des rayons ioniques (Shannon, 1976): Yb^{3+}(VII)—S^{2-} 2,76 Å. Comme habituellement, la septième liaison Yb—S 3,11 Å est significativement plus longue. Bien que ce type de configuration se retrouve aussi dans le composé $CeYb_3S_6$ (Rodier & Laruelle, 1973) avec des distances du même ordre de grandeur (2,67 à 2,88 Å), il est relativement peu répandu dans les sulfures où l'ytterbium possède de préférence un environnement octaédrique.

Cette structure peut donc être considérée comme constituée de colonnes de prismes à section triangulaire, perpendiculaires au plan *ab* et reliées entre elles par des rubans plans d'octaèdres. Si les symboles '*O*' et '*P*' représentent respectivement un octaèdre et un prisme, cet enchaînement correspond au motif *O–O–P* (Fig. 1). En désignant les atomes de manganèse et d'ytterbium par le symbole *M*, on peut faire correspondre au motif *O–O–P*, la formule chimique M_3S_4.

Cette structure présente donc des caractères analogues à celles des sulfures ternaires de terres rares (Er, Yb) et de métaux de transition du groupe 3*d* (Cr, Mn) précédemment étudiées.

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Structure of Cobalt Sulfate Tetrahydrate

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Abstract. Cobalt(II) sulfate tetrahydrate-d_8, $CoSO_4.4D_2O$, mineralogical name aplowite, $M_r = 235.10$, monoclinic, $P2_1/n$, $a = 5.952$ (1), $b = 13.576$ (2), $c = 7.908$ (1) Å, $\beta = 90.53$ (1)°, $V = 638.90$ Å^3, $Z = 4$, $D_x = 2.444$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 2.990$ mm^{-1}, $F(000) = 460$, $T = 295$ K, $R(F) = 0.0217$ for 2637 unique observed reflections. The title compound belongs to the rozenite group of minerals. The characteristic structural units are $[Co_2(SO_4)_2(D_2O)_8]$ heteropolyhedral clusters which are linked by hydrogen bonds of medium strength. One of the water molecules is very asymmetrically bonded, with one H (D) atom being involved in a long bifurcated hydrogen bond.

Introduction. The hydrates of many sulfates of divalent metal ions have been well known and comprehensively characterized for a long time. However, this is not fully true for the corresponding cobalt compounds, possibly owing to the limited stability of almost all these hydrates. The structure of the hexahydrate has been solved and refined by single-crystal X-ray methods (Zalkin, Ruben & Templeton, 1962; Elerman, 1988). Very recently, the structure of the heptahydrate has been reported (Kellersohn, Delaplane & Olovsson, 1991). The monohydrate has so far only been characterized by powder methods (Boyat & Bassi, 1963; Le Fur, Boyat & Bassi, 1966; Oswald, 1965).

Our knowledge of the tetrahydrate has until now been very limited: $CoSO_4.4H_2O$ has been reported to be a metastable phase in the $CoSO_4/H_2SO_4/H_2O$ system (Rohmer, 1939), but it occurs during the dehydration of the hepta- and hexahydrates (Guenot, Manoli & Bregeault, 1969). It was prepared by Hammel (1939), who also described a powder photograph and reported approximate lattice param-

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eters. It occurs naturally as a rare mineral and has been given the name aplowite (Jambor & Boyle, 1965).

While growing crystals of the deuterated hexahydrate for an electron-density study (McIntyre, Kellersohn, Delaplane & Olovsson, 1992), single crystals of the deuterated tetrahydrate were obtained as a byproduct. Since its structure has not yet been reported, a single-crystal X-ray study was performed.

Experimental. A saturated solution of previously dried $CoSO_4$ in 10% D_2SO_4/90% D_2O was allowed to evaporate slowly at room temperature in order to grow large crystals of the hexahydrate. On further evaporation, however, these finally dissolved and the monohydrate precipitated as a microcrystalline powder together with very few pink coloured crystals of the tetrahydrate. The degree of deuteration of the tetrahydrate crystal under investigation could not be determined; however, the single-crystal neutron diffraction study on one hexahydrate crystal obtained previously from this batch (McIntyre, Kellersohn, Delaplane & Olovsson, 1992) showed the deuterium content to be higher than 94%, and the situation for the tetrahydrate should be similar. A crystal fragment of size 0.22 × 0.20 × 0.20 mm was coated with a thin layer of polystyrene and mounted on a Huber four-circle diffractometer. Cell parameters were determined from 37 well centered reflections with $25 < 2\theta < 30°$. A total of 8572 reflections up to $2\theta = 80°$, $-11 < h < 11$, $0 < k < 25$, $-14 < l < 14$, were measured in step-scans, ω–2θ mode, with $\Delta\omega = 0.010°$ and a basic number of 70 steps, the time per step varying between 0.3 and 2.0 s. Five monitor reflections were measured every 3 h, and their intensity decreased linearly by 3% during the 286 h of data collection. A decay correction was accordingly applied. Because of the poorly defined boundary planes, a spherical absorption correction was performed; transmission factors were in the range 0.613–0.614. Merging of symmetry-related reflections gave 3949 unique reflections, $R_{\text{int}} = 0.0142$ based on I. 2637 of these had $I > 3\sigma(I)$ and were used in the following refinements.

The structure was solved by direct methods and subsequent Fourier syntheses. H atoms were located by difference Fourier syntheses and refined with isotropic temperature factors. For the final refinements, the same setting as given by Baur (1962, 1964) for $MgSO_4.4H_2O$ was used to enable a convenient comparison, but the atomic numbering scheme was slightly changed. Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All refinements (on F^2) were performed with the *DUPALS* program (Lundgren, 1982). A total of 124 parameters, including a scale factor and an isotropic extinction parameter, type I according to Becker & Coppens (1974, 1975) with a Gaussian distribution of mosaic blocks, final value $g = 0.11\ (2) \times 10^4$, were refined in the last cycles. The ratio of max. least-squares shift to e.s.d. was less than 0.001, final $R(F^2) = 0.0344$, $wR(F^2) = 0.0535$ with $w = [\sigma(F^2) + (0.03F^2)^2]^{-1}$, conventional $R(F) = 0.0217$, $S = 1.30$. A δR plot according to Abrahams & Keve (1971) had a slope of 0.83 and an ordinate intercept of -0.05 with 24 reflections having $|\delta R(\text{observed})| > 4.0$. Max. and min. heights in the final $\Delta\rho$ map were $+0.47$ and -0.53 e Å^{-3}, both within 1 Å from Co. Atomic coordinates and equivalent isotropic displacement parameters are given in Table 1.*

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters U_{eq} (Å$^2 \times 10^2$) with e.s.d.'s in parentheses*

Atoms marked with an asterisk were refined isotropically. The U_{eq} values were estimated according to: $U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
Co	0.06724 (2)	0.10309 (1)	0.21933 (2)	1.27 (1)
S	0.19357 (4)	0.10776 (2)	0.82516 (3)	1.16 (1)
O1	0.00299 (14)	0.04841 (6)	0.75701 (10)	1.76 (3)
O2	0.24967 (14)	0.07409 (6)	0.99928 (10)	1.75 (3)
O3	0.39356 (14)	0.09218 (6)	0.71774 (11)	1.94 (4)
O4	0.12949 (14)	0.21206 (6)	0.82276 (10)	1.81 (3)
O5	0.36309 (15)	0.07547 (7)	0.35563 (12)	2.15 (4)
O6	0.76821 (15)	0.14101 (8)	0.08449 (12)	2.26 (4)
O7	0.88754 (18)	0.12677 (8)	0.44018 (12)	2.78 (5)
O8	0.17624 (16)	0.24891 (6)	0.21772 (12)	2.17 (4)
D51	0.362 (4)	0.081 (2)	0.446 (3)	1.6 (2)*
D52	0.447 (4)	0.026 (2)	0.334 (3)	2.1 (2)*
D61	0.693 (5)	0.178 (2)	0.131 (3)	4.0 (2)*
D62	0.680 (4)	0.098 (2)	0.043 (4)	2.8 (2)*
D71	0.820 (3)	0.175 (2)	0.448 (3)	1.2 (1)*
D72	0.927 (4)	0.107 (2)	0.548 (3)	1.9 (2)*
D81	0.286 (4)	0.257 (2)	0.278 (3)	2.2 (2)*
D82	0.081 (3)	0.297 (2)	0.228 (2)	1.3 (2)*

Discussion. Selected bond distances and angles are listed in Table 2. All atoms occupy the general position 4(*e*) in space group $P2_1/n$. $CoSO_4.4D_2O$ belongs to the rozenite group of minerals with the general formula $MSO_4.4H_2O$, M = Fe (rozenite), Mn (ilesite), Mg (leonhardtite or starkeyite), Zn (boyleite) and Co (aplowite). Its formation seems to be kinetically determined, whereas, once formed, it appears to be quite stable. It is likely that the stability of the deuterated form is different from that of the protonated one, as such a stability difference has been observed for the heptahydrate (Kellersohn, Delaplane & Olovsson, 1991).

The basic structural units are $[CoO_2(D_2O)_4]$ octahedra and SO_4 tetrahedra, which are, due to the

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* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54774 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0252]

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

$[CoO_2(D_2O)_4]$ octahedron

Co—O1^{i}	2.107 (1)	Co—O6^{iii}	2.129 (1)
Co—O2^{ii}	2.097 (1)	Co—O7^{iii}	2.081 (1)
Co—O5	2.090 (1)	Co—O8	2.083 (1)
O1^{i}—Co—O2^{ii}	89.72 (4)	O2^{ii}—Co—O8	90.55 (4)
O1^{i}—Co—O5	86.90 (4)	O5—Co—O7^{iii}	91.84 (5)
O1^{i}—Co—O6^{iii}	96.59 (4)	O5—Co—O8	84.99 (4)
O1^{i}—Co—O7^{iii}	88.42 (4)	O6^{iii}—Co—O7^{iii}	87.09 (5)
O2^{ii}—Co—O5	87.37 (5)	O6^{iii}—Co—O8	91.49 (4)
O2^{ii}—Co—O6^{iii}	93.82 (5)	O7^{iii}—Co—O8	91.19 (4)

Sulfate ion

S—O1	1.488 (1)	S—O3	1.484 (1)
S—O2	1.486 (1)	S—O4	1.466 (1)
O1—S—O2	109.44 (5)	O2—S—O3	108.19 (6)
O1—S—O3	109.16 (6)	O2—S—O4	111.42 (5)
O1—S—O4	108.72 (5)	O3—S—O4	109.89 (5)

Water molecules and hydrogen bonding

O—D···*X*	O—D	D—O—D	O···*X*	D···*X*	O—D···*X*	Co—O—D
O5—D51···O3	0.72 (2)	106 (2)	2.877 (2)	2.16 (2)	174 (2)	119 (2)
O5—D52···O3^{iv}	0.86 (2)		2.762 (2)	1.91 (2)	174 (2)	122 (1)
O6—D61···O4^{v}	0.76 (3)	106 (2)	2.871 (2)	2.17 (3)	153 (3)	114 (2)
O6—D62···O2^{ii}	0.85 (3)		3.281 (2)	2.60 (3)	138 (2)	123 (2)
O6—D62···O2^{iv}			2.996 (2)	2.40 (3)	128 (2)	
O7—D71···O4^{v}	0.77 (2)	108 (2)	2.825 (2)	2.14 (2)	148 (2)	118 (2)
O7—D72···O1^{vi}	0.92 (2)		2.802 (2)	1.89 (2)	172 (2)	127 (1)
O8—D81···O4^{v}	0.81 (2)	111 (2)	2.865 (2)	2.11 (2)	154 (2)	112 (2)
O8—D82···O3^{vii}	0.87 (2)		2.736 (2)	1.87 (2)	171 (2)	121 (1)

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

stoichiometry, not isolated as in the hepta- and hexahydrates, but linked *via* the sulfate O atoms O1 and O2 to form cyclic $[Co_2(SO_4)_2(D_2O)_8]$ entities as 'fundamental building blocks' (Hawthorne, 1990) with a centre of symmetry (see Fig. 1). These fundamental building blocks are interconnected *via* hydrogen bonds of medium strength with O···O distances in the range 2.736 (2)–2.877 (2) Å, with the exception of D62 (see below).

The distortion of the oxygen octahedron around Co is only slight and comparable to that in the hepta- and hexahydrates. All four water molecules have only one divalent metal ion coordinating on the oxygen lone-pair side, but the deviations from an ideal trigonal coordination are significant in each case; see also the discussion given by Kellersohn, Delaplane & Olovsson (1991).

D62 is an exception since it forms a very long bifurcated hydrogen bond to two sulfate O atoms (O2), each bond being strongly bent. The analogous situation in $MgSO_4.4H_2O$ was interpreted by Baur (1964) as indicating the absence of a hydrogen bond. However, since then numerous vibrational spectroscopic studies on solid hydrates have revealed that the distance range [O···*X* as well as H(D)···*X*] where hydrogen bonding takes place has to be extended considerably; for a recent review, see Lutz (1988). It is questionable whether any solid hydrate with 'free' OH groups has been found so far. The view that D62 is also really hydrogen bonded can be supported by bond-valence considerations (Brown, 1981): a deficiency of 0.22 v.u. (valence units) is found for O2 when the two long D···O contacts are excluded from the calculations. The situation is much more balanced when they are included with a neutron-adjusted O6—D62 bond length of 0.963 Å: only a very slight deviation (−0.01 v.u.) from the ideal value of 2.0 v.u. remains. Nevertheless, $D_2O(6)$ is asymmetrically bonded (Fig. 2), but this asymmetry

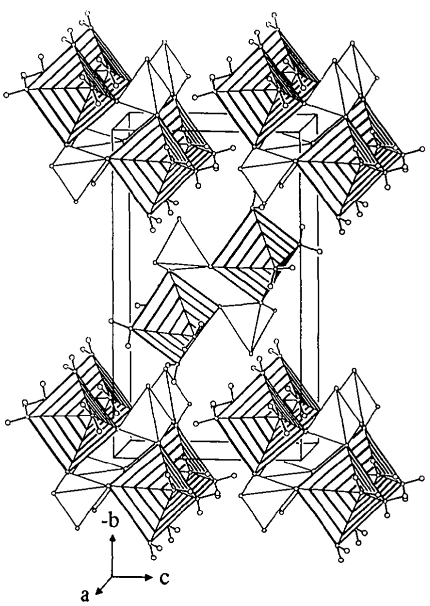

Fig. 1. Polyhedral representation of the structure of $CoSO_4.4D_2O$, projection approximately along [100]. The octahedra around Co are shaded, sulfate tetrahedra are open, Co and S atoms are not drawn, O and D atoms are given arbitrary radii.

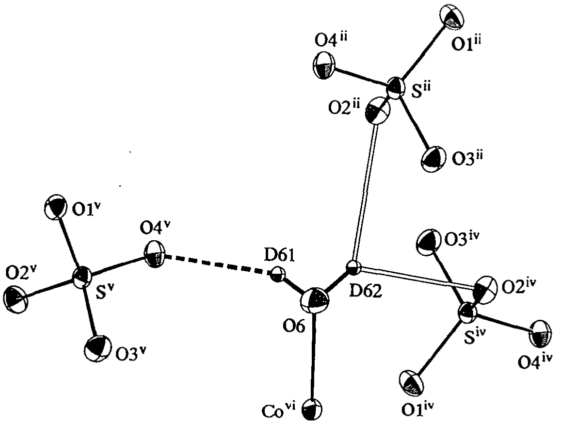

Fig. 2. Environment of $D_2O(6)$ with the long bifurcated hydrogen bond of D62 (open lines). Vibrational ellipsoids (Johnson, 1976) are drawn with 50% probability, except D with arbitrary radii. See Table 2 for symmetry codes.

is not as pronounced as *e.g.* in the $Sr(OH)Cl.4H_2O$-type compounds (Kellersohn, Beckenkamp & Lutz, 1991) where, in addition to large differences in the hydrogen-bond lengths, the acceptor strengths of X are also very different. For a more quantitative evaluation of the situation in $CoSO_4.4D_2O$, however, further vibrational spectroscopic studies will be essential.

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Synthesis and Structure Determination of $SrCa(edta).5H_2O$

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Abstract. Tetraaqua(ethylenediaminetetraacetato)-calciumstrontium monohydrate, $[SrCa(C_{10}H_{12}N_2O_8)(H_2O)_4].H_2O$, $M_r = 505.9$, monoclinic, $C2/c$, $a = 19.568\ (2)$, $b = 11.535\ (8)$, $c = 16.028\ (2)$ Å, $\beta = 95.565\ (8)°$, $V = 3600\ (3)$ Å^3, $Z = 8$, $D_m = 1.82\ (2)$, $D_x = 1.86$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 32.5$ cm^{-1}, $F(000) = 2064$, $T = 296$ K, $R = 0.040$ for 2918 unique observed reflections. The geometry of the compound consists of a three-dimensional linkage of ligand-bridged metal ions and hydrogen bonds. The Ca ion is octacoordinated by four O and two N atoms of edta (ethylenediaminetetraacetic acid), one O atom of another edta molecule and one water molecule. The Sr ion displays nearly square antiprismatic coordination, being bound to three water molecules and five O atoms from different edta molecules.

Introduction. edta has long been known and studied as a calcium binding agent, not only with respect to

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