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Powder and single-crystal X-ray diffraction study of the structure of $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$

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From powder pattern indexing it has been demonstrated that $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$, yttrium oxalate carbonate, crystallizes with orthorhombic symmetry, space group $C222_1$, a = 7.8177 (7), b = 14.943 (1), c = 9.4845 (7) Å, V = 1108.0 (1) $Å^3$, Z = 4. This unit cell displays a doubling of the c parameter, arising from weak diffraction lines observed in the powder diffraction pattern, with respect to results reported in the literature. The crystal structure has been solved *ab initio* using direct methods from powder data and has been confirmed by additional single-crystal data collected with a CCD area detector. The overall crystal structure is similar for both unit cells, except that an alternation of the carbonate groups in the direction parallel to the screw axis is displayed in the larger cell, while with the suggested half unit cell (space group *C2mm*) the carbonate groups would show only one orientation. The unit-cell determination strategy from single-crystal diffraction, collected with Nonius CAD-4 and Nonius Kappa CCD diffractometers, is discussed with respect to the results extracted from the powder diffraction pattern. The study demonstrates the power and usefulness of the full trace of a powder pattern for the detection of subtle structure details.

1. Introduction

Recent studies on the synthesis and crystal chemistry of mixed lanthanum or yttrium oxalates with monovalent elements have revealed two crystal structure types, *i.e.* a three-dimensional structure has been found for $YK(C_2O_4)_2{\cdot}4H_2O$ (Bataille *et al.*, 1999), and a layered-type structure has been identified for $Y(H_2O)Na(C_2O_4)_2{\cdot}3H_2O$ (Bataille & Louër, 1999) and $La(H_2O)_2M(C_2O_4)_2{\cdot}H_2O$ (M = K, NH_4; Bataille *et al.*, 2000). Attempts to extend the family to a mixed yttrium and silver oxalate failed, always giving a different phase in powder form. This compound has been identified from its powder diffraction pattern as a mixed yttrium oxalate carbonate. It belongs to a series of phases $[Ln(H_2O)]_2(C_2O_4)(CO_3)_2$, with Ln = Eu, Gd, Tb, Dy, Y and Ho, recently discovered by Roméro *et al.* (1997). The unit-cell dimensions reported for these phases suggested isostructural properties and the crystal structure type was determined by these authors from single-crystal diffraction data for $[Gd(H_2O)]_2(C_2O_4)(CO_3)_2$ only (space group *C2mm*). In the course of our analysis of the yttrium compound the powder diffraction pattern revealed that a few diffraction lines with low intensity were not indexed by the orthorhombic unit cell reported by Roméro *et al.* (Table V in Roméro *et al.*, 1997). This subtle observation has motivated a thorough analysis of the powder diffraction data to determine the crystal structure of $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$, in spite of a sample made of a mixture of the oxalate carbonate and metallic silver. Furthermore, during the progress of the study and in order to validate the structure details derived from powder data with higher precision, single crystals have been synthesized and used for structure determination and refinement.

2. Experimental

2.1. Synthesis

$[Y(H_2O)]_2(C_2O_4)(CO_3)_2$ was obtained in powder form under hydrothermal conditions. A suspension of 0.37 mmol of $Y_2(C_2O_4)_3{\cdot}10H_2O$ and 1 mmol of $Ag_2C_2O_4$ in 7 ml of water was introduced in a 23 ml Teflon-lined acid digestion bomb (Parr) and acidified (pH = 2) with concentrated HNO_3. The solution was heated to 423 K for 3 d and cooled by quenching to room temperature. $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$ was mixed with small aggregates of silver, according to the reactions due to the oxalate decomposition (Boldyrev, 1993; Roméro *et al.*, 1997). Crystals of $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$ containing inclusions of metallic silver were obtained with the same conditions, except that the solution was cooled slowly to room temperature over 1 d.

2.2. Powder data collection

High-quality X-ray powder diffraction data were obtained with a Siemens D500 diffractometer using monochromatic Cu $K\alpha_1$ radiation (λ = 1.5406 Å) selected with an incident beam curved-crystal germanium monochromator, using the parafocusing Bragg–Brentano geometry, whose characteristics have been reported elsewhere (Louër & Langford, 1988). The powder was ground for 1 h and mounted in a top-loaded sample holder (Swanson *et al.*, 1964) to minimize the preferred orientation effects. The pattern was scanned over the angular range 10–145° (2θ), with a step length of 0.02° (2θ) and a counting time of 75 s per step. After data collection, the stability of the X-ray source was checked by recording again the diffraction lines at low angles. For pattern indexing, the extraction of the peak positions was carried out with the Socabim program *PROFILE*, which is a part of the *DIFFRAC-AT* software package supplied by Bruker AXS. Pattern indexing was performed with the program *DICVOL*91 (Boultif & Louër, 1991). The structure was solved *ab initio* by means of the program *SHELX*97 (Sheldrick, 1997) and the structure refinement was carried out with *FULLPROF*99 (Rodriguez-Carvajal, 1990), available in the software package *WINPLOTR* (Rodriguez-Carvajal & Roisnel, 1998).

2.3. Single-crystal data collection

2.3.1. Nonius CAD-4. A crystal with an average hexagonal-prism shape (0.113 × 0.038 × 0.038 mm) was mounted on an Enraf–Nonius CAD-4 diffractometer using Mo $K\alpha$ radiation (λ = 0.71073 Å) and θ–2θ scan mode. Only SEARCH procedures were carried out for orientation matrix determination and peak indexing, on the basis of 25 observed reflections (Enraf–Nonius, 1989).

2.3.2. Nonius KappaCCD. The same crystal was mounted on a four-circle Nonius Kappa CCD diffractometer, using Mo $K\alpha$ radiation (λ = 0.71073 Å) and equipped with a CCD area detector. The experiment was carried out in the resolution range 20.40–0.62 Å with a crystal-to-detector distance of 32 mm. For the cell determination, a first set of 20 frames was collected with an exposure time per frame of 30 s and a step rotation of the φ angle of 1°. Data collection was performed by collecting 131 frames with a step rotation of 2° for the ω angle. Each frame was obtained with a total exposure time of 60 s, from two iterations of 30 s. Reflection indexing, peak integration and background determination were carried out with the program *DENZO*, available in the KappaCCD software package (Nonius, 1998). The unit-cell parameters were refined with the program *SCALEPACK* of the Nonius software package, on the basis of 2298 reflections in the θ range 1.00–34.97°. A numerical absorption correction was applied by Gaussian integration over the crystal volume, according to the procedure described by Coppens & Hamilton (1970). (For further details on data collection, see, for instance, Kuntzinger *et al.*, 1999.) The structure was solved with the direct-methods program *SIR*97 (Altomare *et al.*, 1999) and refined by least-squares with *SHELXL*97 (Sheldrick, 1997).

3. Structure solution and refinement

3.1. Powder pattern indexing

The first 20 lines of the powder pattern were indexed, using an absolute error of 0.02° (2θ) on the peak positions, on the basis of an orthorhombic solution with the unit-cell dimensions a = 7.821 (1), b = 14.948 (2), c = 9.486 (2) Å and V = 1109.02 Å^3 [M_{20} = 44, F_{20} = 79(0.005,51)]. This result compares well with the cell reported by Roméro *et al.* (1997) of $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$ [a = 7.822 (2), b = 14.948 (4), c = 4.742 (1) Å], except that the c parameter found from the powder data has twice the reported value. In order to validate the correctness of the solution obtained in the present study, a powder diffraction pattern was generated on the basis of the structural data reported for the related gadolinium phase. Fig. 1 shows parts of the pattern of $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$ observed in the present study and the calculated pattern. From the powder pattern indexing, some weak diffraction lines observed in the experimental data are perfectly indexed with the new cell. These lines correspond to reflections hkl with $l = 2n + 1$. It is clear that they are not observed in the calculated pattern and, consequently, their presence involves a unit cell volume of $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$, which is twice as large as the cell volume reported by Roméro *et al.* (1997). The systematic absences of reflections hkl with $h + k = 2n + 1$ and $00l$ with $l = 2n + 1$ were found to be compatible with the non-centrosymmetric space group $C222_1$ only. According to the conditions for non-extinction, a refinement of all diffraction lines available led to the unit-cell dimensions given in Table 1, with the figures of merit M_{20} = 54 and F_{30} = 86(0.008,43).

Table 1
Crystallographic data and details of the refinements.

For the definition of agreement factors from the Rietveld refinement, see McCusker *et al.* (1999).

	Powder	Single crystal
a (Å)	7.8177 (7)	7.8198 (5)
b (Å)	14.943 (1)	14.949 (1)
c (Å)	9.4845 (7)	9.4908 (5)
V (Å^3)	1108.0 (1)	1109.4 (1)
Wavelength (Å)	1.5406	0.71073
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.62	0.81
No. of measured reflections	650	2431
No. of observed reflections [$I > 2\sigma(I)$]	–	1517
No. of structural parameters	37	90
No. of profile parameters	21	–
R_p	0.088	–
$R_{\rm wp}$	0.118	–
R_B	0.075	–
R_F	0.062	–
R_1	–	0.046
wR	–	0.082
GoF	2.42	1.09

3.2. *Ab initio* structure determination from powder data

Integrated intensities were extracted from the iterative pattern decomposition algorithm available in *FULLPROF*99, from which the yttrium atoms only were located from direct methods by using the program *SHELXS*97 (Sheldrick, 1997). The model was found from several difference Fourier calculations by means of *SHELXL*97, except the carbonate oxygen atom O22 for which no unambiguous peak was detected on the Fourier map. Consequently, its theoretical position was calculated according to the geometry of the carbonate anion. A peak (height 2.93 e Å^{-3}) close to the calculated position was detected at 1.21 Å from C2. Its position was introduced into the model and was softly constrained to an actual C—O distance of 1.29 Å. A least-squares Rietveld refinement of the structure of $[\mathrm{Y(H_2O)}]_2(\mathrm{C_2O_4})(\mathrm{CO_3})_2$ was carried out in the angular range 10–145° (2θ) using 650 reflections. The presence of Ag in the pattern was taken into account by refining the profile parameters of its diffraction pattern as a second phase. A pseudo-Voigt function was used to describe line profiles, with a possible variation of the mixing factors η as a linear function of the 2θ angle. The refinement involved 34 atomic parameters, 2 scale factors, 1 overall isotropic atomic displacement parameter for Ag, 1 zero point, 4 cell parameters, 3 half-widths for each phase and 4 line asymmetry parameters modelled according to the procedure introduced by Bérar & Baldinozzi (1993) for the carbonato-oxalate. The background was interpolated using 17 intensity points. One preferred orientation parameter was refined for $[\mathrm{Y(H_2O)}]_2(\mathrm{C_2O_4})(\mathrm{CO_3})_2$ in the direction parallel to the c axis. In addition, one preferred orientation parameter parallel to [111] was selected for Ag. The final Rietveld refinement converged to the residual factors $R_F = 0.062$ and $R_{\rm wp} = 0.118$. Crystallographic data and details of the Rietveld refinement are given in Table 1. The final Rietveld plot (Fig. 2) shows the best agreement between experimental and calculated patterns. Final atomic coordinates and isotropic atomic displacement parameters are displayed in Table 2.

3.3. Structure solution from single-crystal data

3.3.1. Unit-cell determination. An orthorhombic cell was initially found from the 25 reflections collected with the Nonius CAD-4 diffractometer, with the unit-cell parameters a = 7.8077 (7), b = 14.926 (2), c = 4.7364 (7) Å, V = 552.0 (1) Å^3. This cell corresponds to that reported by Roméro *et al.* (1997). The actual unit cell obtained from powder pattern indexing was found after repeating the data acquisition for cell determination three times. The unit-cell dimensions were thus a = 7.8075 (6), b = 14.926 (1), c = 9.477 (1) Å, V = 1104.4 (2) Å^3.

The indexing by *DENZO* from the first 20 data frames collected with the Kappa CCD diffractometer gave the actual orthorhombic cell found from powder data. The refinement

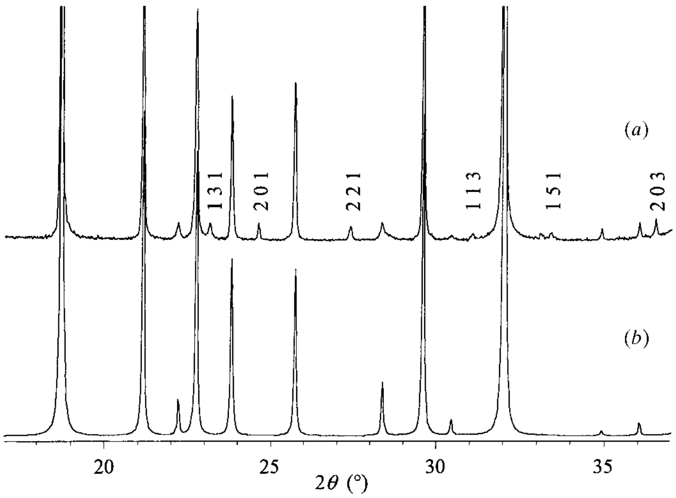

Figure 1
Parts of (a) the experimental powder diffraction pattern of $[\mathrm{Y(H_2O)}]_2(\mathrm{C_2O_4})(\mathrm{CO_3})_2$ and (b) of the powder pattern calculated from the atomic coordinates of the gadolinium related compound.

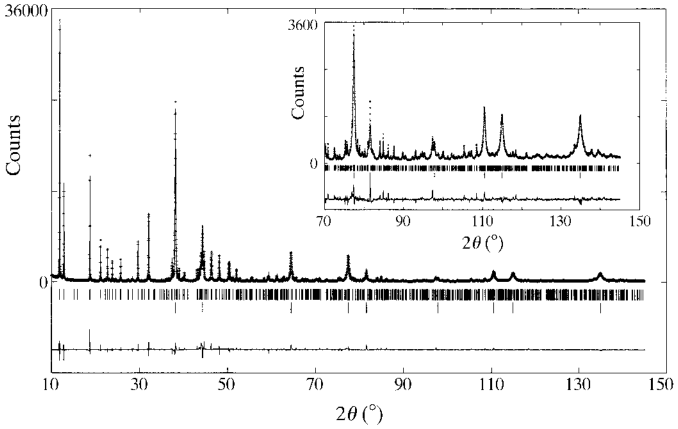

Figure 2
Final Rietveld plot for $[\mathrm{Y(H_2O)}]_2(\mathrm{C_2O_4})(\mathrm{CO_3})_2$. The experimental data are given by crosses, while the calculated pattern is represented by the solid line. The lower trace corresponds to the difference curve. The Bragg reflections are indicated by vertical bars (the lower bars correspond to Ag).

Table 2
Atomic coordinates and isotropic atomic displacement parameters (Å^2) for $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$.

p: powder data set, *c*: single-crystal data set. Isotropic atomic displacement parameters from single-crystal data have been calculated according to $B_{iso} = 8\pi^2 \times U_{eq}$.

		x	y	z	B_{iso}
Y1	*p*	0	0.2932 (5)	1/4	1.6 (2)
	c	0	0.29284 (7)	1/4	0.75 (2)
Y2	*p*	1/2	0.2074 (5)	1/4	1.8 (2)
	c	1/2	0.20723 (7)	1/4	0.75 (2)
O11	*p*	0.331 (2)	−0.0710 (9)	0.246 (3)	0.2 (4)
	c	0.330 (1)	−0.0726 (3)	0.2630 (9)	1.4 (1)
O12	*p*	0.334 (3)	0.0815 (9)	0.283 (2)	1.3 (5)
	c	0.332 (1)	0.0772 (3)	0.2639 (8)	1.5 (1)
C1	*p*	0.400 (1)	0.007 (1)	0.253 (5)	1.7 (4)
	c	0.4007 (5)	0.0011 (6)	0.2573 (5)	1.22 (6)
O21	*p*	0.747 (2)	0.263 (1)	0.387 (1)	0.9 (2)
	c	0.756 (1)	0.2466 (4)	0.3803 (7)	1.7 (1)
O22	*p*	0.5498 (9)	0.1851 (6)	0.505 (2)	0.6 (3)
	c	0.5543 (4)	0.1802 (2)	0.4968 (8)	1.22 (5)
O23	*p*	0.770 (2)	0.237 (1)	0.623 (1)	0.9 (2)
	c	0.756 (1)	0.2474 (4)	0.6186 (7)	1.7 (1)
C2	*p*	0.692 (1)	0.225 (1)	0.503 (2)	−0.2 (3)
	c	0.6951 (5)	0.2246 (3)	0.500 (1)	1.03 (6)
O*w*1	*p*	0	0.143 (3)	1/4	3.1 (3)
	c	0	0.1358 (7)	1/4	4.8 (4)
O*w*2	*p*	1/2	0.371 (3)	1/4	3.1 (3)
	c	1/2	0.3630 (7)	1/4	6.5 (6)
H1	*p*	–	–	–	
	c	0.065 (8)	0.101 (4)	0.317 (6)	1.97
H2	*p*	–	–	–	
	c	0.601 (6)	0.398 (4)	0.226 (7)	1.97

from the complete data set led to the cell dimensions reported in Table 1.

3.3.2. Structure determination from Nonius Kappa CCD data. The complete model, except H atoms, was indicated by the direct-methods program *SIR*97 with a reliability factor R = 0.086. The atomic positions were introduced in the program *SHELXL*97 and refined from a least-squares calculation. The H atoms were found from the last difference Fourier map and added in the model. They were refined with soft constraints on the distances to their water O atoms, *i.e.* 0.980 (15) Å, and with a fixed isotropic displacement parameter [U_{eq} = 0.025 Å^2]. Crystallographic data and details of the final least-squares refinement are displayed in Table 1. Atomic positions and isotropic atomic displacement parameters B are given in parentheses in Table 2, together with the results obtained from powder diffraction data. Bond lengths and angles are listed in Table 3. Although the quality of the powder data for structure refinement was adversely affected by the presence of broadened lines of metallic Ag, it is of interest to comment briefly on the two sets of results. On average, the precision on the atomic coordinates derived from the powder data is lowered by an order of magnitude. The atomic coordinates of the heavy atoms are in accordance within one combined e.s.d. and most light atoms agree within three combined e.s.d.'s.[1]

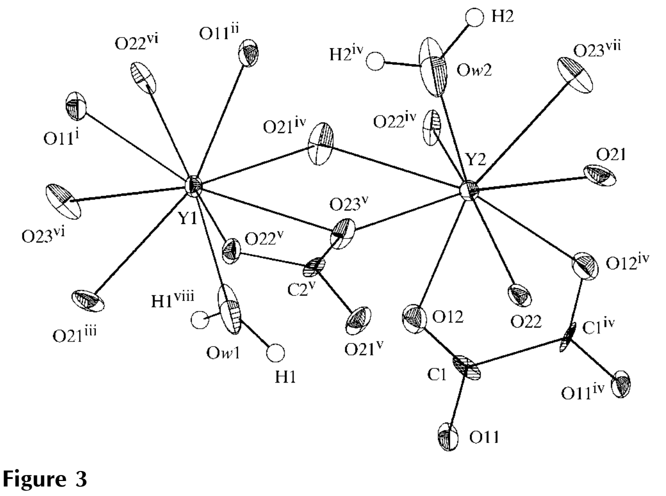

Figure 3
Part of the crystal structure of $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$, showing the environment of the Y atoms, as well as the carbonate and oxalate groups. Displacement ellipsoids are drawn at the 50% probability level.

4. Discussion

A part of the crystal structure of $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$, including the two ninefold coordination polyhedra of Y, is shown in Fig. 3. The crystal structure shows strong similarities with that of the chemically related gadolinium compound reported by Roméro *et al.* (1997). However, the doubling of the *c* parameter found for the yttrium phase involves modifications of the equivalent positions of the carbonate atoms. Fig. 4 is a projection of the structure along [010] for $[Gd(H_2O)]_2(C_2O_4)(CO_3)_2$ (Roméro *et al.*, 1997) and for $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$, showing the arrangement of the carbonate group. It is immediately apparent from the structure of the yttrium phase that the carbonate ligands alternate in the [001] direction, according to the screw axis 2_1 of the space group $C222_1$. This major feature is the origin of the double cell found in the present study. Indeed, only half of the C2 and O22 atoms are shifted from the positions displayed in the small cell. As a result of this subtle change, combined with the low scattering power of the atoms involved (carbon and oxygen), the intensity of the reflections is moderately affected with respect to that calculated with a model based on the small cell. It should also be noted that although all anisotropic displacement parameters are positive-definite, the C1 atom has an excessively elongated ellipsoid, which is likely due to weak reflection intensities not sufficiently accurately measured. The low intensity of the reflections from which the double cell arises can also explain why they were missed in the first data set collected with the Nonius CAD-4 diffractometer for $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$. This result demonstrates that the use of pre-selected input parameters for routine measurements can be responsible for incomplete data collection. Indeed, the first collection of single-crystal data for $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$ with the Nonius CAD-4 diffractometer was carried out with the default speed value of the φ scan (197.8° min^{-1}). The peak/background ratio discrimina-

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0567). Services for accessing these data are described at the back of the journal.

Table 3
Bond lengths (Å) and angles (°) for $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$ obtained from single-crystal data.

$Y1-O11^{i}$	2.415 (7)	$Y2-O12$	2.352 (7)
$Y1-O11^{ii}$	2.415 (7)	$Y2-O12^{iv}$	2.352 (7)
$Y1-O21^{iii}$	2.377 (7)	$Y2-O21$	2.424 (7)
$Y1-O21^{iv}$	2.377 (7)	$Y2-O21^{iv}$	2.424 (7)
$Y1-O22^{v}$	2.474 (7)	$Y2-O22$	2.415 (7)
$Y1-O22^{vi}$	2.474 (7)	$Y2-O22^{iv}$	2.415 (7)
$Y1-O23^{v}$	2.433 (7)	$Y2-O23^{v}$	2.379 (7)
$Y1-O23^{vi}$	2.433 (7)	$Y2-O23^{vii}$	2.379 (7)
$Y1-Ow1$	2.35 (1)	$Y2-Ow2$	2.33 (1)
$C1-C1^{iv}$	1.559 (8)	$O11-C1-O12$	127.6 (4)
$C1-O11$	1.235 (9)	$O11-C1-C1$	116.8 (5)
$C1-O12$	1.26 (1)	$O12-C1-C1$	115.6 (4)
$C2-O21$	1.27 (1)	$O21-C2-O22$	115.9 (9)
$C2-O22$	1.286 (5)	$O21-C2-O23$	125.6 (4)
$C2-O23$	1.27 (1)	$O22-C2-O23$	118.4 (8)

(i) $-\frac{1}{2}+x, \frac{1}{2}+y, z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-1+x, y, z$; (iv) $1-x, y, \frac{1}{2}-z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}-y, -\frac{1}{2}+z$; (vii) $\frac{3}{2}-x, \frac{1}{2}-y; -\frac{1}{2}+z$.

tion factor, selected here to be 2, reduced the time spent to centre diffuse and noisy peaks, but also decreased the sensitivity. In this particular case, the presence of Y atoms (wavelength of K absorption edge 0.72672 Å) involves a strong scattering with the Mo $K\alpha$ radiation arising from X-ray fluorescence. It thus contributes to a high background and the discrimination factor should be less than 2 in this proper case. On the other hand, the choice of small step lengths and high counting times in the powder data collection strategy is helpful for accurate indexing and structure determination, provided that there is no fluorescence background, as is the case here with Cu $K\alpha$ radiation.

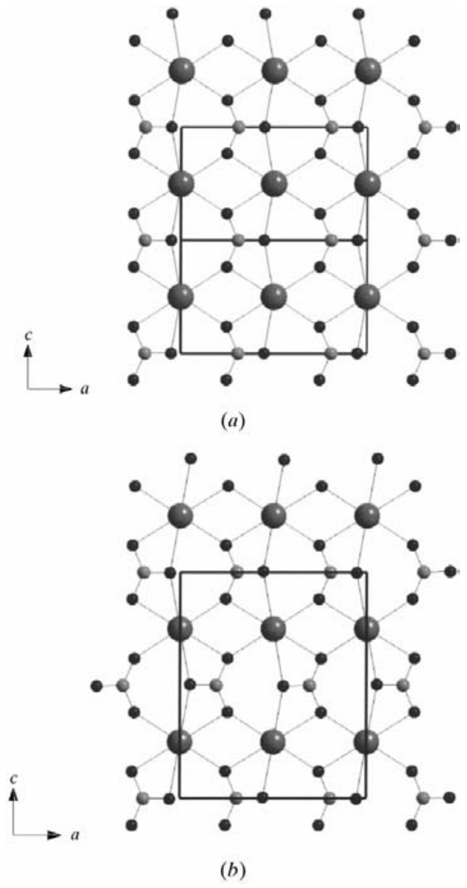

Figure 4
Projections of the crystal structures of (*a*) $[Gd(H_2O)]_2(C_2O_4)(CO_3)_2$ and (*b*) $[Y(H_2O)]_2(C_2O_4)(CO_3)_2$, showing the arrangement of the carbonate group. The oxalate ligand and the water molecules are omitted for clarity. Large grey spheres: Gd or Y; small grey spheres: C; small dark spheres: O.

To conclude this study demonstrates the power of the full trace of a high-quality powder diffraction pattern, which contains all the information on the crystal structure (and the microstructure) of a material, for the detection of subtle details, such as weak diffraction lines. As explained above these lines can be missed with an automatic diffractometer if a routine data collection strategy is used. It also shows the power of the indexing methods and structure determination methods applied to powder diffraction data. The structure solutions derived from powder data and single-crystal diffraction data have explained the effect of the doubling of one cell parameter on the crystal structure. Finally, the study demonstrates that the structure of the yttrium phase shows slight differences with respect to that of the chemically related gadolinium compound.

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