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GEORGEROBINSONITE, $Pb_4(CrO_4)_2(OH)_2FCl$, A NEW CHROMATE MINERAL FROM THE MAMMOTH – ST. ANTHONY MINE, TIGER, PINAL COUNTY, ARIZONA: DESCRIPTION AND CRYSTAL STRUCTURE

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Abstract

Georgerobinsonite, $Pb_4(CrO_4)_2(OH)_2FCl$, is a new chromate mineral species from the Mammoth – St. Anthony mine, Tiger, Pinal County, Arizona. It occurs as minute intergrowths of thin tabular orange crystals less than 0.1 mm across with {001} dominant and minor {010} and {110}, associated with caledonite, a cerchiaraite-related mineral, cerussite, diaboleite, Cr-bearing leadhillite, matlockite, murdochite, pinalite, wulfenite and yedlinite, in vugs in a silicified matrix. Georgerobinsonite is orange-red, transparent and has a pale orange streak and an adamantine luster, and it does not fluoresce under ultraviolet light. No cleavage or parting was observed. The Mohs hardness is 2½–3; georgerobinsonite is brittle with an uneven fracture. The calculated density is 6.23 g/cm^3. The indices of refraction are $\alpha \approx 2.07$, $\beta > 2.11$, $\gamma > 2.11$; $2V$(obs) = 84(2)°; it is strongly pleochroic, α orange, γ yellow; optical orientation: $X = \mathbf{a}$, $Y = \mathbf{c}$ and $Z = \mathbf{b}$, and the dispersion is strong with $r > v$. Georgerobinsonite is orthorhombic, space group *Pmmn*, *a* 7.613(2), *b* 11.574(3), *c* 6.883(2) Å, *V* 606.5(3) Å^3, *Z* = 2, *a*:*b*:*c* = 0.6578:1:0.5947. The strongest six lines in the X-ray powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 2.131(100)(232), 3.308(80)(012), 3.195(80)(211, 220), 6.371(60) (110), 3.357(60)(031, 201) and 3.143(60)(102). Chemical analysis with an electron microprobe gave CrO_3 14.79, PbO 77.99, SO_3 1.64, F 1.47, Cl 3.39, H_2O (calc.) 1.52, sum 99.42 wt.%; the valence states of Pb, Cr and S, and the amount of H_2O, were determined by crystal-structure analysis. The resulting empirical formula, on the basis of 12 (O, F, Cl, OH) anions, is $Pb_{4.09}(Cr^{6+}_{1.73}S^{6+}_{0.24})_{\Sigma 1.97}\,O_8\,(OH)_{1.98}\,F_{0.90}\,Cl_{1.12}$. The crystal structure of georgerobinsonite was solved by direct methods and refined to an R_1 index of 2.0% based on 574 observed reflections collected on a four-circle diffractometer with Mo$K\alpha$ X-radiation. There are two Pb^{2+} cations coordinated by eight and nine anions, and both show prominent lone-pair stereoactive behavior. The Pb polyhedra share faces and edges to form layers parallel to {001} that are linked into a heteropolyhedral framework by (CrO_4) groups, with hydrogen bonding between OH and Cl anions. The mineral is named after Dr. George Willard Robinson (b. 1946), mineral curator, researcher, teacher and field collector.

Keywords: georgerobinsonite, new mineral species, chromate, crystal structure, Mammoth – St. Anthony mine, Tiger, Pinal County, Arizona.

Sommaire

Nous décrivons la georgerobinsonite, $Pb_4(CrO_4)_2(OH)_2FCl$, un chromate, nouvelle espèce minérale provenant de la mine Mammoth – St. Anthony, à Tiger, comté de Pinal, en Arizona. Elle se présente en infîmes intercroissances de minces cristaux tabulaires orangés ayant une largeur inférieure à 0.1 mm, avec les formes {001} dominante, et {010} et {110} mineures, associés à la calédonite, un minéral lié à la cerchiaraïte, cérussite, diaboléite, leadhillite chromifère, matlockite, murdochite, pinalite,

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wulfenite et yedlinite, dans les cavités d'une matrice silicifiée. La georgerobinsonite est orange-rouge, transparente, avec une rayure orange pâle et un éclat adamantin; elle ne montre aucune fluorescence sous la lumière ultraviolette. Nous n'avons décelé aucun clivage ou plan de séparation. La dureté de Mohs est égale à 2½–3; la georgerobinsonite est cassante, avec une fracture inégale. La densité calculée est 6.23 g/cm^3. Les indices de réfraction sont $\alpha \approx 2.07$, $\beta > 2.11$, $\gamma > 2.11$; $2V$(obs) = 84(2)°. Le minéral est fortement pléochroïque, α orange, γ jaune; l'orientation optique est: $X = \mathbf{a}$, $Y = \mathbf{c}$ et $Z = \mathbf{b}$, et la dispersion est forte, avec $r > v$. La georgerobinsonite est orthorhombique, groupe spatial *Pmmn*, *a* 7.613(2), *b* 11.574(3), *c* 6.883(2) Å, *V* 606.5(3) Å^3, $Z = 2$, $a:b:c$ = 0.6578:1:0.5947. Les six raies les plus intenses du spectre de diffraction X, méthode des poudres [*d* en Å(*I*)(*hkl*)] sont: 2.131(100)(232), 3.308(80)(012), 3.195(80)(211, 220), 6.371(60)(110), 3.357(60)(031, 201) et 3.143(60)(102). Une analyse chimique effectuée avec une microsonde électronique a donné CrO_3 14.79, PbO 77.99, SO_3 1.64, F 1.47, Cl 3.39, H_2O (calc.) 1.52, pour un total de 99.42% (poids); les valences de Pb, Cr et S, et la quantité de H_2O, ont été établies par analyse structurale. La formule empirique qui en résulte, calculée sur une base de 12 anions (O, F, Cl, OH), est $Pb_{4.09}(Cr^{6+}_{1.73}S^{6+}_{0.24})_{\Sigma 1.97}O_8(OH)_{1.98}F_{0.90}Cl_{1.12}$. La structure de la georgerobinsonite a été résolue par méthodes directes et affinée jusqu'à un résidu R_1 de 2.0% en utilisant 574 réflexions observées prélevées avec un diffractomètre à quatre cercles et un rayonnement Mo$K\alpha$. Il y a deux cations Pb^{2+} en coordinence avec huit et neuf anions, et les deux ont un comportement dû aux paires d'électrons stéréoactifs isolés. Les polyèdres Pb partagent des faces et des arêtes pour former des couches parallèles à {001} liées en trame hétéropolyédrique par des groupes CrO_4, avec liaisons hydrogène impliquant anions OH et Cl. Le minéral met à l'honneur George Willard Robinson (né en 1946), conservateur, chercheur, professeur et collectioneur averti.

(Traduit par la Rédaction)

Mots-clés: georgerobinsonite, nouvelle espèce minérale, chromate, structure cristalline, mine Mammoth – St. Anthony, Tiger, comté de Pinal, Arizona.

INTRODUCTION

In the early 1970s, one of the authors (WHP) obtained the specimen that contains the new mineral species through an exchange with the late Prof. Dr. Heinrich Meixner, at that time Director of the Institute of Mineralogy and Petrography, University of Salzburg, Austria. Several years ago, re-examination of this specimen revealed the presence of an orange-red mineral (= georgerobinsonite) in very minor amounts. On the basis of the platy habit of the tiny crystals, the mineral was macroscopically identified as possibly wulfenite, already known from the deposit. However, no attempt was made to confirm this visual determination by other methods. Recently, a few fragments were extracted from the specimen and examined by X-ray powder-diffraction methods. The results strongly suggested a new mineral species, and this was confirmed by further work. The new mineral and mineral name were approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2009–068). The mineral is named *georgerobinsonite* after Dr. George Willard Robinson (born 1946), Curator, A.E. Seaman Mineral Museum, and Professor, Geological Engineering and Sciences, Michigan Technological University, Houghton, Michigan, an internationally renowned curator, researcher, teacher and field collector who has contributed to the descriptions of nine new mineral species. The electron-microprobe mount has been deposited in the mineral collection of the Royal Ontario Museum, Toronto, Ontario, under catalogue number M54947. The holotype specimen (7 × 8 × 3 cm) carries the (old) number "M 117". It was obtained in the 1950s by exchange from C. Frondel (Harvard University) and is held by one of the co-authors (WHP), and registered as #636–379 in his systematic mineral collection.

SAMPLE PROVENANCE

The specimen is reportedly from the Mammoth – St.Anthony mine, Tiger, Pinal County, Arizona. This mine is ~5 km southwest of the town of Mammoth, and operated between 1889 and 1953, producing gold, silver, molybdenum, lead, zinc and vanadium. A series of fault-controlled veins with sulfide mineralization have been oxidized to considerable depth, giving rise to a spectacular suite of secondary oxysalt minerals (Bideaux 1980).

The history of the specimen with the new mineral species is remarkable and should be summarized here. It carries the number M 117, written in black ink on a white label. Numerous attempts were made by one of the authors (WHP) to locate the collection from which the specimen originated. Dr. Carl A. Francis, Harvard Mineralogical Museum, explained the possible origin of the specimen. The "M" on the specimen containing georgerobinsonite stands for Dan Mayers, a graduate student at the Department of Mineralogy at Harvard from 1946 to 1949. He had attended the University of Arizona, College of Mines, during the period 1943 to 1944 and had made regular weekend visits to the Mammoth mine to collect mineral specimens. He is the probable source of the bulk of Mammoth mineral specimens distributed to collectors and museums throughout the World. During his stay in Arizona, most of the mining at Tiger was done at those levels of the Collins vein where so many exotic minerals, classified as the "anomalous sequence" by Bideaux (1980), were found. Dan Mayers donated much of his material from

Tiger to the Department of Mineralogy at Harvard. The specimen with the new mineral species was acquired in the 1950s by the late Prof. H. Meixner as part of an exchange with Prof. C. Frondel, at that time curator of the mineral collections at Harvard. A recent contact with Mr. Dan Mayers, who currently resides in Idaho, confirmed the source of the specimen. However, he was unable to provide any further information about the location of the specimen within the mine.

Physical and Optical Properties

The holotype specimen measures 9 × 7 × 3 cm and weighs 182 grams. It also contains pinalite (Dunn *et al.* 1989), yedlinite (McLean *et al.* 1974) and an unnamed cerchiaraite-related mineral, all of which are very rare mineral species known only from Tiger. The strongly silicified matrix of the specimen contains numerous irregularly shaped vugs up to 10 mm across, occasionally containing elongate crystals of cerussite. Other cavities have abundant tablets of diaboleite, locally encrusted with clusters of mm-sized rectangularly shaped crystals of matlockite. Two vugs in the type specimen contain sprays of twinned pinalite crystals, and one vug carries tiny crystals of yedlinite. Grass-green caledonite, small (less than 1 mm) octahedral crystals of murdochite, and rare wulfenite also occur in this specimen. Georgerobinsonite occurs at three different places on the specimen. The most prominent area is 4 × 4 mm where georgerobinsonite is intimately associated with yellowish green leadhillite (which also is abundant in other vugs on the specimen). The second area contains isolated crystals of georgerobinsonite (Fig. 1) in a tiny vug, associated with quartz crystals. At the third location, georgerobinsonite is associated with leadhillite. The total weight of georgerobinsonite on this specimen is less than 0.01 μg.

According to the description of the mineralogy of this deposit (Bideaux 1980), the silicification of the specimens and mineral associations are strong evidence for it originating from the Collins vein (500 level), possibly from the east wall of the main haulage tunnel. This assumption is supported by the siliceous matrix and the green (not blue) color of the associated caledonite, which is typical for that location (Bideaux 1980).

Crystals of georgerobinsonite may be isolated or occur as fan-like clusters. Georgerobinsonite is transparent, orange-red (Fig. 1), similar to Cr-bearing wulfenite for which it may be mistaken, and has a pale orange streak and an adamantine luster, and it does not fluoresce under ultraviolet light. Crystals are small (less than 0.10 mm) and have a thin tabular habit (Fig. 2), with {001} dominant and minor {010} and {110}. Georgerobinsonite is brittle with an uneven fracture, and no cleavage or parting was observed. The Mohs hardness is estimated to be between 2½ and 3. The density could not be measured because of the extremely small size of the crystals. The calculated density (based on the empirical formula) is 6.23 g/cm^3, slightly higher than that of yedlinite. Georgerobinsonite is associated with caledonite (minor), a cerchiaraite-related mineral (trace), cerussite (major), diaboleite (major), Cr-bearing leadhillite (common), matlockite (common), murdochite (trace), pinalite (trace), wulfenite (trace) and yedlinite (trace), all in vugs in a silicified matrix. The indices of refraction (λ = 590 nm) are $\alpha \approx 2.07$, $\beta > 2.11$, $\gamma > 2.11$; $2V$(obs) = 84(2)°; georgerobinsonite is strongly pleochroic, $\alpha = \beta$ orange, γ yellow. The optical orientation is $X = \mathbf{a}$, $Y = \mathbf{c}$ and $Z = \mathbf{b}$, and the dispersion is strong, with $r > v$.

Chemical Composition

Crystals were analyzed with a Cameca SX–100 electron microprobe operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 10 μm. The following standards were used: PbTe (Pb), chromite (Cr), barite (S), fluorapatite (F), tugtupite (Cl); Ca, V, As, Mo and W were sought and are below detection limits. The data were reduced and corrected by the PAP method of Pouchou & Pichoir (1985). The presence and quantity of (OH) were established by crystal-structure solution and refinement. In addition, infrared spectroscopy indicated a broad intense band centered at ~3310 cm^{-1}, and a lack of any band in the region of 1630 cm^{-1} indicative of H_2O. Table 1 gives the chemical composition (mean of five determinations) and formula unit based on 12 (O, OH, F, Cl) anions [including two (OH) groups per formula unit (*pfu*)]. The empirical formula for georgerobinsonite is $Pb_{4.09}(Cr^{6+}_{1.73}S_{0.24})_{\Sigma 1.97}O_8(OH)_{1.98}F_{0.90}Cl_{1.12}$, and the end-member formula is $Pb_4(CrO_4)_2(OH)_2FCl$.

X-Ray Powder Diffraction

The powder-diffraction pattern of georgerobinsonite (Table 2) was recorded with Ni-filtered Cu$K\alpha$ X-radiation (λ = 1.54178 Å) and a 114.6 mm diameter Debye–Scherrer camera. The intensities were visually estimated, and the data were not corrected for shrinkage, nor was there an internal standard. The unit-cell parameters were refined by least squares, giving the following values: a 7.613(2), b 11.574(3), c 6.883(2) Å, V = 606.5(3) Å^3, Z = 2, a:b:c = 0.6578:1:0.5947.

TABLE 1. CHEMICAL COMPOSITION OF GEORGEROBINSONITE

PbO wt%	77.99(27)	H_2O*	1.52
CrO_3	14.79(11)	O=F	–0.62
SO_3	1.64(17)	O=Cl	–0.76
F	1.47(3)		
Cl	3.39(1)	Total	99.42

* assuming 2(OH) groups *pfu.*

FIG. 1. Georgerobinsonite (orange) in a vug, associated with quartz; the size of the aggregate of georgerobinsonite is ~0.10 mm across.

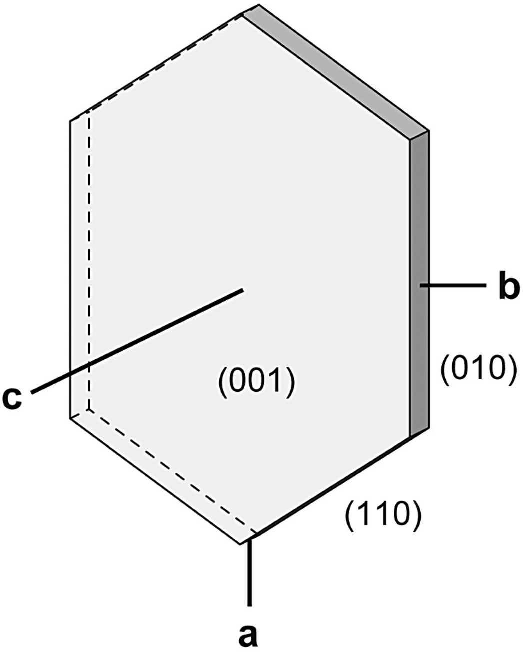

FIG. 2. Crystal drawing of georgerobinsonite showing the habit and crystal forms.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR GEORGEROBINSONITE

I_{est}	d_{meas} Å	d_{calc} Å	h	k	l	I_{est}	d_{meas} Å	d_{calc} Å	h	k	l
20	6.889	6.883	0	0	1	* 10	2.250	2.251	0	1	3
60	**6.371**	**6.360**	**1**	**1**	**0**	15	2.196	2.197	1	0	3
10	5.791	5.787	0	2	0			2.194	0	5	1
20	5.118	5.106	1	0	1	5	2.162	2.158	1	1	3
20	4.677	4.671	1	1	1	* **100**	**2.131**	**2.129**	**2**	**3**	**2**
50	4.445	4.430	0	2	1	* 20	2.040	2.042	3	0	2
3	3.802	3.807	2	0	0	* 40	1.972	1.972	0	3	3
* 30	3.443	3.441	1	3	0	* 50	1.936	1.937	2	1	3
60	**3.357**	**3.365**	**0**	**3**	**1**	* 30	1.905	1.903	4	0	0
		3.331	**2**	**0**	**1**	5	1.840	1.839	3	4	1
* **80**	**3.308**	**2.999**	**0**	**1**	**2**	* 15	1.804	1.805	1	6	1
80	**3.195**	**3.201**	**2**	**1**	**1**	* 10	1.748	1.749	4	2	1
		3.180	**2**	**2**	**0**	10	1.720	1.721	0	0	4
* **60**	**3.143**	**3.136**	**1**	**0**	**2**			1.715	2	5	2
* 30	3.079	3.078	1	3	1	3	1.699	1.702	0	1	4
1	3.023	3.027	1	1	2			1.702	3	0	3
* 10	2.959	2.958	0	2	2	* 30	1.670	1.669	2	6	1
* 50	2.889	2.887	2	2	1	20	1.650	1.657	4	3	1
* 20	2.757	2.757	1	2	2			1.649	4	1	2
* 30	2.669	2.667	0	4	1	10	1.626	1.630	0	5	3
* 30	2.517	2.517	1	4	1			1.626	2	4	3
5	2.496	2.493	2	1	2	3	1.601	1.601	4	2	2
1	2.431	2.434	1	3	2	5	1.571	1.573	1	7	1
5	2.377	2.381	3	0	1			1.572	0	3	4
3	2.334	2.336	2	2	2			1.568	2	0	4
		2.332	3	1	1	25	1.553	1.554	2	1	4
* 50	2.302	2.304	2	4	0			1.549	4	4	1

* lines used for refinement of unit-cell dimensions.

INFRARED SPECTROSCOPY

The infrared-powder-absorption spectrum was recorded using a Hyperion 2000 microscope interfaced to a Bruker Tensor 27 spectrometer in the range 4000–430 cm^{-1} (Fig. 3). In the principal OH-stretching region (3800–3000 cm^{-1}), the spectrum shows a prominent absorption at ~3310 cm^{-1} in accord with a single OH group in the structure. The lack of any significant absorption in the 1630 cm^{-1} region is in accord with the absence of any H_2O in the proposed chemical formula. Other absorptions at 1200–700 cm^{-1} are attributable to symmetric and asymmetric vibrations of the (CrO_4) group.

CRYSTAL-STRUCTURE SOLUTION AND REFINEMENT

A crystal of georgerobinsonite was attached to a glass fiber and mounted on a Bruker *P*4 diffractometer equipped with an Apex CCD detector and graphite-monochromated Mo*K*α X-radiation. A total of 7947 reflections was measured out to 50° 2θ using 60 s per 0.2° frame, with a crystal-to-detector distance of 5 cm. Unit-cell dimensions were determined by least-squares refinement of 4040 reflections $I > 10\sigma I$, and are given in Table 3, together with other information pertaining to data collection and structure refinement. Of the 615 unique reflections, 574 reflections were considered as observed [$\lvert F\text{o}\rvert > 4\sigma\lvert F\rvert$]. Absorption corrections were done using the program SADABS (Sheldrick 1998). The data were then corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors.

All calculations were done with the SHELXTL PC (Plus) system of programs; *R* indices are of the form given in Table 3 and are expressed as percentages. Systematic absences in the single-crystal X-ray diffraction data are consistent with space group *Pmmn*, and the structure was solved with this symmetry by direct methods and refined by full-matrix least-squares to an R_1 index of 2.0%. At the final stages of refinement, one H (hydrogen) site was identified in difference-Fourier maps approximately 1 Å from the O(4) anion and was inserted into the refinement. The O(donor)–H distance was softly constrained to be close to 0.98 Å during refinement. Refined coordinates and anisotropic-displacement parameters of the atoms are listed in Table 4, selected interatomic distances are

TABLE 3. MISCELLANEOUS INFORMATION ABOUT GEORGEROBINSONITE

a (Å)	7.6256(6)	Crystal size (μm)	80 × 50 × 10
b	11.6081(9)	Radiation	Mo*K*α
c	6.8961(5)	No. of reflections	7947
V (Å^3)	610.43(14)	No. in Ewald sphere	3684
Space group	*Pmmn*	No. unique reflections	615
Z	2	No. $\lvert F_o\rvert > 4\sigma\lvert F\rvert$	574
		R_{merge} %	2.9
		R_1 %	2.0
		wR_2 %	4.6

Cell content: $2[Pb_4(Cr^{6+}O_4)_2(OH)_2FCl]$
$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{½}$.

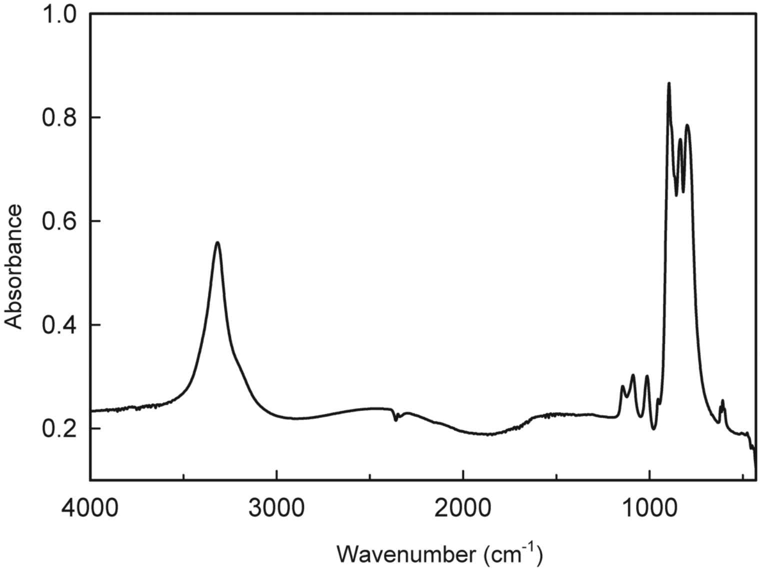

FIG. 3. The infrared spectrum of georgerobinsonite.

TABLE 4. POSITIONS AND DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN GEORGEROBINSONITE

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	¼	0.59690(4)	0.12642(7)	0.02183(15)	0.0256(2)	0.0233(3)	0.0166(3)	–0.0031(2)	0	0
Pb(2)	0.50242(6)	¼	0.41670(7)	0.02025(14)	0.0147(2)	0.0239(3)	0.0221(3)	0	–0.00089(18)	0
Cr	¼	0.49812(15)	0.6485(3)	0.0129(7)	0.0134(10)	0.0135(11)	0.0117(11)	–0.0015(8)	0	0
Cl*	¼	0.2284(5)	0.0720(8)	0.0217(13)						
F	¾	¼	0.1327(15)	0.027(2)	0.035(5)	0.034(6)	0.011(5)	0	0	0
O(1)	0.4226(8)	0.5121(5)	0.7804(9)	0.0264(14)	0.023(3)	0.033(3)	0.023(3)	–0.006(3)	–0.003(3)	0.006(3)
O(2)	¼	0.6070(7)	0.4931(13)	0.0232(19)	0.028(4)	0.021(4)	0.021(5)	–0.000(4)	0	0
O(3)	¼	0.3763(7)	0.5289(14)	0.0235(19)	0.023(4)	0.016(4)	0.032(5)	–0.003(4)	0	0
O(4)(OH)	0.4388(10)	¾	0.2306(12)	0.0166(17)	0.014(3)	0.019(4)	0.016(4)	0	–0.001(3)	0
H	0.550(8)	¾	0.159(16)	0.02**						

* site occupancy = 0.5; ** fixed during refinement.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN GEORGEROBINSONITE

Pb(1)–O(1) c,d	2.871(6)	×2	*Pb*(2)–O(1) d,i	3.131(6)	×2
Pb(1)–O(1) e,f	2.898(6)	×2	*Pb*(2)–O(2) d,h	2.590(6)	×2
Pb(1)–O(2)	2.531(9)		*Pb*(2)–O(3) ,g	2.540(5)	×2
Pb(1)–O(4) ,a	2.398(5)	×2	*Pb*(2)–O(4) d	2.473(8)	
Pb(1)–F b	2.520(7)		*Pb*(2)–F	2.721(7)	
Pb(1)–Cl g	3.795(5)		*Pb*(2)–Cl	3.069(4)	
Pb(1)–Cl	4.294(5)				
			Cr–O(1),j	1.608(6)	×2
			Cr–O(2)	1.657(9)	
			Cr–O(3)	1.638(8)	
			<*Cr*–O>	1.628	
		Hydrogen-bonding			
O(4)–H	0.98		H….Cl b	2.22(4)	
O(4)…Cl b	3.170(9)		O(4)–H–Cl b	163(10)	

a: $\bar{x}+½, \bar{y}+3/2, z$; b: $\bar{x}+1, \bar{y}+1, \bar{z}$; c: $x-½, \bar{y}+1, \bar{z}+1$; d: $\bar{x}+1, \bar{y}+1, \bar{z}+1$; e: $\bar{x}+½, y, z-1$; f: $x, y, z-1$; g: $\bar{x}+½, \bar{y}+½, z$; h: $x+½, y-½, \bar{z}+1$; i: $\bar{x}+1, y-½, \bar{z}+1$; j: $\bar{x}+½, y, z$.

TABLE 6. BOND-VALENCE* (*vu*) TABLE FOR GEORGEROBINSONITE

	Pb(1)	*Pb*(2)	*Cr***	H	Σ
O(1)	$0.15^{\times2\downarrow}$ $0.15^{\times2\downarrow}$	$0.10^{\times2\downarrow}$	$1.54^{\times2\downarrow}$		1.94
O(2)	0.31	$0.27^{\times2\downarrow\rightarrow}$	1.35		2.20
O(3)		$0.30^{\times2\downarrow\rightarrow}$	1.42		2.02
O(4)	$0.42^{\times2\downarrow\rightarrow}$	0.35		0.80	1.99
F	$0.27^{\times2\rightarrow}$	$0.15^{\times2\rightarrow}$			0.84
Cl	$0.03^{\times½\downarrow\rightarrow}$ $0.01^{\times½\downarrow\rightarrow}$	$0.23^{\times2\rightarrow}$		$0.20^{\times2\rightarrow}$	0.88
Σ	2.04	2.07	5.85	1.00	

* using curves of Brown (1981) and Brese & O'Keeffe (1991);
** using $Cr_{0.83}S_{0.17}$ from site-occupancy refinement.

given in Table 5, and bond valences are given in Table 6. Structure factors and the digitized infrared spectrum may be obtained from the Depository of Unpublished Data, MAC website [document Georgerobinsonite CM49_865].

CRYSTAL STRUCTURE

Coordination of cations

The single *Cr* site is occupied predominantly by Cr^{6+} that is tetrahedrally coordinated by oxygen anions O(1) ×2, O(2) and O(3) with a <*Cr*–O> distance of 1.628 Å. The formula calculated from the electron-microprobe analysis indicates an occupancy of $Cr^{6+}_{0.88}$ + $S^{6+}_{0.12}$, and site-occupancy refinement gave an occupancy of $Cr^{6+}_{0.83}$ + $S^{6+}_{0.17}$.

There are two *Pb* sites, both of which are occupied by Pb^{2+} cations. The *Pb*(1) site is coordinated by four anions [F, O(2), O(4) ×2] to one side of the site, with *Pb*(1)–Φ (Φ: unspecified ligand) distances from 2.398 to 2.531 Å (Fig. 4a, Table 5). The Pb(1) atom also bonds to four more distant O(1) anions on the opposite side (2.871–2.898 Å). In addition, there is a very long approach to a disordered Cl anion at 3.795 and 4.294 Å beyond the O(1) sites. In Figure 4a, the *Pb*(1), F, O(2) and Cl sites lie on the (100) mirror, and the pairs of O(1) and O(4) anions lie to either side of this mirror. The *Pb*(2) site is coordinated by five anions [O(2) ×2, O(3) ×2, O(4)] on one side of the site, with *Pb*(2)–Φ distances from 2.473 to 2.590 Å (Fig. 4b, Table 5). The Pb(2) atom also bonds to four more distant anions [O(1) ×2, F, Cl] on the opposite side (2.721–3.131 Å). The *Pb*(2), F, O(4) and H sites lie on the (010) mirror, and the pairs of O(1), O(2) and O(3) anions lie to either side of this mirror. Moreover, Cl is disordered off this mirror. The asymmetric coordination of the Pb^{2+} cations indicates that they are both lone-pair stereoactive; details of this behavior in a wide range of compounds have been summarized by Shimoni-Livny *et al.* (1998).

Structure topology

Two *Pb*(1)Φ_8 polyhedra share a triangular face consisting of two (OH) groups and one F anion to form a [$Pb_2\Phi_{13}$] dimer. These dimers link by sharing O–O edges to form an open sheet parallel to {001} that is decorated by (CrO_4) tetrahedra (Fig. 5a). The *Pb*(2) Φ_9 polyhedra share triangular faces, alternately two O atoms and one Cl, and two O atoms and one F, to form columns that extend in the **a** direction and are cross-linked by (CrO_4) tetrahedra to form sheets parallel to {001} (Fig. 5b). These sheets alternate in the **c** direction (Fig. 6) to form a heteropolyhedral framework. Each *Pb*(1) polyhedron shares edges with two *Pb*(1) polyhedra and four *Pb*(2) polyhedra, and each *Pb*(2) polyhedron, in turn, shares faces with two *Pb*(2) polyhedra and edges with four *Pb*(1) polyhedra; in combination with edge and corner-sharing to (CrO_4) tetrahedra, this results in a fairly dense framework.

The OH group and hydrogen bonding

Inspection of the bond-valence table (Table 6) shows that the O(4) anion bonds to two Pb(1) and one Pb(2) cations for an incident bond-valence sum of ~1.2 *vu* (valence units), indicating that O(4) is an OH group. In accord with this conclusion, a small electron-density peak was found ~1 Å from O(4) in the final stages of refinement and was inserted as H into the refinement. The H…Cl distance, 2.22 Å, and the O(4)–H…Cl angle, 163°, indicate a hydrogen bond of medium strength, and Cl is an acceptor of two symmetrically related hydrogen bonds (Tables 5, 6).

Related structures

Yedlinite, which is present on the same sample, was originally described as a chromate, but recent investigation of its crystal structure shows that Cr^{3+} is present in octahedral coordination (McCarthy *et al.* 2006). A listing of the known lead chromate minerals is given in Table 7; the structures of cassedanneite, embreyite and santanaite are still unknown. Both georgerobinsonite and phoenicochroite have a Pb:(XO_4) ratio of 2 (where *X* denotes a tetrahedrally coordinated cation) and both are simple lead chromates without additional cations. In addition to the anions belonging to the (XO_4) groups, some of the minerals in Table 7 contain additional anions {O, (OH), F} that form bonds to Pb (and possibly Cu or Zn). Siidra *et al.* (2008) showed that these additional anions commonly are coordinated by four Pb^{2+} cations to form (OPb_4) tetrahedra that link together to form anion-centered structural units. Similar F-centered (FPb_4) tetrahedra have been described by Krivovichev *et al.* (1998) and Krivovichev & Filatov (1999). Iranite and hemihedrite contain an isolated ($O_2Pb_4CuH_2$) dimer of tetrahedra in which two (OPb_2CuH) tetrahedra share a corner at the Cu atom (Fig. 7a). Fornacite, macquartite and vauquelinite contain an [OPbCuH] chain comprised of ($OPbCu_2H$) tetrahedra that link through their Cu vertices (Fig. 7b). Phoenicochroite contains an [OPb_2] chain comprised of (OPb_4) tetrahedra that share *trans* Pb–Pb edges (Fig. 8a). Georgerobinsonite contains a complex oxy-fluoro- chain, [$O_2FPb_4H_2$], comprised of two (OPb_3H) tetrahedra that share a Pb–Pb edge with each other, and with a neighboring (FPb_4) tetrahedron (Fig. 8b).

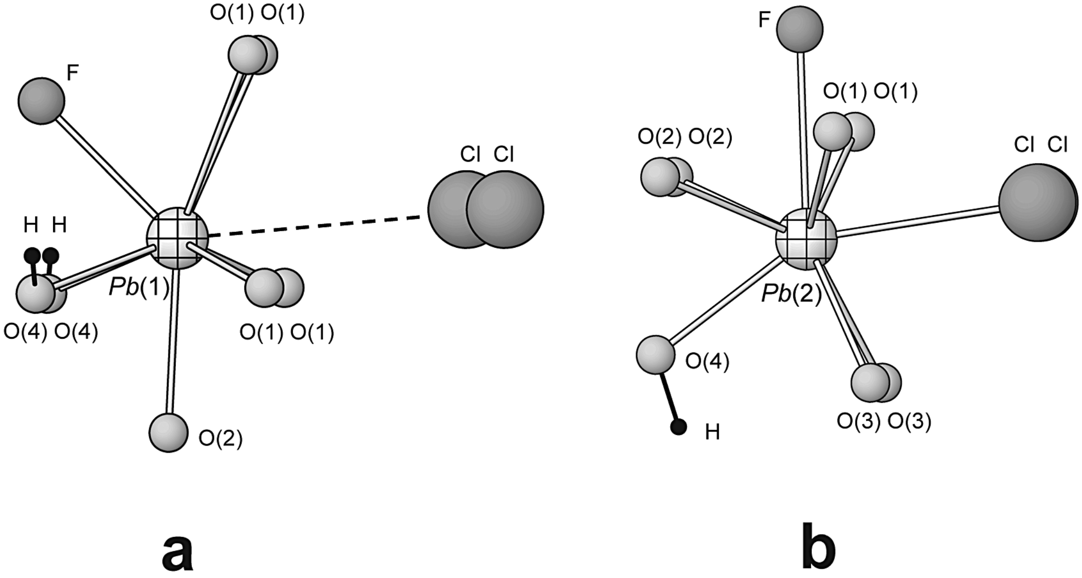

FIG. 4. The coordination of Pb in georgerobinsonite: (a) *Pb*(1); (b) *Pb*(2).

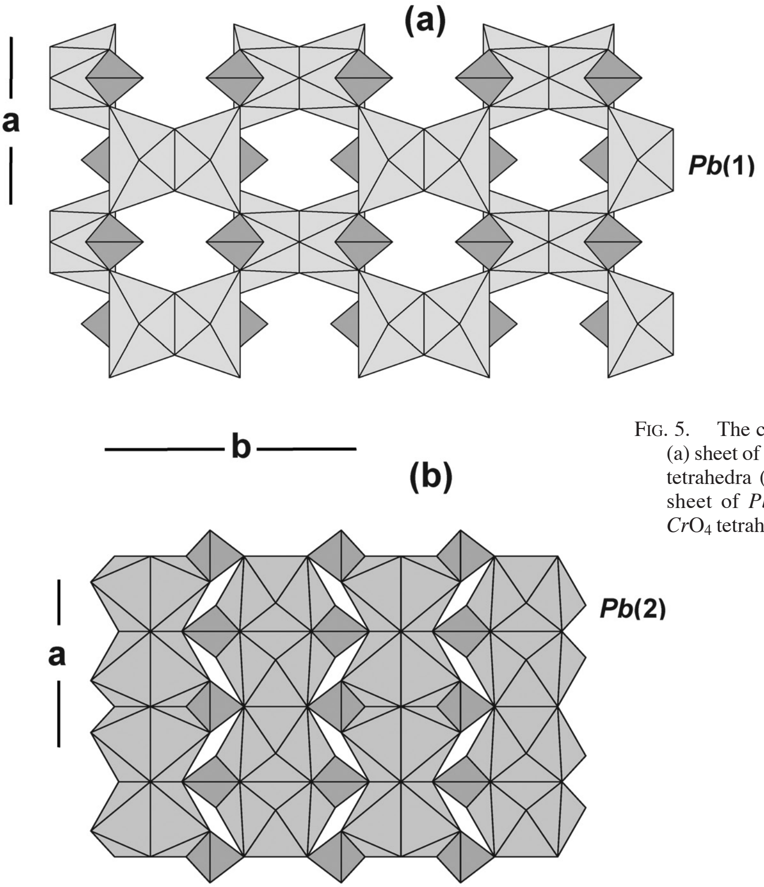

FIG. 5. The crystal structure of georgerobinsonite: (a) sheet of *Pb*(1) polyhedra (pale grey) and CrO_4 tetrahedra (dark grey) projected onto (001); (b) sheet of *Pb*(2) polyhedra (medium grey) and CrO_4 tetrahedra (dark grey) projected onto (001).

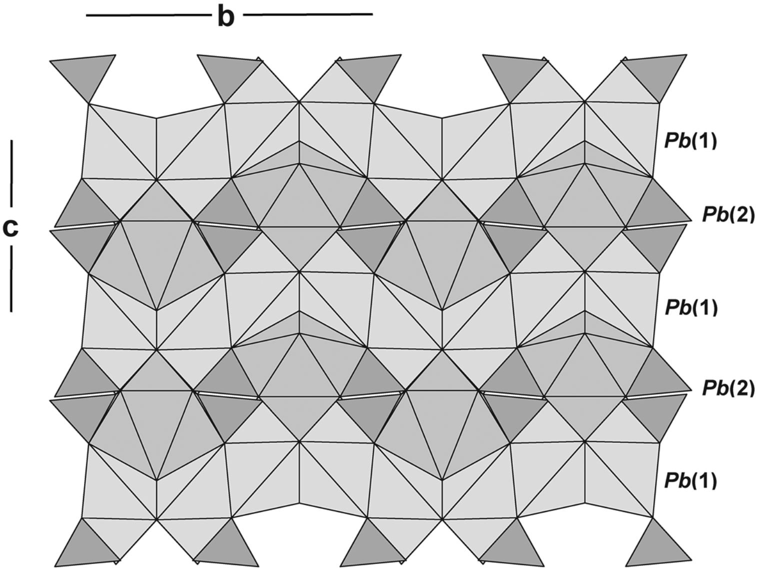

FIG. 6. The crystal structure of georgerobinsonite projected onto (100); legend as in Figure 5.

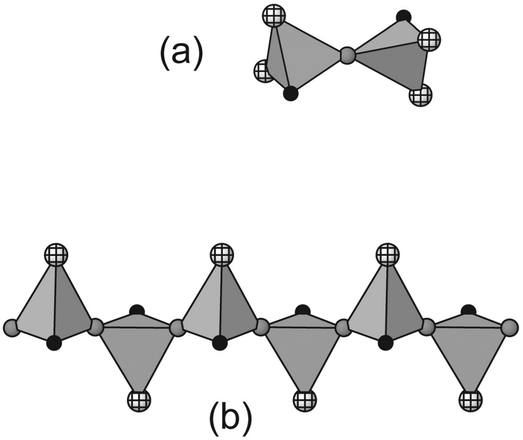

FIG. 7. Anion-centered structural units: (a) the ($O_2Pb_4CuH_2$) dimer of tetrahedra in iranite and hemihedrite; (b) the [OPbCuH] chain in fornacite, macquartite and vauquelinite. Cross-hatched circles: *Pb* atoms; black circles: H atoms; shaded circle: *Cu* atoms.

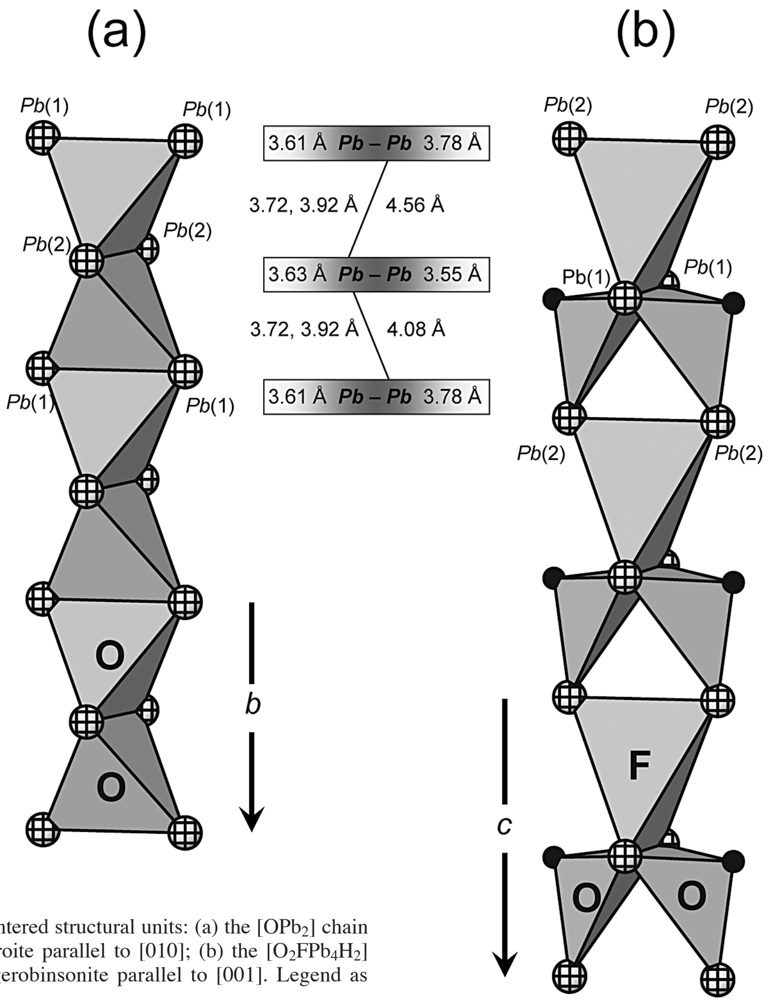

FIG. 8. Anion-centered structural units: (a) the [OPb_2] chain in phoenicochroite parallel to [010]; (b) the [$O_2FPb_4H_2$] chain in georgerobinsonite parallel to [001]. Legend as in Figure 7.

Inspection of the anion-centered chains in georgerobinsonite and phoenicochroite reveals the same pattern of Pb distribution along the chain, but with different Pb–Pb separations. The (FPb_4) tetrahedron in georgerobinsonite is substantially elongate along the chain axis (Fig. 8b). In georgerobinsonite, every second O atom along the phoenicochroite chain is replaced by a F atom, and the other O atom position along the phoenicochroite chain is vacant; this anion vacancy is accompanied by occupancy of two neighboring (OH) sites off the central axis of the chain. Relative to four Pb atoms, the chains have anion compositions $\{(OH)_2F\}^{3-}$ in georgerobinsonite and $\{OO\}^{4-}$ in phoenicochroite, with an additional Cl anion present in georgerobinsonite that serves to maintain electroneutrality. The structures of georgerobinsonite and phoenicochroite are compared in Figure 9 looking down the anion-centered chains. The positioning of the chains is similar in both structures; however, in phoenicochroite, the chains are noticeably rotated about their central axes compared

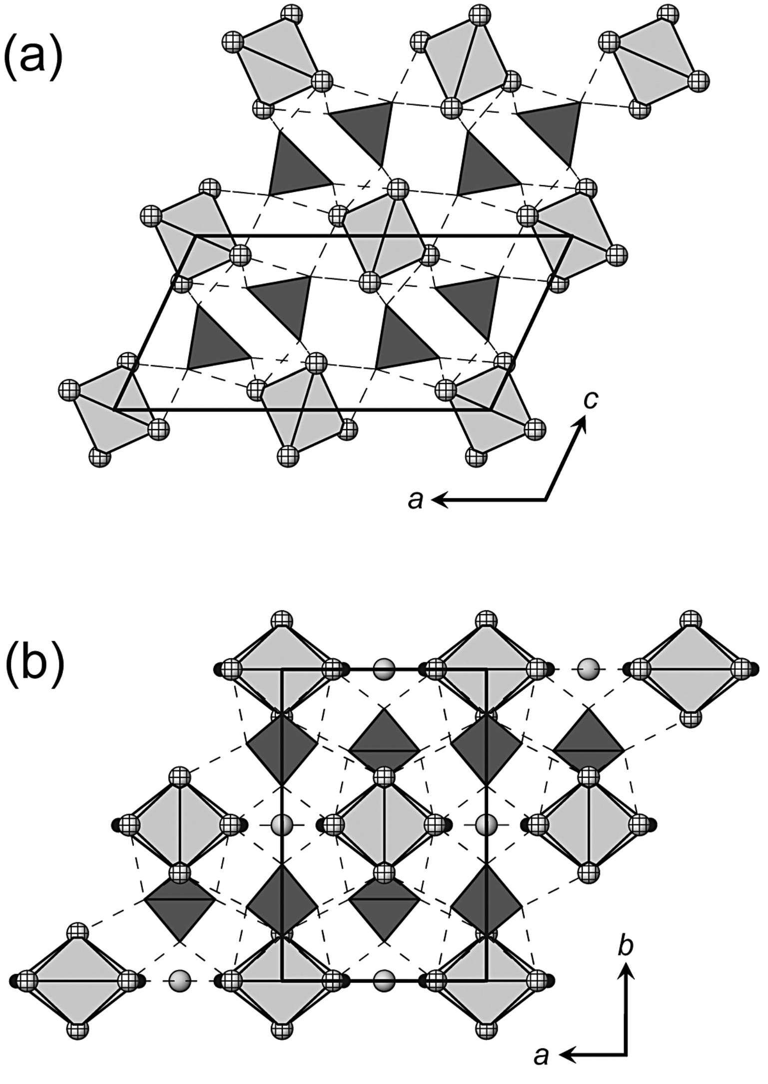

FIG. 9. The crystal structure of (a) phoenicochroite, and (b) georgerobinsonite looking down the anion-centered chains of Figure 8, with flanking (CrO_4) groups shown as darker-shaded polyhedra. Marked unit cells (heavy lines) are displaced from their origins by (½ 0 ½) for phoenicochroite, and (¼ 0 ¼) for georgerobinsonite. Legend as in Figure 8, with large shaded circles indicating Cl anions.

TABLE 7. LEAD CHROMATE MINERALS: FORMULAE AND STRUCTURAL UNITS

		Pb:(XO$_4$)	anion-centered structural unit	Ref.
Cassedanneite	$Pb_5(CrO_4)_2(VO_4)_2\ H_2O$	1.25	–	
Crocoite	$PbCrO_4$	1	–	
Embreyite	$Pb_5(CrO_4)_2(PO_4)_2\ H_2O$	1.25	–	
Fornacite	$Pb_2Cu(CrO_4)(AsO_4)OH$	1	chain [$OPbCuH$]	[1]
Georgerobinsonite	$Pb_4(CrO_4)_2(OH)_2FCl$	2	chain [$O_2FPb_4H_2$]	[2]
Hemihedrite	$Pb_{10}Zn(CrO_4)_6(SiO_4)_2F_2$	1.25	dimer [$O_2Pb_4CuH_2$]	[3]
Iranite	$Pb_{10}Cu(CrO_4)_6(SiO_4)_2\ (OH)_2$	1.25	dimer [$O_2Pb_4CuH_2$]	[4]
Macquartite	$Pb_7Cu_2(CrO_4)_2(SiO_4)_2\ (OH)_2$	1.75	chain [$OPbCuH$]	[5]*
Phoenicochroite	$Pb_2(CrO_4)O$	2	chain [OPb_2]	[6]
Santanaite	$Pb^{2+}{}_9Pb^{4+}{}_2(CrO_4)O_{12}$	11	–	
Vauquelinite	$Pb_2Cu(CrO_4)(PO_4)(OH)$	1	chain [$OPbCuH$]	[7]

* Macquartite and wherryite are isostructural.

References: [1] Cocco *et al.* (1967), [2] this study, [3] McLean & Anthony (1970), [4] Yang *et al.* (2007), [5] Cooper & Hawthorne (1994), [6] Williams *et al.* (1970), [7] Fanfani & Zanazzi (1968).

to those in georgerobinsonite. In response to the relative difference in anion-centered chain rotations in the two structures, the flanking (*Cr*O$_4$) tetrahedra occupy somewhat different positions such that the bonding requirements of the (CrO$_4$) oxyanion and the Pb atoms are mutually satisfied.

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