 (2)	P7—O9^{xii}	1.488 (2)
Cr3—O8^{xi}	1.980 (2)	P7—O17^{xii}	1.575 (3)

P1—O19^x	1.489 (3)	P7—O12^{xiii}	1.588 (3)
P1—O13^x	1.490 (2)	P8—O8	1.480 (2)
P1—O15^x	1.572 (2)	P8—O14	1.488 (3)
P1—O6^x	1.588 (2)	P8—O1	1.571 (3)
P2—O20^x	1.480 (2)	P8—O2^{ii}	1.590 (2)
P2—O25^i	1.497 (3)	P9—O3^{viii}	1.485 (3)
P2—O12^x	1.574 (3)	P9—O4^{viii}	1.491 (3)
P2—O21^x	1.580 (2)	P9—O2^{xiv}	1.583 (2)
P3—O5^{viii}	1.480 (2)	P9—O24^{xi}	1.592 (3)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, y - \frac{1}{2}, z - 1$; (iv) $x, y, z - 1$; (v) $x, y, 1 + z$; (vi) $x, -y, \frac{1}{2} + z$; (vii) $1 + x, 1 + y, 1 + z$; (viii) $x, 1 - y, \frac{1}{2} + z$; (ix) $1 + x, 1 - y, \frac{1}{2} + z$; (x) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (xi) $x, 1 + y, z$; (xii) $1 + x, y, 1 + z$; (xiii) $1 + x, y, z$; (xiv) $x - \frac{1}{2}, \frac{1}{2} + y, z$.

The non-centrosymmetric crystal structure of $Cr(PO_3)_3$ has been refined as a racemic twin using *SHELXL93* (Sheldrick, 1993) following a procedure described by Flack & Schwarzenbach (1988; Flack, 1983).

Data collection: *STADI*-4 (Stoe & Cie, 1995). Cell refinement: *STADI*-4. Data reduction: *STADI*-4. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1995), *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL93*.

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Tetracarbonyl(tetraphosphorus hexaoxide)iron

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Abstract

The title [Fe(CO)$_4$(P$_4$O$_6$)] molecule consists of a trigonal-bipyramidally coordinated Fe atom, with the adamantane-like P$_4$O$_6$ cage in an axial position. As a consequence of the electronic effects of the iron–carbonyl group on the P$_4$O$_6$ cage, the P—O bond lengths show distortions similar to those observed within the series P$_4$O$_7$ → P$_4$O$_6$S → P$_4$O$_6$Se, but the effects are slightly less pronounced.

Comment

P$_4$O$_6$Fe(CO)$_4$ is the first transition metal complex of P$_4$O$_6$ to be investigated by single-crystal X-ray diffraction. An earlier structural investigation of the complex P$_4$O$_6$[Ni(CO)$_3$]$_4$ by means of powder diffraction (Pierron, Wheatley & Riess, 1966) did not reveal accurate bond lengths and angles, and more recent structural data on P$_4$O$_6$–transition metal complexes are not available.

The goal of the present work was to compare the influences of group VIA substituents and the isolobal iron–tetracarbonyl group on the distortion of the P$_4$O$_6$ unit (for crystal structures of the compounds P$_4$O$_6$X, where X is O, S and Se, see Jansen & Voss, 1981; Jost & Schneider, 1981; Jansen & Möbs, 1984a; Frick, Jansen, Bruna & Peyerimhoff, 1991; Clade, Jansen, Engels & Marian, 1995). The Fe atom is coordinated trigonal bipyramidally by four carbonyl groups and the P$_4$O$_6$ cage, the cage being in an axial position. The C$_{ax}$—Fe—C$_{eq}$ and C$_{eq}$—Fe—P$_{coord}$ angles are almost 90°. This means that the P$_4$O$_6$ cage, due to the considerably long