Lead-tellurium oxysalts from Otto Mountain near Baker, California: IV. Markcooperite, Pb(UO₂)Te⁶⁺O₆, the first natural uranyl tellurate

ANTHONY R. KAMPF,1,* STUART J. MILLS,2 ROBERT M. HOUSLEY,3 JOSEPH MARTY,4 AND BRENT THORNE5

¹Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Blvd., Los Angeles, California 90007, U.S.A.
 ²Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada
 ³Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, U.S.A.
 ⁴3457 E. Silver Oak Road, Salt Lake City, Utah 84108, U.S.A.
 ⁵3898 S. Newport Circle, Bountiful, Utah 84010, U.S.A.

ABSTRACT

Markcooperite, Pb₂(UO₂)Te⁶⁺O₆, is a new tellurate from Otto Mountain near Baker, California, named in honor of Mark A. Cooper of the University of Manitoba for his contributions to mineralogy. The new mineral occurs on fracture surfaces and in small vugs in brecciated quartz veins. Markcooperite is directly associated with bromian chlorargyrite, iodargyrite, khinite-40, wulfenite, and four other new tellurates: housleyite, thorneite, ottoite, and timroseite. Various other secondary minerals occur in the veins, including two other new secondary tellurium minerals: paratimroseite and telluroperite. Markcooperite is monoclinic, space group $P2_1/c$, a = 5.722(2), b = 7.7478(2), c = 7.889(2) Å, $\beta =$ 90.833(5)°, V = 349.7(2) Å³, and Z = 2. It occurs as pseudotetragonal prisms to 0.2 mm with the forms {100} and {011} and as botryoidal intergrowths to 0.3 mm in diameter; no twinning was observed. Markcooperite is orange and transparent, with a light orange streak and adamantine luster, and is non-fluorescent. Mohs hardness is estimated at 3. The mineral is brittle, with an irregular fracture and perfect {100} cleavage. The calculated density is 8.496 g/cm³ based on the empirical formula. Markcooperite is biaxial (+), with indices of refraction $\alpha = 2.11$, $\beta = 2.12$, $\gamma = 2.29$ calculated using the Gladstone-Dale relationship, measured α - β birefringence of 0.01 and measured 2V of 30(5)°. The optical orientation is $X = \mathbf{c}$, $Y = \mathbf{b}$, $Z = \mathbf{a}$. The mineral is slightly pleochroic in shades of orange, with absorption: X > Y = Z. No dispersion was observed. Electron microprobe analysis provided PbO 50.07, $TeO_3 22.64$, $UO_3 25.01$, Cl 0.03, O = Cl -0.01, total 97.74 wt%; the empirical formula (based on O+Cl = 8) is $Pb_{2.05}U_{0.80}Te_{1.18}^{6+}O_{7.99}Cl_{0.01}$. The strongest powder X-ray diffraction lines are $[d_{obs}$ in Å (hkl) I]: 3.235 $(120, 102, \overline{1}02)$ 100, 2.873 (200) 40, 2.985 $(\overline{1}21, 112, 121)$ 37, 2.774 (022) 30, 3.501 (021, 012) 29, 30, 3.5012.220 (221, $\overline{2}21$, 212) 23, 1.990 (222, $\overline{2}22$) 21, and 1.715 (320) 22. The crystal structure ($R_1 = 0.052$) is based on sheets of corner-sharing uranyl square bipyramids and tellurate octahedra, with Pb atoms between the sheets. Markcooperite is the first compound to show Te⁶⁺ substitution for U⁶⁺ within the same crystallographic site. Markcooperite is structurally related to synthetic Pb(UO₂)O₂.

Keywords: Markcooperite, new mineral, tellurate, uranyl, crystal structure, Otto Mountain, California

Introduction

Markcooperite, $Pb_2(UO_2)Te^{6+}O_6$, is one of seven new secondary lead-tellurium minerals discovered recently at Otto Mountain near Baker, California. Detailed information on the mining history, geology, mineralogy, and mineral paragenesis of the deposit, as well as the discovery of the new minerals, is provided in Kampf et al. (2010a). Markcooperite is the first natural uranyl tellurate discovered; however, three uranyl tellurites are known: cliffordite, $UTe^{4+}O_9$ (Gaines 1969), moctezumite, $PbUO_2(Te^{4+}O_3)_2$ (Gaines 1965), and schmitterite $UO_2Te^{4+}O_3$ (Gaines 1971).

Markcooperite is named in honor of Mark A. Cooper (b. 1963) of the University of Manitoba for his contributions to mineralogy. He has been involved in the description of many new minerals (~35), and the determination of the crystal structures of many minerals containing uranium (e.g., schoepite, guillemi-

nite, marthozite, rutherfordine) and tellurium (e.g., khinite-4*O*, khinite-3*T*, spiroffite). Cooper has agreed to the naming of the mineral in his honor. The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2009-045). Three cotype specimens are deposited in the Natural History Museum of Los Angeles County, catalog numbers 62510, 62511, and 62512.

OCCURRENCE

Markcooperite was found at the Aga mine, (35° 16.399'N 116° 05.665'W) on Otto Mountain, ~2 km northwest of Baker, San Bernardino County, California, U.S.A., and in the Bird Nest drift on the southwest flank of Otto Mountain, 0.7 km northwest of the Aga mine (35° 16.606'N 116° 05.956'W).

Markcooperite is very rare and occurs on fracture surfaces and in small vugs in quartz veins. Species observed in direct association with the new mineral include bromine-rich chlorar-

^{*} E-mail: akampf@nhm.org

gyrite, iodargyrite, khinite-40, wulfenite and four new tellurates: housleyite [Pb₆Cu²⁺Te₄⁶⁺O₁₈(OH)₂] (IMA2009-024; Kampf et al. 2010c), ottoite $[Pb_2Te^{6+}O_5]$ (IMA2009-063; Kampf et al. 2010b), thorneite $[Pb_6(Te_2^{6+}O_{10})(CO_3)Cl_2(H_2O)]$ (IMA2009-023; Kampf et al. 2010a), and timroseite $[Pb_2Cu_5^{2+}(Te^{6+}O_6)_2(OH)_2]$ (IMA2009-064; Kampf et al. 2010d). Other species identified in the assemblages include acanthite, anglesite, atacamite, boleite, brochantite, burckhardtite, calcite, caledonite, celestine, cerussite, chalcopyrite, chrysocolla, devilline, diaboleite, eztlite, fluorite, fornacite, galena, goethite, gold, hessite, jarosite, kuranakhite, linarite, malachite, mimetite, mottramite, munakataite, murdochite, muscovite, perite, phosphohedyphane, plumbojarosite, pyrite, schieffelinite, vanadinite, vauquelinite, and two other new minerals: paratimroseite [Pb₂Cu₄²⁺(Te⁶⁺O₆)₂(H₂O)₂] (IMA2009-065; Kampf et al. 2010d) and telluroperite [Pb₃Te⁴⁺O₄Cl₂] (IMA2009-044; Kampf et al. 2010e). Other potentially new species are still under investigation.

Markcooperite and most of the other secondary minerals of the quartz veins are interpreted as having formed from the partial oxidation of primary sulfides (e.g., galena) and tellurides (e.g., hessite) during or following brecciation of the quartz veins. The U may have originated from one or more primary U-bearing phases (possibly uraninite in the form of inclusions); however, the source of the U is yet to be determined.

PHYSICAL AND OPTICAL PROPERTIES

Markcooperite crystals are pseudotetragonal prisms exhibiting $\{100\}$ as the basal form and $\{011\}$ as the prism form. Crystals range from tiny, thin, tapering prisms, $<5~\mu m$ in length (Fig. 1), to larger squat prisms to 0.2 mm in length. Most commonly, the mineral occurs as botryoidal aggregates to 0.3 mm in diameter, which consists of tightly intergrown crystals (Fig. 2).

Markcooperite is orange and transparent, with a light orange streak and adamantine luster. It is non-fluorescent and has an estimated Mohs hardness of 3. The tenacity is brittle, the fracture is irregular, and the cleavage is perfect on {100}. Density could not be measured because it is greater than those of available high-density liquids and there is insufficient material for physical measurement. The calculated density is 8.496 g/cm³ for the empirical formula. In dilute HCl, markcooperite immediately decomposes, turning white and opaque, and then dissolves slowly.

Optically, markcooperite is biaxial (+); however, the indices of refraction are higher than the available high-density liquids. The Gladstone-Dale relationship (Mandarino 1981) predicts $n_{av} = 2.175$ from the empirical formula. This value can be used with the measured 2V of $30(5)^{\circ}$ and the α - β birefringence (0.01) to predict the indices of refraction: $\alpha = 2.11$, $\beta = 2.12$, $\gamma = 2.29$. The optical orientation is $X = \mathbf{c}$, $Y = \mathbf{b}$, $Z = \mathbf{a}$. The mineral is slightly pleochroic in shades of orange, with absorption: X > Y = Z. No dispersion was observed.

CHEMISTRY

Five chemical analyses were carried out using a JEOL8200 electron microprobe (WDS mode, 15 kV, 10 nA, focused beam) at the Division of Geological and Planetary Sciences, California Institute of Technology. The standards used were PbS, UO₂, Te metal, and sodalite (for Cl). No other elements were detected

in EDS analyses, and in the microprobe S, Cr, Cu, and Bi were below detection limits. Crystal structure and bond-valence considerations (see below) indicate the absence of H₂O and OH in the structure. The averages (and ranges) of the analyses are: PbO 50.07 (49.23–51.60), TeO₃ 22.64 (21.11–23.18), UO₃ 25.01 (24.22–25.83), Cl 0.03 (0.01–0.06), O≡Cl −0.01, total 97.74 wt%. Although no damage was noted in a subsequent SEM examination of the probe mount, tellurates are prone to electron beam damage. This and sample porosity contributes to the low analytical total, even though we used the mildest analytical conditions feasible. This problem of sample instability in the electron beam appears to be common in tellurates, cf. Grundler et al. (2008), Mills et al. (2009c),

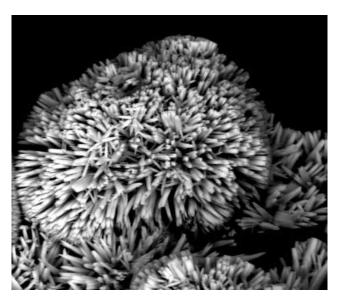


FIGURE 1. Backscatter SEM image of a cluster markcooperite crystals (FOV $30 \mu m$).

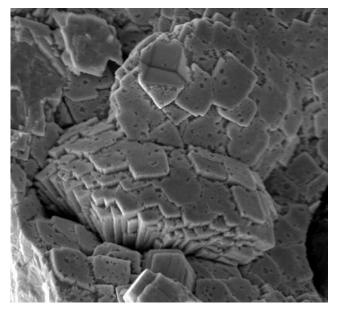


FIGURE 2. SEM image of the surface of a botryoidal aggregate of markcooperite crystals (FOV 75 μ m).

and Mills et al. (2010).

The empirical formula (based on O+Cl = 8) is $Pb_{2.05}U_{0.80}$ $Te_{1.18}^{6+}O_{7.99}Cl_{0.01}$. The simplified formula is $Pb_2(UO_2)TeO_6$, which requires 49.16 PbO, 19.34 TeO_3 , and 31.50 UO_3 , total 100.00 wt%.

X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATIONS

Both powder and single-crystal X-ray diffraction data were obtained on a Rigaku R-Axis Spider curved imaging plate microdiffractometer utilizing monochromatized $MoK\alpha$ radiation.

TABLE 1. X-ray powder-diffraction data for mark-cooperite

cooperite							
lobs	$d_{ m obs}$		d_{calc}	$I_{\rm calc}$	hkl		
12	3.993	ſ	4.002	10	111*		
		ſ	3.970	10	111*		
29	3.501	ſ	3.514	26	012		
		l	3.489	45	<u>0</u> 21*		
		•	3.266	71	102		
100	3.235	1	3.231	67	102		
		1	3.221	100	<u>1</u> 20*		
		(3.011	14	<u>1</u> 12		
		(2.988	28	121*		
37	2.985	₹	2.984	18	112		
		Ĺ	2.975	27	121*		
40	2.873		2.871	58	200*		
30	2.774		2.768	46	022*		
9	2.490		2.488	10	013		
7	2.462		2.464	8	031		
6	2.279		2.274	5	<u>1</u> 13		
16	2.239		2.235	9	<u>2</u> 12		
		(2.222	14	2 21		
23	2.220	₹	2.212	4	212		
		Ĺ	2.211	12	221		
5	2.177		2.177	5	023		
4	2.043		2.042	3	<u>1</u> 23		
21	1.990	ſ	2.001	18	222		
		ſ	1.985	16	<u>2</u> 22		
13	1.881	{	1.891	4	213		
		ſ	1.889	7	041		
18	1.838		1.843	18	<u>1</u> 40*		
12	1.817	ſ	1.818	8	114		
12	1.017	ſ	1.806	6	<u>1</u> 14		
13	1.795	{	1.796	7	1 41		
		l	1.793	7	<u>1</u> 41		
16	1.764	ſ	1.761	10	1 33*		
		l	1.744	10	<u>0</u> 42		
18	1.731		1.729	10	302*		
22	1.715		1.718	15	<u>3</u> 20*		
		(1.682	5	321		
15	1.673	₹	1.675	5	124*		
		Ĺ	1.675	5	321*		
_		(1.582	5	<u>2</u> 14		
9	1.577	₹	1.580	3	241		
		Ĺ	1.576	3	<u>2</u> 41		
8	1.497		1.494	5	242		
6	1.440		1.436	5	400*		

Notes: $I_{\rm obs}$ based upon peak heights. $I_{\rm calc}$ calculated from the crystal structure using Powder Cell (Kraus and Nolze 1996). $d_{\rm calc}$ based on the cell refined from the powder data (*) using UnitCell (Holland and Redfern 1997). Refined cell: a=5.7427(6), b=7.782(1), c=7.878(2) Å, $\beta=90.66(2)$ ° and V=352.06(9) ų.

The powder data presented in Table 1 show good agreement with the pattern calculated from the structure determination.

The Rigaku CrystalClear software package was used for processing the structure data, including the application of an empirical absorption correction. The structure was solved by direct methods using SHELXS-97 and refined, with neutral atom scattering factors, using SHELXL-97 (Sheldrick 2008). The details of the data collection and the final structure refinement are provided in Table 2. The final atomic coordinates and displacement parameters are in Table 3. Selected interatomic distances are listed in Table 4 and bond valences in Table 5. CIF and structure factors are available on deposit¹.

DESCRIPTION OF THE STRUCTURE

In the markcooperite structure (Fig. 3), uranyl square bipyramids and tellurate octahedra link to one another by sharing corners along **b** and **c** to form sheets parallel to (100). The sheets are linked in the **a** direction via bonds to Pb atoms residing between the sheets. The $[\frac{1}{2}(\text{TeO}_6)^{2-}_{\infty} \cdot \frac{1}{2}(\text{UO}_2\text{O}_4)^{2-}_{\infty}]$ sheet is unique,

TABLE 2. Data collection and structure refinement details for mark-cooperite

Diffractometer	Rigaku R-Axis Spider		
X-ray radiation/power	MoK α (λ = 0.71075 Å)/50 kV, 40 mA		
Temperature	298(2) K		
Structural formula	$Pb_2(U_{0.75}Te_{0.25}^{6+}O_2)TeO_6$		
Space group	P2 ₁ /c		
Unit-cell dimensions	a = 5.722(2) Å		
	b = 7.748(2) Å		
	c = 7.889(2) Å		
	$\beta = 90.833(5)^{\circ}$		
Z	2		
Volume	349.7(2) Å ³		
Density (for above formula)	8.361 g/cm ³		
Absorption coefficient	70.483 mm ⁻¹		
F(000)	724		
Crystal size	$45 \times 45 \times 15 \mu m$		
θ range	3.56° to 20.76°		
Index ranges	$-5 \le h \le 5, -7 \le k \le 7, -7 \le l \le 7$		
Reflections collected/unique	$3886/362 [R_{int} = 0.1058]$		
Reflections with $F_o > 4\sigma F$	287		
Completeness to $\theta = 27.50^{\circ}$	99.5%		
Max. and min. transmission	0.4178 and 0.1436		
Refinement method	Full-matrix least-squares on F ²		
Parameters refined	60		
GoF	1.083		
Final R indices $[F_o > 4\sigma F]$	$R_1 = 0.052$, $wR_2 = 0.131$		
R indices (all data)	$R_1 = 0.064$, $wR_2 = 0.139$		
Largest diff. peak/hole	3.052/–2.335 <i>e</i> /ų		
	·		

Notes: $R_{\rm int} = \Sigma [F_0^2 - F_0^2 ({\sf mean})]/\Sigma [F_0^2]$. GoF = S = $\{\Sigma [w(F_0^2 - F_0^2)^2]/(n-p)\}^{1/2}$. $R_1 = \Sigma [|F_0| - |F_c|]/\Sigma [F_0]$. $wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2]/\Sigma [w(F_0^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where a is 0.0945, b is 0, and P is $[2F_c^2 + {\sf Max}(F_0^2,0)]/3$.

TABLE 3. Atomic positions and displacement parameters for markcooperite

	X	у	Z	$U_{ m eq}$	U ₁₁	U_{22}	U_{33}	U_{23}	U_{13}	U ₁₂
U/Te*	0.0000	0.0000	0.0000	0.0386(12)	0.035(2)	0.039(2)	0.042(2)	0.002(1)	0.003(1)	0.003(1)
Te	0.0000	0.5000	0.0000	0.0339(13)	0.029(2)	0.034(3)	0.039(2)	0.002(2)	-0.001 (2)	-0.003(2)
Pb	0.4972(3)	0.1689(3)	0.6919(2)	0.0531(10)	0.044(1)	0.051(2)	0.064(2)	0.002(1)	-0.003(1)	-0.003(1)
01	0.699(5)	-0.068(4)	-0.061(3)	0.054(8)	0.05(2)	0.05(2)	0.07(2)	0.01(2)	-0.03(1)	0.01(2)
O2	-0.137(5)	0.234(3)	0.505(3)	0.038(7)	0.06(2)	0.02(2)	0.03(2)	0.00(1)	-0.02(1)	0.00(1)
O3	0.295(4)	0.085(4)	0.429(3)	0.045(7)	0.02(1)	0.05(2)	0.06(2)	0.03(2)	0.00(1)	0.00(1)
04	-0.114(4)	0.532(3)	-0.237(3)	0.040(7)	0.03(1)	0.02(2)	0.07(2)	0.01(1)	-0.01(1)	-0.00(1)

^{*} Occupancy: 0.75(2)/0.25(2).

¹ Deposit item AM-10-046, CIF and structure factors. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

in that it has not been described in any natural or synthetic structure; however, it is derived from the more fundamental sheet $[(UO_2O_4)_{\text{loc}}^{2-}]$ found in synthetic $\text{Li}_2[(UO_2O_2)]$ (Gebert et al. 1978), $\text{Ba}[(UO_2O_2)]$ (Reis et al. 1976), $\text{Sr}[(UO_2O_2)]$ (Loopstra and Riet-

TABLE 4. Selected bond lengths (Å) in markcooperite

IADLE 7.	selected bolld left	Juis (A) in markcoopenie	
Pb-O3	2.45(3)	Te-O3 (×2)	1.90(2)
Pb-O4	2.46(2)	Te-O2 (×2)	1.98(2)
Pb-O3	2.49(3)	Te-O4 (×2)	1.98(3)
Pb-O1	2.54(3)	<te-o></te-o>	1.95
Pb-O2	2.63(3)		
Pb-O1	2.90(3)	U/Te-O1 (×2)	1.86(3)
Pb-O3	2.92(3)	U/Te-O2 (×2)	2.20(3)
Pb-O1	3.23(3)	U/Te-O4 (×2)	2.20(3)
Pb-O2	3.30(3)	<u te-o=""></u>	2.09
Pb-O4	3.63(3)		
<pb-o></pb-o>	2.86		

TABLE 5. Bond-valence analysis for markcooperite

	01	02	O3	04	Sum
Pb	0.31, 0.15, 0.08	0.26, 0.07	0.37, 0.34, 0.14	0.36, 0.03	2.10
Te		$0.84 \times 2 \rightarrow$	1.05 ×2→	$0.84 \times 2 \rightarrow$	5.46
U/Te	1.40 ×2→	$0.71 \times 2 \rightarrow$		0.71 ×2→	5.64
Sum	1.94	1.88	1.90	1.95	

Notes: Values are expressed in valence units. Multiplicity is indicated by $\times \rightarrow$; Pb²⁺-O bond strengths from Krivovichev and Brown (2001); Te⁶⁺-O bond strengths from Brown and Altermatt (1985); ^[6]U⁶⁺-O bond strengths (r_0 = 2.074, b = 0.554) from Burns et al. (1997); U/Te site occupancy (0.75/0.25) used in calculations.

veld 1969), Pb[(UO₂O₂)] (Cremers et al. 1986), γ -[(UO₂(OH)₂)] (Siegel et al. 1972), β -[(UO₂(OH)₂)] (Taylor and Bannister 1972), and β -Na₂[(UO₂O₂)] (Kovba 1971). No natural mineral has thus far been described with this [(UO₂O₄) $_{\infty}^{2-}$] sheet, although the parent sheet, as described by Burns (2005), is found in the autunite structure-type (Burns et al. 1996).

The structure of markcooperite is topologically equivalent to the orthorhombic (Pbcm) structure of Ba[(UO₂O₂)], Sr[(UO₂O₂)], and Pb[(UO₂O₂)] (Fig. 3) in which there is only one U site located on the origin. The replacement of alternating (UO₂O₄) square bipyramids by TeO₆ octahedra to form the markcooperite sheet leads to a reduction in symmetry to the monoclinic space group, $P2_1/c$. The increase in the β angle to 90.833(5)° also apparently serves to better accommodate the smaller TeO₆ octahedra within the sheet. During structure analysis, we tested an orthorhombic Pbcm model in which U and Te were refined on the origin; however, it yielded unreasonable bond lengths and higher R-factors.

Another interesting feature of markcooperite is the partial substitution of Te for U on the origin. The refined U:Te occupancy of 0.75(2):0.25(2) matches very closely the empirical formula, Pb_{2.05}U_{0.80}Te_{1.18}O_{7.99}Cl_{0.01}. To the best of our knowledge, this is the first case of Te⁶⁺ for U⁶⁺ substitution. In spite of the

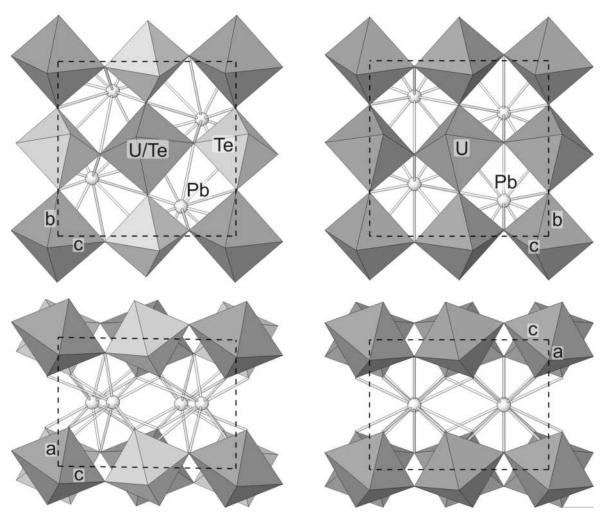


FIGURE 3. Structures of markcooperite (left) and Pb[(UO₂O₂)] (right; Cremers et al. 1986), viewed along a (top) and along b (bottom).

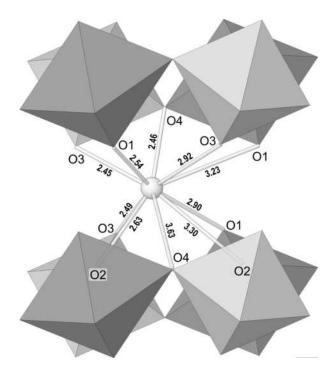


FIGURE 4. Coordination of the Pb atom in markcooperite viewed along **b**. The lopsided distribution of bond lengths is attributable to the localization of the lone-pair electrons. Bond lengths are given in angstroms.

25% occupancy by Te, the bond lengths for the site are reasonably normal for a uranyl group. The apical bond lengths of 1.86 Å, are slightly longer than the average of 1.79 Å noted by Burns et al. (1997), but are consistent with the structure type $\{e.g., 1.85 \text{ Å for Pb}[(UO_2O_2)]$ —Cremers et al. (1986) $\}$ and the equatorial U-O bond lengths, 2.20 Å, are also consistent with those in Pb $[(UO_2O_2)]$, 2.19 Å (Cremers et al. 1986).

It is typical for square bipyramidal uranyl groups to link to one another via their more distant equatorial corners, as this best accommodates the repulsion between the highly charged U⁶⁺ cations. This is the case in the Ba $[(UO_2O_2)]$, Sr $[(UO_2O_2)]$, and Pb[(UO₂O₂)] structures, and it is also noted in the markcooperite structure for the linkages between the uranyl square pyramids and the tellurate octahedra. Furthermore, in markcooperite the repulsion between U⁶⁺ and Te⁶⁺ results in significant distortion of the tellurate octahedron, manifest in four long equatorial Te-O bonds of 1.98 Å, corresponding to the corners shared with the uranyl square bipyramids, and two short apical Te-O bonds of 1.90 Å projecting into the interlayer region. The average Te-O bond length of 1.95 Å is quite normal for octahedrally coordinated Te⁶⁺ (e.g., Mills et al. 2010; Kampf et al. 2010a). We note that the U and Pb bond-valence parameters have been refined with a new r_0 -b pair with $b \neq 0.37$, whereas Te⁶⁺ has not. Fixing b = 0.37 also contributes to large displacements in the bond-valence fits (Burns et al. 1997; Locock and Burns 2004; Mills et al. 2009a).

The Pb atom is in 10-fold lopsided coordination (Fig. 4), which is indicative of the $6s^2$ lone-pair being stereochemically active. This feature is often noted in Pb oxysalts (e.g., Moore 1988; Cooper and Hawthorne 1994; Kharisun et al. 1997; Mills et al. 2009b) and, in fact, the Pb atoms in the structures of all seven

recently discovered new minerals from Otto Mountain exhibit this feature. All 10 Pb-O bonds are unique and range from 2.45 to 3.63 Å, with an average of 2.86 Å. In Pb[(UO₂O₂)] (Cremers et al. 1986), Pb is in 10-fold coordination and also exhibits a steroactive lone-electron-pair, with Pb-O bonds ranging from 2.48 to 3.81 Å and with an average bond length of 2.89 Å.

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