Iranite, $\text{CuPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2(\text{OH})_2$, isomorphous with hemihedrite

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This study presents the first structural report of iranite, ideally $\text{CuPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2(\text{OH})_2$ [copper decalead hexachromate bis(orthosilicate) dihydroxide], based on single-crystal X-ray diffraction data. Iranite is isomorphous with hemihedrite, with substitution of Cu for Zn and OH for F. The Cu atom is situated at the special position with site symmetry 1. The CrO$_4$ and SiO$_4$ tetrahedra and CuO$_4$(OH)$_2$ octahedra form layers that are parallel to (120) and are linked together by five symmetrically independent Pb$^{2+}$ cations displaying a rather wide range of bond distances. The CuO$_4$(OH)$_2$ octahedra are corner-linked to two CrO$_4$ and two SiO$_4$ groups, while two additional CrO$_4$ groups are isolated. The mean Cr—O distances for the three nonequivalent CrO$_4$ tetrahedra are all slightly shorter than the corresponding distances in hemihedrite, whereas the CuO$_4$(OH)$_2$ octahedron is more distorted than the ZnO$_4$F$_2$ octahedron in hemihedrite in terms of octahedral quadratic elongation.

Comment

Iranite was first discovered in Sébarz, Anarak (central Iran), and incorrectly described as a lead chromate with chemical formula PbCrO$_4$·H$_2$O (Bariand & Herpin, 1963). Adib & Ottemann (1970) reported several new lead chromates from Iran, one of which was called khuniite, with chemical formula (Pb$_{1.6}$Zn$_{0.2}$Cu$_{0.2}$)CrO$_5$. However, further studies of khuniite by Adib et al. (1972) suggested a new chemical formula, viz. Pb$_4$(Cu,Zn)(CrO$_4$)$_6$SiO$_4$, for this mineral. Concurrently, the new mineral hemihedrite, ZnPb$_{10}$(CrO$_4$)$_6$(SiO$_4$)$_2$F$_2$, was discovered (Williams & Anthony, 1970) and its crystal structure reported (McLean & Anthony, 1970). Fleischer (1973) noted that the chemical formula given by Adib et al. (1972) for khuniite was not charge-balanced and that this mineral might be isostructural with hemihedrite on the basis of similar X-ray powder diffraction data. A re-examination of the type mineral of iranite by Williams (1974) showed that it was probably the Cu analog of hemihedrite and that khuniite was misidentified and is actually iranite. A synthetic hydroxide analogue of iranite and synthetic hemihedrite were found to have the formulae $\text{CuPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2(\text{OH})_2$ and $\text{ZnPb}_{10}(\text{CrO}_4)_6(\text{SiO}_4)_2(\text{OH})_2$, respectively, and analyses of natural materials indicated that there is probably a solid solution between the two minerals (Cesbron & Williams, 1980; Bariand & Poullen, 1980). While the crystal structure of hemihedrite was determined by McLean & Anthony (1970), the crystal structure of iranite remained undetermined until now. This paper reports the first structural refinement of natural iranite based on single-crystal X-ray diffraction data.

Iranite is isotypic with hemihedrite, with substitution of Cu for Zn and OH for F. The view down the [211] direction (Fig. 1) demonstrates that iranite can be regarded as a layered structure of CrO$_4$ and SiO$_4$ tetrahedra, along with CuO$_4$(OH)$_2$ octahedra that lie parallel to (120) and are linked together by five symmetrically independent Pb$^{2+}$ cations. Within a polyhedral layer, each CuO$_4$(OH)$_2$ octahedron shares opposite corners with two SiO$_4$ tetrahedra as well as opposite corners with two CrO$_4$ tetrahedra, while the two OH groups are oriented towards the Pb layer. The CrO$_4$ and Cr$_2$O$_4$ tetrahedra are isolated in the polyhedral layer (Fig. 2). Owing mostly to the Jahn–Teller effect of Cu$^{2+}$, the Cu$^{2+}$—O$^{11}$ bond length [$2.290$ (5) Å] in iranite is longer than the Zn—O$^{11}$ length ($2.17$ Å) in hemihedrite, whereas the Cu$^{2+}$—O$^{17}$ bond distance [$1.950$ (5) Å] is shorter than the Zn—F distance ($2.05$ Å). As a consequence, the CuO$_4$(OH)$_2$ octahedron in iranite is more distorted ($1.0150$) than the ZnO$_4$F$_2$ octahedron ($1.0075$) in hemihedrite in terms of the octahedral quadratic elongation (Robinson et al., 1971). The mean Cr—O distances for the Cr$_1$, Cr$_2$ and Cr$_3$ tetrahedra are $1.640$, $1.650$ and $1.648$ Å, respectively, which are all slightly shorter than the corresponding mean distances ($1.659$, $1.662$ and $1.658$ Å) in hemihedrite (McLean & Anthony, 1970) but are comparable to most values in the literature, such as those reported for tarapacaite (K$_2$CrO$_4$; $1.643$ Å; McGinney, 1972), lopezite...
(K₂Cr₂O₇; ~1.65 Å; Brunton, 1973), dietzeite [Ca₃(PO₄)₂·
CrO₄·H₂O; 1.647 Å; Burns & Hawthorne, 1993] and edoylerite
(Hg₂CrO₄·S₂; 1.643 Å; Burns, 1999). Within 3.2 Å, the coordi-
nation numbers of the five nonequivalent Pb²⁺ cations vary
from 7 to 9.

There have been considerable discussions about the effects
of F—OH substitution on the crystal structures and prop-
eties of minerals (e.g. Groat et al., 1990; Cooper & Hawthorne,
1995; Yang et al., 2007). For some minerals, the OH and F members may form a complete solid solution, such as
for the amblygonite [LiAl(PO₄)F]—montebrasite [LiAl-
(PO₄)(OH)] and fluorapatite [Ca₅(PO₄)₃F]—hydroxylapatite
[Ca₅(PO₄)₃(OH)] series. However, there are also many examples in which F—OH substitution results in structural
transformations or symmetry changes, such as the cases
between transformations or symmetry changes, such as the examples in which F—OH substitution results in structural
between the hemihedrite–iranite series.

Experimental

The iranite specimen used in this study is from Chapacase mine,
Sierra Cerillos district, Tocopilla, Chile, and is in the collection of the
RRUFF project (deposition No. R060781; http://rruff.info), donated
by Mike Scott. The average chemical composition of the studied
sample, viz. CuPb₁₀[(Cr₀.⁹⁹⁹][⁰.⁰⁰¹)]₂(OH)(OH)₀·₃3 [O₃(PO₄)(OH)₀·₃₃] [SiO₄]₂(OH)₂,
determined with a CAMECA SX50 electron microprobe (http://
rruff.info).

Crystal data

CuPb₁₀(CrO₄)₆(SiO₄)₂(OH)₂
Mᵣ = 3049.64
Triclinic, P₁
a = 9.5416 (4) Å
b = 11.3992 (5) Å
c = 10.7465 (4) Å
α = 120.472 (2)°
β = 112.300°
ν = 56.58 mm⁻¹
T = 293 (2) K
\( \mu = 55.531 \) (2)
\( \rho = 7.0086 \) (6) Å³
\( \chi(T) = 1 \)
\( \omega = 0.05 \times 0.05 \times 0.04 \) mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan
(SADABS; Sheldrick, 2005)
\( T_{\text{min}} = 0.083, T_{\text{max}} = 0.104 \)
\( T_{\text{min}} = 0.083, T_{\text{max}} = 0.104 \)

Refinement

\( R(F²) = 0.034 \)
\( wR(F²) = 0.070 \)
\( S = 1.01 \)
\( \Delta θ_{\text{max}} = 3.50 \) e Å⁻³
\( \Delta θ_{\text{max}} = 3.50 \) e Å⁻³

The H atoms were not located in the final difference Fourier
syntheses. The chemical analysis showed a little deficiency in Cr when
compared with the ideal value of six per chemical formula, but the
refinement assumed an ideal chemistry, as the overall effects of such a
small amount of vacancy on the final structure results are negligible.
The highest residual peak in the difference Fourier map was located
0.71 Å from atom Pb4 and the deepest hole was located 0.88 Å from
Pb2.

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT
(Bruker, 2005); data reduction: SAINT; program(s) used to solve
structure: SHELX97 (Sheldrick, 1997); program(s) used to refine
structure: SHELXL97 (Sheldrick, 1997); molecular graphics: Xtal-
Draw (Downs & Hall-Wallace, 2003); software used to prepare
material for publication: SHELXTL (Bruker, 1997).
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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3032). Services for accessing these data are described at the back of the journal.

References
