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Single crystals of tetracalcium iridium hexaoxide, Ca_4IrO_6, tricalcium magnesium iridium hexaoxide, Ca_3MgIrO_6, and tricalcium zinc iridium hexaoxide, Ca_3ZnIrO_6, were prepared *via* high-temperature flux growth and structurally characterized by single-crystal X-ray diffraction. The three compounds are isostructural and adopt the K_4CdCl_6 structure type, comprised of chains of alternating face-shared [CaO_6], [MgO_6] or [ZnO_6] trigonal prisms and [IrO_6] octahedra, surrounded by columns of Ca^{2+} ions.

Comment

Ternary and quaternary transition metal oxides belonging to a family of pseudo-one-dimensional oxides derived from the K_4CdCl_6 structure type (Bergerhoff & Schmitz-Dumont, 1959), with the general formula $A_3A'BO_6$, have attracted widespread attention in recent years. This interest can be attributed to their compositional flexibility (Smith & zur Loye, 2000), their low dimensionality, the intriguing magnetic properties exhibited by members of this family of oxides (Nguyen & zur Loye, 1995) and their ability to stabilize high oxidation states (Carlson & Stacy, 1992). While there are several published powder X-ray diffraction studies for these materials, only a few calcium iridates with this structure type, for example, Ca_3CuIrO_6 (Tomaszewska & Müller-Buschbaum, 1993), Ca_3NaIrO_6 (Claridge *et al.*, 1997), and $Ca_{3.75}Ni_{0.25}IrO_6$ (Claridge *et al.*, 1998), have been characterized by single-crystal X-ray diffraction.

In an effort to synthesize novel compounds with the general formula $A_3A'BO_6$, exploratory work has been carried out in the calcium–(metal)–iridium–oxygen phase space, which has resulted in the preparation of single crystals of Ca_4IrO_6, (I), Ca_3MgIrO_6, (II), and Ca_3ZnIrO_6, (III) (nominal compositions). Small dark rhombohedral-shaped crystals of (I), (II) and (III) were grown from a eutectic halide flux of $CaCl_2$, KCl and NaCl at high temperature. While the structure of (I) has previously been determined by powder X-ray diffraction (Sarkozy *et al.*, 1974; Segal *et al.*, 1996), (II) and (III) have not been structurally characterized prior to the present work. The occurrence of Zn in the trigonal prismatic coordination is notable in (III), since the common coordination environment for Zn in oxides is tetrahedral (Greenwood & Earnshaw, 1989).

The structures of the title compounds consist of infinite one-dimensional chains of alternating face-shared [$A'O_6$] trigonal prisms and rhombohedrally elongated [BO_6] octahedra running parallel to the *c* axis (Fig. 1). These chains are surrounded by six spiral columns of distorted square [CaO_8] antiprisms, and these Ca^{2+} columns are in turn surrounded by three one-dimensional chains (Fig. 2). Located just off the threefold axis, the Ca–O square antiprisms are highly distorted [Ca—O 2.371 (2)–2.699 (3) Å for (I), 2.359 (2)–2.689 (2) Å for (II) and 2.349 (3)–2.675 (3) Å for (III)].

The [IrO_6] octahedra are regular, with Ir—O distances ranging from 2.012 (3) to 2.020 (2) Å, in agreement with other octahedral Ir^{4+} compounds, *e.g.* 1.98 (1) Å in Ca_3SrIrO_6 (Segal *et al.*, 1996) and 2.024 (3) Å in $Ca_{3.5}Ni_{0.5}IrO_6$ (Claridge *et al.*, 1998). The [CaO_6] [in (I)], [MgO_6] [in (II)] or [ZnO_6] [in (III)] trigonal prisms are also regular (Tables 1–3), although they exhibit a significant twisting distortion from an ideal eclipsed conformation [φ = 19.4 (2), 15.8 (2) and 17.7 (2)° for (I)–(III), respectively]. These distances are also typical for M—O bond lengths for elements in trigonal prismatic coordinations in this structure type, *e.g.* 2.20 (1) Å in Sr_3MgIrO_6 (Nguyen & zur Loye, 1995) and 2.199 (4) Å in Sr_3ZnPtO_6 (Lampe-Önnerud & zur Loye, 1996).

One would expect that the substitution of either Mg or Zn for Ca would affect the lattice parameters and the unit-cell size. Since the ionic radii for these elements in sixfold coordination are 0.72 Å for Mg^{2+}, 0.74 Å for Zn^{2+} and 1.00 Å for Ca^{2+} (Shannon, 1976), we would expect a decrease in the overall unit-cell volume. Two recent studies of the size effect of the A' cation using a series of rare earths (Layland *et al.*, 1998; Smith & zur Loye, 2000) indicated that both the unit-cell volume and the ratio of *c*/*a* tend to decrease when smaller cations are substituted for larger ones. In this particular case, we find that indeed the unit-cell volume decreases, as expected, and the *c*/*a* ratio also decreases. The unit-cell volume change, however, is not the same for Mg and Zn, as

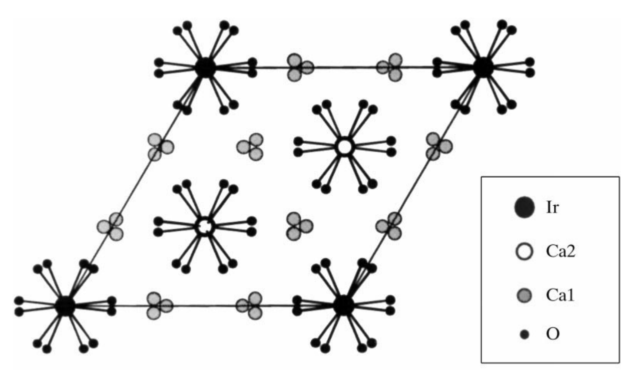

Figure 1
The [001] projection of Ca_4IrO_6.

one might have expected from their very similar ionic radii. Sr analogues of this structure type exhibit a similar trend (Segal *et al.*, 1996; Núñez *et al.*, 1997). There seems to be a difference between main group (filled *d* shell) elements and either transition metals or alkaline earth metals. In the study by Layland *et al.* (1998), In also did not follow the expected trend.

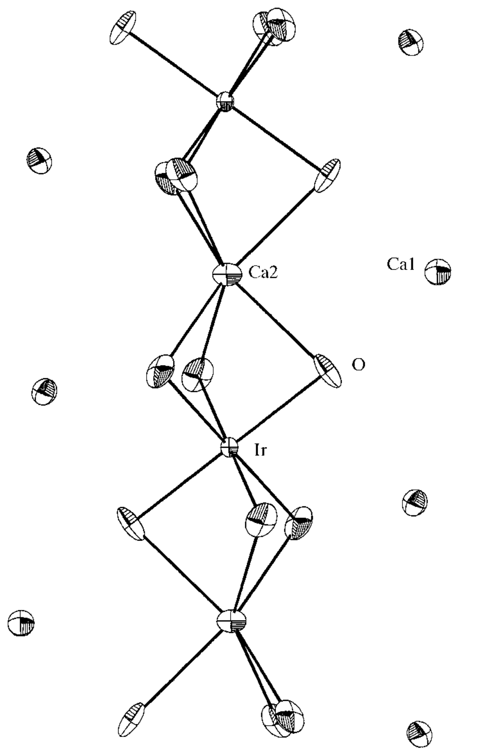

Figure 2
The structure of a chain in Ca_4IrO_6 showing 80% probability displacement ellipsoids.

Experimental

Single crystals of the title compounds were grown from a tenfold excess eutectic flux of $CaCl_2$, KCl and NaCl (all Fisher, reagent grade). $Ca(OH)_2$ (Mallinckrodt, reagent grade), either MgO (Alfa, 99.998%) or ZnO (Alfa, 99.998%) for (II) and (III), respectively, and Ir (Engelhard, 99.95%) were used as reagents. The starting materials were placed in covered alumina crucibles and heated in air at 1198 K for 24 h, and then cooled to 873 K at a rate of 15 K h^{-1}, at which point the furnace was shut off. The flux was dissolved in distilled water and dark rhombohedral crystals were isolated for analysis.

Compound (I)

Crystal data

Ca_4IrO_6
$M_r = 448.52$
Trigonal, $R\bar{3}c$
$a = 9.3030$ (5) Å
$c = 11.0864$ (8) Å
$V = 830.93$ (9) Å^3
$Z = 6$
$D_x = 5.378$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1993 reflections
$\theta = 3.1$–$36.3°$
$\mu = 27.77$ mm^{-1}
$T = 293$ (2) K
Irregular, black
0.08 × 0.06 × 0.04 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.112$, $T_{max} = 0.168$
2592 measured reflections
450 independent reflections
408 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 36.3°$
$h = -10 \rightarrow 14$
$k = -14 \rightarrow 13$
$l = -8 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.061$
$S = 1.07$
450 reflections
20 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 3.25$ e Å^{-3}
$\Delta\rho_{min} = -3.59$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00062 (14)

Table 1
Selected bond distances (Å) for (I).

Ca1—O1 (× 2)	2.371 (2)	Ca2—O1^{iv} (× 6)	2.263 (2)
Ca1—O1^{i} (× 2)	2.493 (2)	Ca2—Ir (× 2)	2.7716 (2)
Ca1—O1^{ii} (× 2)	2.519 (2)	Ir—O1^{v} (× 6)	2.020 (2)
Ca1—O1^{iii} (× 2)	2.699 (3)		

Symmetry codes: (i) $-\frac{1}{3}-x, \frac{1}{3}-y, \frac{1}{3}-z$; (ii) $-\frac{1}{3}-y, \frac{1}{3}+x-y, \frac{1}{3}+z$; (iii) $x-y-\frac{1}{3}, \frac{1}{3}+x, \frac{1}{3}-z$; (iv) $1-x, -x+y, \frac{1}{2}-z$; (v) $1-x+y, -x, z$.

Compound (II)

Crystal data

$Ca_{3.34}Mg_{0.66}IrO_6$
$M_r = 438.16$
Trigonal, $R\bar{3}c$
$a = 9.2876$ (4) Å
$c = 11.0200$ (8) Å
$V = 823.23$ (8) Å^3
$Z = 6$
$D_x = 5.303$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1830 reflections
$\theta = 3.1$–$33.1°$
$\mu = 27.49$ mm^{-1}
$T = 293$ (2) K
Rhombohedron, black
0.10 × 0.06 × 0.05 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.104$, $T_{max} = 0.137$
2382 measured reflections
350 independent reflections
326 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 33.1°$
$h = -9 \rightarrow 14$
$k = -13 \rightarrow 12$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.034$
$S = 1.09$
350 reflections
20 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.19$ e Å^{-3}
$\Delta\rho_{min} = -1.13$ e Å^{-3}

Table 2
Selected bond distances (Å) for (II).

Ca1—O^{i} (× 2)	2.3590 (19)	Mg—O^{v} (× 6)	2.2310 (19)
Ca1—O^{ii} (× 2)	2.4967 (19)	Mg—Ir (× 2)	2.7550 (2)
Ca1—O^{iii} (× 2)	2.5301 (19)	Ir—O (× 6)	2.0128 (18)
Ca1—O^{iv} (× 2)	2.689 (2)		

Symmetry codes: (i) $\frac{2}{3}-x+y, \frac{1}{3}+y, z-\frac{7}{6}$; (ii) $\frac{1}{3}+x-y, \frac{2}{3}-y, -z+\frac{7}{6}$; (iii) $\frac{1}{3}-y, \frac{2}{3}-x, z-\frac{5}{6}$; (iv) $\frac{1}{3}-x, \frac{2}{3}-x+y, -z+\frac{7}{6}$; (v) $-y, -x, z-\frac{1}{2}$.

Compound (III)

Crystal data

$Ca_{3.50}Zn_{0.50}IrO_6$	Mo $K\alpha$ radiation
$M_r = 461.17$	Cell parameters from 1927 reflections
Trigonal, $R\overline{3}c$	$\theta = 4.4–36.3°$
$a = 9.2641$ (3) Å	$\mu = 29.82$ mm^{-1}
$c = 11.0298$ (5) Å	$T = 293$ (2) K
$V = 819.79$ (5) Å^3	Block, black
$Z = 6$	0.10 × 0.06 × 0.05 mm
$D_x = 5.605$ Mg m^{-3}	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	448 independent reflections
ω scans	398 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)	$R_{int} = 0.034$
$T_{min} = 0.171$, $T_{max} = 0.344$	$\theta_{max} = 36.3°$
2889 measured reflections	$h = -14 \rightarrow 7$
	$k = -10 \rightarrow 15$
	$l = -10 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.077$	$\Delta\rho_{max} = 4.57$ e Å^{-3}
$S = 1.13$	$\Delta\rho_{min} = -3.54$ e Å^{-3}
448 reflections	
19 parameters	

Table 3
Selected bond distances (Å) for (III).

Ir—O^{i} (×6)	2.012 (3)	Ca1—O^{iv} (× 3)	2.536 (3)
Ir—Zn (×3)	2.75745 (13)	Ca1—O^{v} (× 3)	2.675 (3)
Ca1—O^{ii} (×3)	2.349 (3)	Zn—O^{vi} (× 5)	2.223 (3)
Ca1—O^{iii} (×3)	2.501 (3)		

Symmetry codes: (i) $1-y, 2+x-y, z$; (ii) $\frac{4}{3}-x, \frac{5}{3}-y, \frac{2}{3}-z$; (iii) $1+x, y, z$; (iv) $y, -x+y, 1-z$; (v) $-x+y, 1-x, z$; (vi) $-x, -x+y, \frac{1}{2}-z$.

The patterns of systematic absences in the data confirmed a *c*-glide operation, indicating the space groups $R3c$ and $R\overline{3}c$. Preliminary powder X-ray diffraction showed the compounds to be isostructural with K_4CdCl_6 (space group $R\overline{3}c$). Therefore, the expected centrosymmetric space group was chosen and confirmed by the solution of the structures. The structure solution and refinement of compound (I) proceeded without incident, and all atomic positions were found to be fully occupied by the constituent atoms. However, refinement of compound (II) using a fully occupied Ca_3MgIrO_6 model resulted in an isotropic displacement parameter value of zero for the Mg atom in the trigonal prismatic site (Wyckoff symbol 6*a*). Previous reports of quaternary calcium iridium oxides have shown mixing of alkaline earth cations and the metal on the trigonal prismatic site (Claridge *et al.*, 1998), and therefore this model was adopted for (II). The final refinement yielded site-occupancy factors (SOFs) of 0.662 (10) for Mg and 0.338 (10) for Ca on the 6*a* site. Both the SOFs and anisotropic displacement parameters for these atoms could be refined simultaneously, subject to the constraints that the total SOF was equal to 1.0 and that the anisotropic displacement parameters for both atoms were set equal. Similar mixing on the trigonal prismatic site was also observed for compound (III). Values for the SOF of 50% Zn and 50% Ca on the trigonal prismatic site were obtained from refinement with isotropic displacement parameters. However, since even constrained simultaneous refinement of the SOFs with the anisotropic displacement factors proved unstable, the SOF values were fixed at 50% Ca and 50% Zn before the final anisotropic refinement was completed. The largest difference peaks for the three compounds were 3.25 e Å^{-3} for (I), 2.19 e Å^{-3} for (II) and 4.57 e Å^{-3} for (III), all located less than 0.8 Å from Ir.

For all compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1140). Services for accessing these data are described at the back of the journal.

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