COSKRENITE-(Ce), (Ce,Nd,La)$_2$(SO$_4$)$_2$(C$_2$O$_4$)•8H$_2$O, A NEW RARE-EARTH OXALATE MINERAL FROM ALUM CAVE BLUFF, TENNESSEE: CHARACTERIZATION AND CRYSTAL STRUCTURE*

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ABSTRACT

The new mineral species coskrenite-(Ce) [(Ce,Nd,La)$_2$(SO$_4$)$_2$(C$_2$O$_4$)•8H$_2$O] occurs as transparent, pink- to cream-colored clusters of tabular crystals 0.1 to 1.0 mm across embedded within, or in cavities in, epsomite and "hair salts" (principally apjohnite) at Alum Cave Bluff, Great Smoky Mountains, Tennessee. A complex suite of sulfates occurs in the soil or on the ceiling of a rock shelter, as a result of weathering of pyritic phyllite and evaporation of the resulting solutions. Coskrenite-(Ce) is closely associated with two other new minerals, levinsonite-(Y) [(Y,Nd,Ce)Al(SO$_4$)$_2$(C$_2$O$_4$)•12H$_2$O] and zugshunstite-(Ce) [(Ce,Nd,La)Al(SO$_4$)$_2$(C$_2$O$_4$)•12H$_2$O]. They are the first natural examples of rare-earth oxalate salts. Coskrenite-(Ce) is triclinic, space group $P\bar{1}$, a 6.007(1), b 8.368(2), c 9.189(2) Å, α 99.90(2), β 105.55 (2), γ 107.71(2)°, V 407.4(2) Å^3, and Z = 1. The basic structural unit is a four-membered ring of two REE(O,H$_2$O)$_9$ polyhedra and two SO$_4$ tetrahedra, each sulfate tetrahedron sharing two of its vertices with two REE polyhedra. These rings are linked into chains, and adjacent chains are linked by oxalate groups and hydrogen bonds into sheets oriented parallel to {001}. Adjacent sheets are weakly bonded together through hydrogen bonds. The REE site is nine-coordinated by a distorted monocapped square antiprism of five O and four H$_2$O, with an average REE–O distance of 2.518 Å. The strongest lines in the powder-diffraction pattern [d in Å(I)(hkl)] are: 5.48(100)(1$\bar{1}$0), 8.52(70)(001), 6.72(60)(01$\bar{1}$), 3.84(60)(020,110), 4.26(50)(002,01$\bar{2}$), 3.35(40)(02$\bar{2}$), and 2.744(40)(12$\bar{2}$,2$\bar{1}$$\bar{2}$,1$\bar{3}$0,2$\bar{2}$0). Coskrenite-(Ce) is biaxial negative, α = 1.544(4), β = 1.578(4), γ = 1.602(4), 2V(obs.) = 65(10)°, 2V(calc.) = 69(3)° dispersion medium ($r > v$), and $Z' \wedge c$ = 21° (in plane of cleavage). The mineral is named after its discoverer, T. Dennis Coskren.

Keywords: coskrenite-(Ce), new mineral species, rare-earth oxalate, X-ray data, crystal-structure determination, Alum Cave Bluff, Tennessee.

SOMMAIRE

La coskrenite-(Ce) [(Ce,Nd,La)$_2$(SO$_4$)$_2$(C$_2$O$_4$)•8H$_2$O], nouvelle espèce minérale, se présente en amas de cristaux transparents tabulaires, de couleur rose ou crème, de 0.1 à 1.0 mm, encastrés dans l'epsomite et les sels capillaires, surtout l'apjohnite, à Alum Cave Bluff, dans les montagnes Great Smoky, au Tennessee. Une association complexe de sulfates se trouve dans le sol ou sur le plafond d'un abri naturel, résultat de l'altération de surface de phyllite pyriteuse et de l'évaporation des solutions. La coskrenite-(Ce) est étroitement associée à deux autres nouvelles espèces minérales, levinsonite-(Y) [(Y,Nd,Ce)Al(SO$_4$)$_2$(C$_2$O$_4$)•12H$_2$O] et zugshunstite-(Ce) [(Ce,Nd,La)Al(SO$_4$)$_2$(C$_2$O$_4$)•12H$_2$O]. Ce sont les premiers exemples naturels d'oxalates de terres rares (*TR*). La coskrenite-(Ce) est triclinique, groupe spatial $P\bar{1}$, a 6.007(1), b 8.368(2), c 9.189(2) Å, α 99.90(2), β 105.55 (2), γ 107.71(2)°, V 407.4(2) Å^3, et Z = 1. L'unité structurale de base est un anneau à quatre membres, composé de deux polyèdres *TR*(O,H$_2$O)$_9$ et deux tétraèdres SO$_4$, chaque tétraèdre SO$_4$ partageant deux des coins avec deux polyèdres à terres rares. Ces anneaux sont agencés en chaînes, et les chaînes adjacentes sont liées par des groupes oxalate et des liaisons hydrogène pour former des feuillets orientés parallèles à {001}. Les feuillets adjacents sont faiblement interliés grâce à d'autres liaisons hydrogène. Le site occupé par les terres rares a une coordinence neuf, les liaisons définissant un antiprisme carré difforme à terminaison unique, avec cinq atomes d'oxygène et quatre molécules H$_2$O, et une distance *TR*–O moyenne de 2.518 Å. Les raies les plus intenses du spectre de diffraction (méthode des poudres) [d en Å(I)(hkl)] sont: 5.48(100)(1$\bar{1}$0), 8.52(70)(001), 6.72(60)(01$\bar{1}$), 3.84(60)(020,110), 4.26(50) (002,01$\bar{2}$), et 3.35(40)(02$\bar{2}$), et 2.744(40)(12$\bar{2}$,2$\bar{1}$$\bar{2}$,1$\bar{3}$0,2$\bar{2}$0). La coskrenite-(Ce) est biaxe négative, α = 1.544(4), β = 1.578(4),

$\gamma = 1.602(4)$, $2V$(obs.) $= 65(10)°$, $2V$(calc.) $= 69(3)°$, dispersion moyenne ($r > v$), and $Z' \wedge c = 21°$ (dans le plan du clivage). Le nom choisi honore T. Dennis Coskren, qui en a fait la découverte.

(Traduit par la Rédaction)

Mots-clés: coskrenite-(Ce), nouvelle espèce minérale, oxalate de terres rares, données de diffraction X, détermination de la structure cristalline, Alum Cave Bluff, Tennessee.

INTRODUCTION

T. D. Coskren recently undertook a study of the unusual minerals that occur at Alum Cave Bluff, a locality that is now a popular tourist site in the Great Smoky Mountains National Park, Tennessee. That study resulted in the identification of a great variety of minerals typical of an evaporite environment (Coskren & Lauf 2000). Several of these minerals could not initially be identified, however, and were therefore studied using scanning electron microscopy at the Oak Ridge National Laboratory (Lauf 1997), the resulting data indicating the presence of several new species. Among these, three minerals seemed to be *REE* sulfates on the basis of qualitative energy-dispersion analytical (EDS) data. Specimens of these minerals were submitted to the Mineralogical Laboratory at the University of Michigan for further characterization. The resultant data confirmed that the three *REE* minerals are indeed new species, but crystal-structure analyses showed that they are all highly hydrated sulfate oxalates, the oxalate component having gone undetected in the EDS study. These minerals are named coskrenite-(Ce) $[(Ce,Nd,La)_2(SO_4)_2(C_2O_4)\cdot 8H_2O]$, levinsonite-(Y) $[(Y,Nd,Ce)Al(SO_4)_2(C_2O_4)\cdot 12H_2O]$, and zugshunstite-(Ce) $[(Ce,Nd,La)Al(SO_4)_2(C_2O_4)\cdot12H_2O]$. We take pleasure in naming the first of these after Dr. T. Dennis Coskren (b. 1942), geochemist and geologist from Columbia, Maryland, whose efforts to characterize the minerals at Alum Cave Bluff led to the discovery of the new minerals. All three minerals and their names have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. With these additions, the list of oxalate minerals (Gaines *et al.* 1997) numbers well over a dozen, but the new species are unique in two respects: they are the first natural rare-earth oxalates and the first natural double salts of two acids, one organic and the other inorganic. Levinsonite-(Y) and zugshunstite-(Ce) will be described elsewhere (Peacor *et al.*, in prep.), as they have a special crystal-chemical significance in having the same complex formula type, but different crystal structures, representing the extremes of differentiation of *LREE* and *HREE*. In this report, we confine ourselves to the characterization of coskrenite-(Ce) and its crystal structure. Type samples have been deposited in the collections of the U.S. National Museum of Natural History and the Department of Geological Sciences of the University of Michigan.

OCCURRENCE

Coskrenite-(Ce) occurs in the soil at Alum Cave Bluff, a locality whose name is actually a misnomer in that there is no cave; rather, there is a rock shelter defined by an overhanging steep cliff (Coskren & Lauf 2000). The cliff and surrounding bedrock are part of the Precambrian Anakeesta Formation, a metapelite with the texture of a phyllite, whose major minerals are muscovite, biotite, chlorite, quartz, and pyrite. The area is affected by an especially high rainfall, ~200 cm per year. The resultant weathering of the rock in the cliff face involves oxidation of pyrite and dissolution of the dominant rock-forming silicates, resulting in sulfate-rich, low-pH solutions with dissolved elements such as Fe, Mg, Al, K, Na, Ca, and Mn. As these solutions trickle down the face of the cliff, they pass under the inclined upper surface of the rock shelter, where partial evaporation leads to precipitation of sulfates, especially those of iron. Most of the water then passes down to the soil at the base of the rock shelter, where complete evaporation results in precipitation of a variety of minerals, most of which are hydrous or hydrated sulfates. The bulk of the precipitates consists of epsomite and members of the "hair-salt" family, of which apjohnite is the most abundant. There is also a variety of other minerals, including gypsum, jarosite, tschermigite, and destinezite ("diadochite"). The last of these occurs in exceptional crystals in the range of tens of micrometers, a size large enough to permit the first set of single-crystal X-ray intensity data to be measured for this mineral (Peacor *et al.* 1999). In addition to the new minerals coskrenite-(Ce), levinsonite-(Y), and zugshunstite-(Ce), at least two other phases appear to be new mineral species. These are the probable ammonium analogue of slavikite and an iron phosphate (T.D. Coskren, pers. commun.).

MORPHOLOGY AND PHYSICAL PROPERTIES

Coskrenite-(Ce) occurs as aggregates of tabular, wedge-shaped, euhedral crystals. Individual crystals are up to *ca.* 0.7 mm in width (Fig. 1) and are flattened on {100}, with edges defined by {010} and {001}. The crystals are embedded within epsomite or hair salt, or are found in cavities bounded by those minerals.

Coskrenite-(Ce) is transparent, with a color that is usually pale pink under incandescent light, but it ranges to cream-colored in some material. The pink material displays a weak alexandrite-like effect in becoming pale

blue under fluorescent room lighting. There is no discernable fluorescence under ultraviolet light or the beam of the electron microprobe. The streak is colorless, and the luster, vitreous. It is brittle and has a perfect {001} cleavage, but the hardness could not be measured because of the small size of the crystals. Likewise, the density could not be accurately measured because the crystals are small and intergrown or coated with other minerals, but the density was calculated to be 2.881 g/cm^3 from the combined results of the chemical and crystal-structure analyses. The mineral is readily soluble in water.

The optical properties of coskrenite-(Ce) were measured using oriented crystals on gelatin slides. Immersion oils were employed with an ordinary light source. It is biaxial negative, $\alpha = 1.544(4)$, $\beta = 1.578(4)$, $\gamma = 1.602(4)$, $2V$(obs.) $= 65(10)°$, $2V$(calc.) $= 69(3)°$, dispersion medium ($r > v$), and $Z' \wedge c = 21°$ (in plane of cleavage). No pleochroism was observed.

CHEMICAL COMPOSITION

The chemical analysis of coskrenite-(Ce) by a microbeam technique proved to be difficult because of rapid decomposition of polished samples under the electron beam. In order to minimize beam damage, the electron microprobe was operated at the somewhat unusual conditions of 10 kV, 5 μA, and 5-s counting times, and with a focused beam rastered over an area of 5×5 μm. The standards are listed in Table 1; corrections were made by the PAP method using Cameca software. The

TABLE 1. CHEMICAL DATA FOR COSKRENITE-(Ce)

oxide	60 s analysis	2nd 60 s	3rd 60 s	ave. wt.%	obs. range (std. dev.)	EMP standard
La$_2$O$_3$	4.9	5.3	4.8	4.6	4.4 – 4.8 (0.29)	LaPO$_4$
Ce$_2$O$_3$	24.6	25.3	26.3	25.9	24.1 – 26.6 (0.71)	CePO$_4$
Pr$_2$O$_3$	2.1	2.4	2.8	2.1	2.0 – 2.8 (0.13)	PrPO$_4$
Nd$_2$O$_3$	13.1	13.4	13.2	13.3	12.7 – 13.7 (0.45)	NdPO$_4$
Sm$_2$O$_3$	1.0	1.0	0.8	1.0	0.9 – 1.3 (0.08)	SmPO$_4$
Eu$_2$O$_3$	1.0	1.0	1.2	0.8	0.5 – 0.8 (0.09)	EuPO$_4$
Gd$_2$O$_3$	--	--	--	0.3	0.2 – 0.3 (0.02)	GdPO$_4$
Y$_2$O$_3$	--	--	--	0.1	0.0 – 0.2 (0.04)	Y$_3$Al$_5$O$_{12}$
SO$_3$$^+$	20.3	16.5	14.4	22.6	21.0 – 23.0 (0.29)	SrSO$_4$
F$_2$	--	--	--	0.3	0.1 – 0.4 (0.05)	apatite
C$_2$O$_3$*	10.2	10.2	10.2	10.2		
H$_2$O*	20.4	20.4	20.4	20.4		
Sum	97.6	95.5	94.1	100.0		

* Calculated from stoichiometry.
$^+$ Low value due to beam damage of sample. Note the dramatic decrease of SO$_3$ with repeated 60-s analyses on same spot. The H$_2$O and C$_2$O$_3$ contents may also decrease during the chemical analysis.

proportion of oxygen was provisionally calculated as the difference from 100% in order to provide an adequate matrix for the PAP program. After provisional compositions were obtained, repeated analyses showed some increase in *REE* concentrations due to dehydration, decarbonation, and substantial loss of sulfur (Table 1). Analyses were then repeated using the previous back-
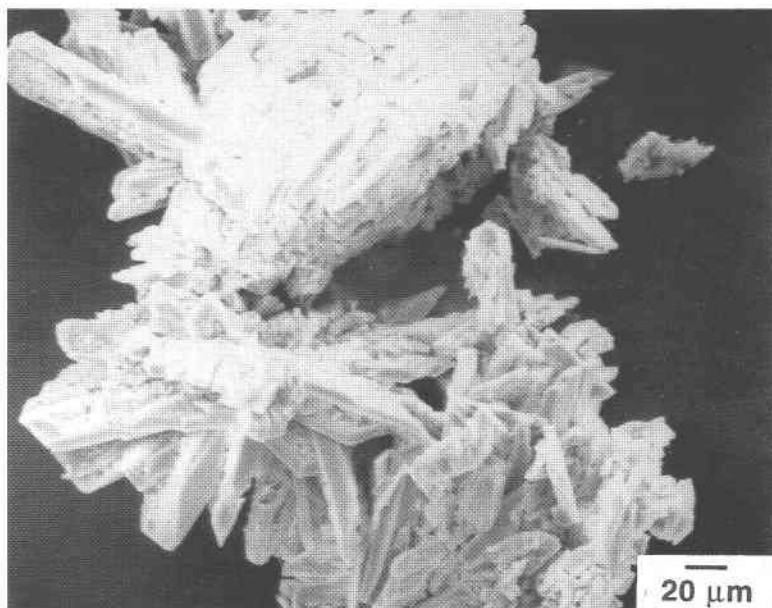

FIG. 1. SEM image of coskrenite-(Ce) crystals in cavities in epsomite.

ground readings to reduce the time of analysis and minimize beam damage. The counts for sulfur were extrapolated back to zero time in order to estimate the original amount before exposure to the electron beam. The apparent levels of the abundant *REE* elements showed some erratic variation with time (Table 1). The analytical results were back-calculated to 100 wt%, assuming the stoichiometric levels of H, C, and O established by the structure analysis, and normalized to $\Sigma REE = 2$. Analysis for Na, Al, P, K, Ca, Fe, Ba, and the *REE* heavier than Gd showed that the concentrations of these elements are less than detectable values (<0.1 wt% for Ba and *HREE*, < 0.04 wt% for the other elements). The combined results of the electron-microprobe analysis (Table 1) and crystal-structure determination yield the empirical formula $(Ce_{1.06}Nd_{0.56}La_{0.20}Pr_{0.09}Sm_{0.04}Eu_{0.03}Gd_{0.01}Y_{0.01})_{\Sigma 2.00}(SO_4)_2(C_2O_4) \cdot 8H_2O$. This may be simplified to $(Ce,Nd,La)_2(SO_4)_2(C_2O_4) \cdot 8H_2O$. Alternative possibilities, based on the failure to locate two of the 16 hydrogen atoms associated with the H_2O molecules, are discussed below.

X-Ray Crystallography

Coskrenite-(Ce) was studied using the precession and Weissenberg methods, which revealed that it is triclinic, with space group $P\bar{1}$ or $P1$. The refined unit-cell parameters, obtained using the optimized setting angles of 25 reflections measured with a CAD4 four-circle diffractometer, are a 6.007(1), b 8.368(2), c 9.189(2) Å, α 99.90(2), β 105.55(2), γ 107.71(2)°, V 407.4(2) Å^3, for which $Z = 1$. Powder-diffraction data, obtained using a 114.6-mm diameter Gandolfi camera, are listed in Table 2. For reflections for which more than one d(calc) corresponded to a given d (obs) within error, intensities from the CAD4 data set were compared with the observed powder-derived intensities. Reflections whose single-crystal intensities were insignificant relative to observed powder-diffraction intensities were deleted from the list of calculated values.

Structure Solution and Refinement

A transparent, lath-shaped crystal of coskrenite-(Ce) was selected for measurement of intensity data after an examination for quality using the precession method. The crystal was mounted on an Enraf–Nonius CAD4 diffractometer and, after a determination of lattice parameters, the intensities of 2512 reflections in one hemisphere of reciprocal space were measured to a maximum 2θ of 60°. The intensities were then reduced to structure factors by correction for the Lorentz, polarization, and

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR COSKRENITE-(Ce)

I(obs)	d(obs)	d(calc)	hkl	I(obs)	d(obs)	d(calc)	hkl
70	8.52	8.51	0 0 1	10	2.152	2.153	2 $\bar{2}$ 2
60	6.72	6.69	0 1 $\bar{1}$			2.130	2 $\bar{2}$ 3
100	5.48	5.45	1 $\bar{1}$ 0	10	2.093	2.099	1 $\bar{3}$ 3
5	5.00	5.04	0 1 1			2.084	1 $\bar{4}$ 1
50	4.26	4.25	0 0 2			2.083	2 $\bar{3}$ 2
		4.25	0 1 $\bar{2}$			2.076	1 2 $\bar{4}$
5	4.04	4.08	1 0 $\bar{2}$	20	2.032	2.034	1 3 0
60	3.84	3.83	0 2 0			2.028	2 1 1
		3.79	1 1 0			2.027	0 2 3
30	3.61	3.63	1 $\bar{1}$ 2			2.021	1 3 $\bar{3}$
		3.58	1 1 $\bar{2}$	10	1.968	1.980	2 $\bar{1}$ 4
40	3.35	3.34	0 2 $\bar{2}$			1.965	2 $\bar{1}$ 4
10	2.846	2.836	0 0 3			1.961	0 $\bar{4}$ 2
40	2.744	2.773	1 2 $\bar{2}$			1.954	2 2 $\bar{3}$
		2.752	2 1 $\bar{2}$	20	1.915	1.920	3 $\bar{2}$ 2
		2.730	1 $\bar{3}$ 0			1.915	0 4 0
		2.724	2 $\bar{2}$ 0			1.915	0 $\bar{3}$ 4
30	2.680	2.715	2 $\bar{2}$ $\bar{1}$			1.909	3 $\bar{1}$ 0
		2.689	2 0 0			1.901	3 0 $\bar{2}$
		2.685	1 $\bar{1}$ 3	5	1.840	1.841	0 $\bar{4}$ 3
		2.657	0 2 $\bar{3}$			1.833	2 $\bar{2}$ 3
		2.656	0 3 $\bar{1}$	10	1.707	1.709	3 1 $\bar{1}$
20	2.431	2.450	2 1 $\bar{1}$			1.706	1 4 $\bar{1}$
		2.427	2 1 $\bar{2}$			1.705	2 3 $\bar{2}$
		2.414	1 1 2			1.703	2 1 $\bar{3}$
5	2.331	2.375	1 $\bar{1}$ 3			1.702	0 0 5
		2.330	1 2 1			1.699	3 1 $\bar{3}$
10	2.266	2.279	0 3 1				
		2.273	2 $\bar{3}$ $\bar{1}$				
		2.259	1 0 $\bar{4}$				
5	2.223	2.228	0 $\bar{3}$ 3				
		2.223	2 $\bar{3}$ 1				
		2.216	1 0 3				
		2.213	0 $\bar{1}$ 4				

Intensities visually estimated. Calculated d-values for which the corresponding observed single-crystal intensities are weak have been excluded.

TABLE 3. EXPERIMENTAL DETAILS

Crystal size	0.047 × 0.078 × 0.188 mm
Data measurement	
Radiation	Monochromatized $MoK\alpha$ at 50 kV, 30 mA
Index limits	$-8 \le h \le 8$, $-11 \le k \le 11$, $0 \le l \le 12$
Maximum 2θ	60.00°
Scan type	$\omega/2\theta$
Scan rates	0.4 to 5.5°/min in ω
Scan widths	$0.88 + 0.35 \tan\theta$
Intensity monitoring	4 reflections every 3 hrs
Orientation monitoring	4 reflections every 400 reflections
Data corrections	Lorentz, polarization, and absorption (μ_l 62.1 cm^{-1}) effects
Structure refinement	
Type	Full-matrix least-squares
Function minimized	$\Sigma w(F\text{obs} - F\text{cal})^2$
Reflection weights	$4F^2\text{obs}/\sigma^2(F^2\text{obs})$
Anomalous dispersion	For all atoms
Observations	2186 reflections with $I > 2\sigma(I)$
Variables	146 parameters
R(observed data)	0.045
wR(observed data)	0.055
R(all data)	0.050
Esd obs. of unit weight	1.615
Largest shift/error	0.01
Largest difference-Fourier peaks	+5.4 e/Å^3 and −1.5 e/Å^3
Diffractometer	Enraf–Nonius CAD4
Crystallographic software	MolEN System

absorption effects, the last of these by the psi-scan method (North *et al.* 1968) using ten reflections between 10° and 53° 2θ. Averaging of symmetry-equivalents (merging $R = 0.013$) resulted in a final data set of 2373 reflections, of which 2186 were considered "observed" at the $I(\text{obs}) > 2\sigma(I)$ threshold. Application of the direct methods program MULTAN11/82 in space group $P\bar{1}$ revealed the locations of the two heaviest atoms in the structure, *REE* and S, and a difference Fourier synthesis led to the location of eleven light atoms, which were initially assumed to be oxygen. This model refined to an unweighted residual of 0.090 using isotropic displacement factors. The scattering power of the *REE* site was approximated by the scattering curve of Ce ($Z = 58$), as the weighted average atomic number of the site is 58.6, and Ce is the dominant *REE* element. Additional details of the structure solution and refinement are given in Table 3.

At this point, a calculation of interatomic distances and angles yielded distances of 1.53, 1.26, and 1.25 Å for O11–O11', O11–O1, and O11–O2, respectively. The first of these was recognized as the length of a C–C single covalent bond, and the other distances and angles were found to be consistent with the configuration of the oxalate ion, $C_2O_4^{2-}$. Recognition of oxalate groups in coskrenite-(Ce), which had initially been assumed on the evidence of the electron-microprobe data to be a simple rare-earth sulfate hydrate, was greatly facilitated by the authors' previous experience with the structure of the natural sodium copper oxalate hydrate wheatleyite (Rouse *et al.* 1986).

With "O11" then correctly attributed to carbon, and converting to anisotropic displacement factors, the

unweighted residual decreased to 0.046. Inspection of the low-theta, high-intensity reflections showed no evidence of extinction. A series of difference Fourier syntheses using both the full dataset and a low-angle dataset truncated at $\sin\theta/\lambda = 0.400$ revealed the locations of seven of the eight hydrogen sites indicated by the chemical formula. All of the sites were associated with those oxygen sites (O5w, O7w, O9w, and O10w) that had been previously identified as belonging to H_2O molecules by their Pauling-type bond-valence sums. The hydrogen parameters refined smoothly to convergence, but the estimated standard deviations were high (*ca.* 0.01), and thus the hydrogen positions reported here are, at best, semi-quantitative. The unlocated hydrogen site is associated with O10w. An alternative interpretation of these results involving O10w as a hydroxyl ion rather than an oxygen atom belonging to H_2O and the reformulation of the coskrenite-(Ce) formula that this would entail are deferred until a later section of this report.

Inclusion of the hydrogen atoms in the structure model reduced the values of the residuals from 0.046 to 0.045 (unweighted) and from 0.059 to 0.055 (weighted). A final difference Fourier synthesis based on the full structure-model showed only one major feature, that being a group of small peaks of height 4 to 5 $e/\text{Å}^3$, clustered around the *REE* site at distances of *ca.* 0.75 Å. This anomaly may indicate residual absorption error in the data due to inadequacy of the psi-scan method in this case.

Table 4 contains the refined atomic positional and equivalent isotropic displacement factors, Table 5 the refined anisotropic displacement factors, Table 6 the observed and calculated structure-factors, and Table 7 some selected interatomic distances and angles. Copies of Table 6 are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

TABLE 4. POSITIONAL AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS IN COSKRENITE-(Ce)

Atom	x	y	z	$B(\text{Å}^2)$
REE	0.77072(4)	0.24583(3)	0.67858(3)	0.766(5)
S	0.8443(2)	0.2947(1)	0.2932(1)	1.13(2)
C	0.1280(8)	0.0646(6)	0.5552(6)	1.01(8)
O1	0.3150(6)	0.0417(5)	0.5326(4)	1.17(6)
O2	0.1334(6)	0.1837(5)	0.6603(5)	1.41(7)
O3	0.2548(8)	0.6990(5)	0.5768(5)	1.88(8)
O4	0.0901(8)	0.5318(5)	0.7364(5)	1.72(8)
O5w	0.4382(7)	0.5364(5)	0.3344(6)	2.26(8)
O6	0.3478(9)	0.8338(5)	0.8501(5)	2.08(9)
O7w	0.7772(8)	0.0061(5)	0.8075(5)	1.88(8)
O8	0.0661(8)	0.2496(5)	0.3333(6)	2.26(9)
O9w	0.1171(9)	0.3468(6)	0.9525(5)	2.25(9)
O10w	0.4107(7)	0.7164(5)	0.1051(5)	1.77(8)
H1	0.486(14)	0.282(10)	0.870(10)	2(2)
H2	0.789(12)	0.540(9)	0.005(8)	2(1)
H3	0.138(14)	0.056(9)	0.230(9)	2(2)
H4	0.368(11)	0.043(8)	0.180(8)	1(1)
H5	0.419(15)	0.440(11)	0.635(11)	3(2)
H6	0.379(15)	0.467(11)	0.345(10)	3(2)
H7	0.096(14)	0.265(10)	0.998(10)	2(2)

The hydrogen atoms were all refined with isotropic displacement parameters.

TABLE 5. ANISOTROPIC ATOMIC DISPLACEMENT PARAMETERS IN COSKRENITE-(Ce)

Atom	$U(11)$	$U(22)$	$U(33)$	$U(12)$	$U(13)$	$U(23)$
REE	0.01336(9)	0.00877(9)	0.00945(9)	0.00378(7)	0.00511(7)	0.00726(8)
S	0.0217(4)	0.0107(4)	0.0125(4)	0.0043(3)	0.0068(3)	0.0090(3)
C	0.015(2)	0.011(2)	0.013(2)	0.004(1)	0.005(1)	0.008(1)
O1	0.013(1)	0.015(1)	0.018(1)	0.005(1)	0.006(1)	0.007(1)
O2	0.015(1)	0.018(1)	0.019(1)	0.006(1)	0.006(1)	0.002(1)
O3	0.035(2)	0.026(2)	0.017(1)	0.012(1)	0.014(1)	0.012(1)
O4	0.028(2)	0.012(1)	0.023(2)	0.002(1)	0.005(1)	0.014(1)
O5w	0.027(1)	0.024(1)	0.050(2)	0.014(1)	0.021(1)	0.027(1)
O6	0.035(2)	0.017(2)	0.016(1)	−0.004(1)	0.007(1)	0.004(1)
O7w	0.032(2)	0.018(1)	0.029(2)	0.009(1)	0.016(1)	0.014(1)
O8	0.031(2)	0.026(1)	0.041(2)	0.016(1)	0.017(1)	0.021(1)
O9w	0.034(2)	0.026(2)	0.016(2)	0.004(2)	0.002(1)	0.007(1)
O10w	0.023(1)	0.033(2)	0.017(1)	0.013(1)	0.007(1)	0.016(1)

The form of the anisotropic displacement parameter is $\exp[-2\pi^2\{h^2a^2U(11) + k^2b^2(U22) + l^2c^2(U33) + 2hkab(U12) + 2hlac(U13) + 2klbc(U23)\}]$, where a, b, and c are the reciprocal cell parameters.

Description of Crystal Structure

The coordination polyhedron for the *REE* site is defined by nine ligands, five oxygen ions and four oxygen atoms of H_2O molecules (Fig. 2). The polyhedron is a monocapped square antiprism, defined by one square face and 12 triangular faces. Figure 3 shows how two such polyhedra are linked by vertex-sharing to two sulfate tetrahedra to form a four-membered ring, which is the fundamental building block (fbb) of the structure.

The fbb units combine to form chains extending parallel to [110] (Fig. 4). The linkage occurs only through the oxalate oxygen atom O1, which is common to two adjacent *REE* polyhedra. Adjacent chains are linked *via* oxalate groups. The oxygen atoms O1 and O2 form one side of a C_2O_4 group, each such pair sharing an edge with *REE* polyhedra in adjacent chains. The interconnected parallel chains thus define a sheet oriented parallel to {001}. Figure 5 shows such sheets oriented normal to the diagram, so that the direction of view is parallel to the sheets. The individual chains are oriented approximately normal to the plane of Figure 5. There are no cation–anion bonds between atoms in adjacent sheets. The only significant short bonds are those between O9w and O10w [2.917(7) Å], which represent hydrogen bonds O9w–H2•••O10w (Table 7). The perfect {001} cleavage is a result of this weak interplanar bonding.

Reference to Table 8 shows more-or-less satisfactory empirical bond-valence sums for all anions except the terminal sulfate oxygen atoms O6 and O8, which appear to be severely underbonded owing to the fact that they are each bonded to only one cation, sulfur (Figs. 3, 4). Their charge-neutralization requirements can only be met by the formation of two hydrogen bonds to each from H_2O molecules of neighboring $REEO_5(H_2O)_4$ groups. For O8, these bonds are O5w–H6•••O8 and O7w–H3•••O8, and for O6, they are O7w–H4•••O6 and O10w–*X*•••O6 (Fig. 4). Here "*X*" represents the unlocated H atom bonded to O10w. Its presence and the existence of an *X*•••O6 bond are implied by the O10w–O6 distance [2.673(7) Å], which is the shortest Ow–O distance in the structure. In addition, the oxalate oxygen atom O2 may be slightly underbonded because it is bonded to C and one *REE* atom, whereas the other oxalate oxygen atom, O1, is bonded to C and two *REE*.

TABLE 7. INTERATOMIC DISTANCES (Å) AND ANGLES (°)
IN COSKRENITE-(Ce)

$REEO_5(H_2O)_4$ Capped Antiprism

REE – O2	2.429(4)	*REE* – O10w	2.529(5)
O4	2.432(4)	O1	2.571(4)
O3	2.443(4)	O9w	2.602(5)
O7w	2.504(4)	O1	2.631(4)
O5w	2.509(5)	Mean	2.517

SO_4 Tetrahedron

S – O8	1.465(5)	O4 – S – O6	108.4(3)
O3	1.470(5)	O3 – S – O4	108.6(3)
O6	1.471(5)	O4 – S – O8	109.4(3)
O4	1.477(4)	O3 – S – O6	109.6(3)
Mean	1.471	O6 – S – O8	110.3(3)
		O3 – S – O8	110.6(3)
		Mean 109.5	

C_2O_4 Group

C – O2	1.249(6) ×2	C – C – O2	117.1(6) ×2
O1	1.258(6) ×2	C – C – O1	117.3(6) ×2
C	1.529(10)	O1 – C – O2	125.6(5) ×2

H_2O and H–O···O*

O5w – H5	0.77(11)	H5···O2ox	2.40(10)
O5w – H6	0.62(11)	O5w – O2ox	2.887(7)
H5 – H6	1.16(13)	O5w – H5···O2ox	127(4)
H5 – O5w – H6	113(13)	H6···O8s	2.14(12)
		O5w – O8s	2.733(7)
		O5w – H6···O8s	159(14)
O7w – H3	0.92(9)	H3···O8s	1.95(9)
O7w – H4	0.89(7)	O7w – O8s	2.840(7)
H3 – H4	1.59(11)	O7w – H3···O8s	161(7)
H3 – O7w – H4	123(7)	H4···O6s	1.83(8)
		O7w – O6s	2.712(7)
		O7w – H4···O6s	173(7)
O9w – H2	0.89(8)	H2···O10w	2.02(8)
O9w – H7	0.86(9)	O9w···O10w	2.917(7)
H2 – H7	1.58(11)	O9w – H2···O10w	175(7)
H2 – O9w – H7	128(8)	H7···O7w	2.41(9)
		O9w – O7w	2.787(7)
		O9w – H7···O7w	107(7)
O10w – H1	0.60(9)	H1···O2ox	2.25(10)
		O10w – O2ox	2.769(6)
		O10w – H1···O2ox	146(12)
		O10w – O6s	2.673(7)

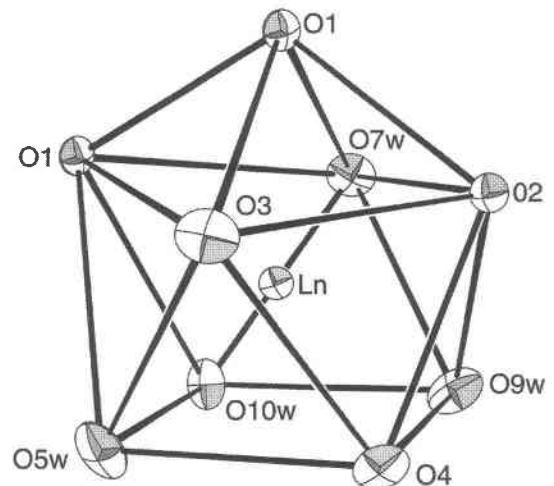*Ow: water oxygen, Os: sulfate oxygen, Oox: oxalate oxygen.

Fig. 2.   ORTEP-generated view of the monocapped square antiprism coordination polyhedron of the *REE*.
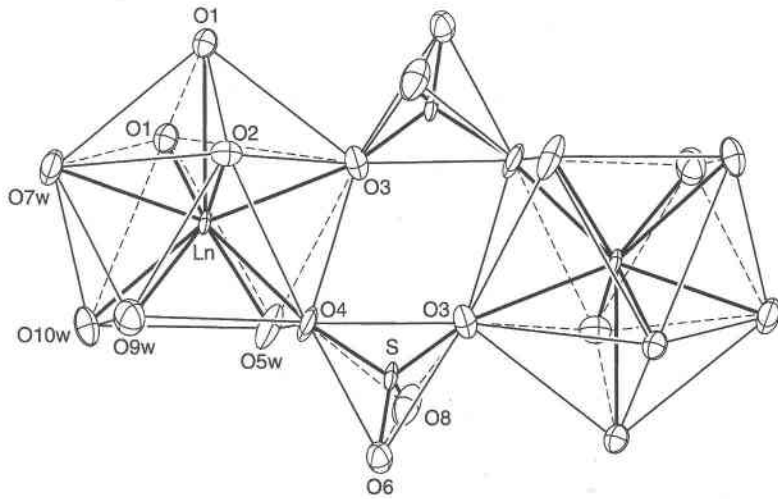
FIG. 3. ORTEP-generated drawing of the fundamental building block of the coskrenite-(Ce) structure, consisting of two *REE* polyhedra bridged by two sulfate tetrahedra. Ln: rare-earth element.
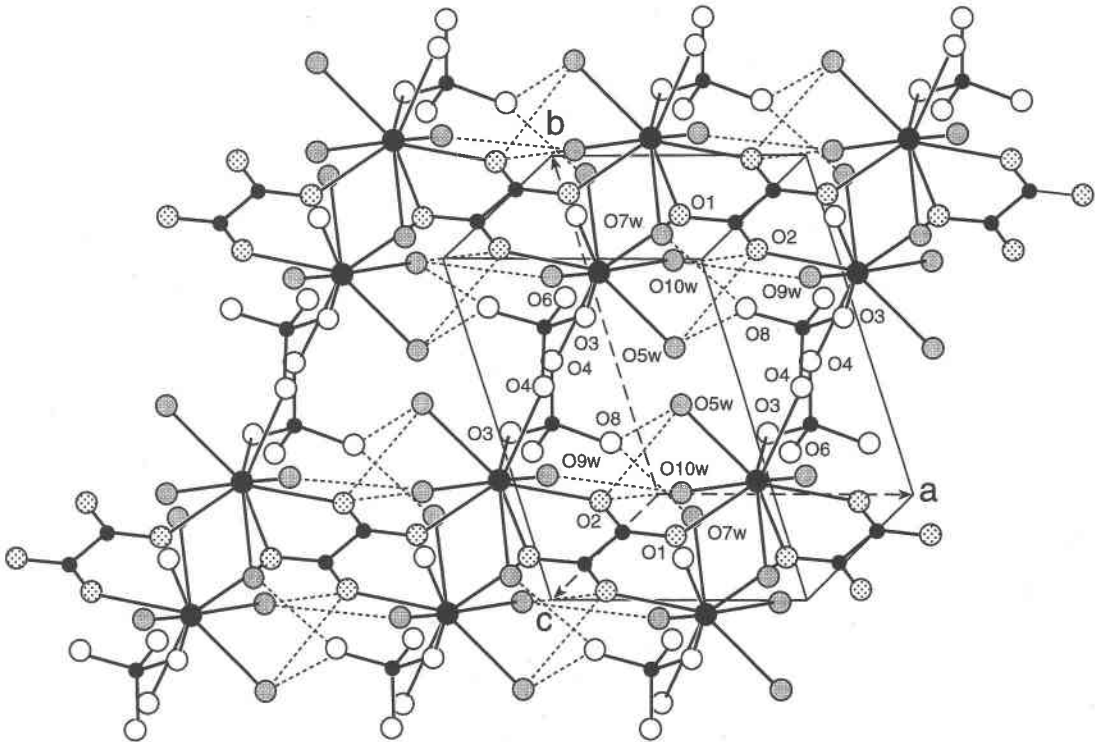

FIG. 4. View of the crystal structure of coskrenite-(Ce) projected parallel to **c***. The bonds of one chain are darkened. Small darkened circles correspond to S or C, larger darkened circles to the *REE*, and the large open circles to oxygen atoms. Oxygen atoms belonging to H₂O are shaded, and those belonging to the oxalate groups are stippled. Only the interchain hydrogen bonds are shown (as dashed lines).

Any charge deficit here is eliminated by the potential hydrogen bonds O5w–H5•••O2 and O10w–H1•••O2.

A calculation of the valence of carbon in the oxalate group, when it is done in the usual way assuming a valence of –2 for oxygen, gives an apparent value of +3 for this element. However, the oxalate group is strictly a covalent bonding system, with the configuration $O_2CF–CO_2$. Each carbon atom forms single bonds to the other carbon atom and one oxygen atom, plus a double bond to the other oxygen atom. This system requires a contribution of four valence electrons from each carbon atom, and carbon therefore has its normal *covalence* of four, *i.e.*, C^{IV} rather than C^{4+}, in the oxalate group. The use of bond-valence constants for C(IV) in the bond-valence calculations reported in Table 8 is therefore justified. Indeed, the bond-valence constant R_o = 1.543 (Brown 1981) used to calculate the C–C bond valence in Table 8 is just the length of a C–C single bond (Urusov 1995).

Coskrenite-(Ce), levinsonite-(Y), and zugshunstite-(Ce) are the first natural members of a small but expanding group of mixed-anion oxalates, data for which are given in Table 9. These compounds adopt a variety of structure types, but most are based on chains and rings of $REEO_8$ or $REEO_9$ polyhedra plus other ions, the chains or rings being linked in various ways to form layer structures. As described above, this is also the case for the structure of coskrenite-(Ce), although the analogy breaks down at the level of the specific kinds of rings and chains.

Possible alternative chemical formulae

Assuming that oxygen atom O10 is correctly attributed to H_2O, the formula of coskrenite-(Ce) is $REE_2(SO_4)_2(C_2O_4)•8H_2O$, which is perfectly charge-balanced, assuming all trivalent *REE*, as is commonly the case. On the other hand, 14 of the 16 hydrogen at-

TABLE 8. EMPIRICAL BOND-VALENCES IN COSKRENITE-(Ce)

Atom	REE	S	C	Σv_a
C			1.04	
O1ox	0.31,0.26		1.43	2.00
O2ox	0.46		1.46	1.92
O3s	0.44	1.52		1.96
O4s	0.45	1.49		1.94
O5w	0.37			0.37
O6s		1.51		1.51
O7w	0.37			0.37
O8s		1.54		1.54
O9w	0.29			0.29
O10w	0.35			0.35
Σv_c	3.30	6.06	3.93	

The bond-valence constants used in the calculations are those of Brown (1981) for the C–C bond, and those of Brese & O'Keeffe (1991) for all other bonds. A weighted average constant was used for the REE site. The letters w, s, and ox appended to the atomic labels have the same meaning as in Table 7. Σv_a, Σv_c: bond valences of anions and cations, respectively.

oms required of that formula were located in a straight-forward manner, but two of the four that would be associated with O10 if it is part of an H_2O molecule could not be found. This implies that the H atoms are positionally disordered or that O10 may be attributed to a hydroxyl ion. In the latter case, two possibilities may be considered to account for the resulting deficiency of positive charge:

1. The REE may occur in the 4+ valence state, resulting in the formula $(REE^{4+}, REE^{3+})_2(SO_4)_2(C_2O_4)(OH)_2 \cdot 6H_2O$. Indeed, Ce^{4+} is known to occur in minerals (Brookins 1989), but it is the only REE with that valence identified in minerals. Cotton & Wilkinson (1988) stated that the oxidation state 4+ is important for Ce, of minor importance for Pr and Tb, and very rare for Nd and Dy. Because Nd is a prominent element in coskrenite-(Ce), charge balance would require that it occur as the ion Nd^{4+}, but that possibility is highly unlikely. Even if Ce, Nd, and Pr occur as ions of charge 4+, the remaining 3+ ions still leave the formula not fully charge-balanced. In addition, atoms O5, O7, O9, and O10 all have the same cation coordination, each being bonded to one REE and no other atom (other than H), and the REE–O bond distances are not markedly different from one another [2.509(5), 2.504(4), 2.602(5), and 2.529(5) Å, respectively]. Because the identification of O5, O7, and O9 as H_2O oxygen atoms is beyond question, it is reasonable to conclude that O10 is of the same species. Lastly, the lanthanide sulfate oxalates that coexist with coskrenite at Alum Cave Bluff, namely zugshunstite-(Ce) and levinsonite-(Y), contain only trivalent REE ions. It is reasonable to expect the same of coskrenite-(Ce), as it is coeval with those minerals.

2. A hydrogen atom may be associated with an oxygen atom that coordinates sulfur, resulting in the for-

TABLE 9. NATURAL AND SYNTHETIC MIXED-ANION OXALATES

Sulfate Oxalates		
$(REE)_2(SO_4)_2(C_2O_4) \cdot 8H_2O$ [1] Coskrenite-(Ce)	Triclinic $P\bar{1}$	a 6.007, b 8.368, c 9.189 Å α 99.90, β 105.55, γ 107.71° $Z = 1$
$(REE)Al(SO_4)_2(C_2O_4) \cdot 12H_2O$ [1] Levinsonite-(Y)	Monoclinic $P2/n$	a 10.289, b 9.234, c 11.015 Å β 108.50°, $Z = 2$
$(REE)Al(SO_4)_2(C_2O_4) \cdot 12H_2O$ [1] Zugshunstite-(Ce)	Monoclinic $C2/c$	a 8.718, b 18.313, c 13.128 Å β 93.90°, $Z = 4$
Phosphate Oxalates		
$Sn_2(PO_4)(C_2O_4)_{0.5}$ [2]	Monoclinic $P2_1/n$	a 4.712, b 5.862, c 22.242 Å β 95.77°, $Z = 4$
$Fe_4(PO_4)_2(C_2O_4) \cdot 2H_2O$ [3]	Monoclinic $P2_1/n$	a 7.974, b 4.817, c 14.169 Å β 94.70°, $Z = 2$
$(NH_3CH_2CH_2NH_3)_{2.5}[Al_4H$ $(HPO_4)_4(H_2PO_4)_2(C_2O_4)_4]$ [4]	Monoclinic $C2/m$	a 19.683, b 12.360, c 16.734 Å, β 110.51°, $Z = 4$
$(C_4H_{12}N_2)[Fe^{2+}_4(C_2O_4)_3(HPO_4)_2]$ [5]	Monoclinic $P2_1/c$	a 7.5573, b 7.8188, c 18.0421 Å, β 98.710°, $Z = 2$
$(C_5H_{14}N_2)[Fe^{3+}_2(C_2O_4)(HPO_4)_3]$ [5]	Triclinic $P\bar{1}$	a 6.3948, b 9.1419, c 16.1585 Å, α 98.758, β 93.443, γ 108.488°, $Z = 2$
$[N_2C_4H_{12}]_{0.5}[Fe_2(HPO_4)(C_2O_4)_{1.5}]$ [6]	Monoclinic $P2_1/c$	a 7.569, b 7.821, c 18.033 Å β 98.8°, $Z = 4$
$Fe_2(OH)_2PO_4(C_2O_4)_{0.5}$ [6]	Monoclinic $P2_1/c$	a 10.240, b 6.375, c 9.955 Å β 117.3°, $Z = 4$
Carbonate and Formate Oxalates		
$(CN_3H_6)_9REE(CO_3)_2(C_2O_4)_2 \cdot nH_2O$ [7]	Not reported	Not reported
$[Ce(H_2O)]_2(C_2O_4)_2(CO_3) \cdot 2.5H_2O$ [8]	Triclinic $P\bar{1}$	a 6.329, b 8.743, c 13.004 Å α 105.59, β 90.47, γ 105.13° $Z = 2$
$[Gd(H_2O)]_2(C_2O_4)(CO_3)_2$ [9]	Orthorhombic $C2mm$	a 7.8941, b 15.127, c 4.7931 Å, $Z = 2$
$Ce(C_2O_4)(HCO_2)$ [7]	Orthorhombic $Pnma$	a 7.322, b 10.825, c 6.738 Å $Z = 8$

References: [1] this study, [2] Natarajan (1998), [3] Lethbridge & Lightfoot (1999), [4] Lightfoot et al. (1999), [5] Lin et al. (1999), [6] Choudhury et al. (1999), [7] Dumonceau et al. (1981), [8] Romero et al. (1996), [9] Romero et al. (1997).

mula $(REE)_2(SO_3OH)_2(C_2O_4)(OH)_2 \cdot 6H_2O$; that is, there is an acid sulfate group. There is precedence for this case, namely in the minerals matteuccite ($NaHSO_4 \cdot H_2O$), mercallite ($KHSO_4$), letovicite [$(NH_4)_3H(SO_4)_2$] (Pushcharovsky et al. 1998), and mitryaevaite {Al_{10} [$(PO_4)_{8.7}(SO_3OH)_{1.3}]\Sigma_{10}AlF_3 \cdot 30H_2O$} (Ankinovich et al. 1997). A search of the difference Fourier synthesis calculated using all atoms in the model, including the seven known hydrogen positions, revealed nothing that might be identified as the hydrogen atom of an (SO_3OH) group.

The above-described relations therefore present no reasonable alternative to the formula $(REE^{3+})_2(SO_4)_2$ $(C_2O_4) \cdot 8H_2O$ for coskrenite-(Ce). The inability to locate two hydrogen atoms of a single equipoint of rank

two during the structure determination is ascribed to the normal difficulty in locating hydrogen atoms, commonly because they may be disordered over alternative sites.

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