Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

$RbCr^{III}(C_2O_4)_2\cdot 2H_2O$, $Cs_2Mg(C_2O_4)_2\cdot 4H_2O$ and $Rb_2Cu^{II}(C_2O_4)_2\cdot 2H_2O$: three new complex oxalate hydrates

Uwe Kolitsch

Universität Wien, Institut für Mineralogie und Kristallographie, Geozentrum, Althanstrasse 14, A-1090 Wien, Austria
Correspondence e-mail: uwe.kolitsch@univie.ac.at

Received 28 July 2003
Accepted 26 January 2004
Online 19 February 2004

Rubidium chromium(III) dioxalate dihydrate [diaquabis(μ-oxalato)chromium(III)rubidium(I)], [$RbCr(C_2O_4)_2(H_2O)_2$], (I), and dicaesium magnesium dioxalate tetrahydrate [tetraaquabis(μ-oxalato)magnesium(II)dicaesium(I)], [$Cs_2Mg(C_2O_4)_2(H_2O)_4$], (II), have layered structures which are new among double-metal oxalates. In (I), the Rb and Cr atoms lie on sites with imposed $2/m$ symmetry and the unique water molecule lies on a mirror plane; in (II), the Mg atom lies on a twofold axis. The two non-equivalent Cr and Mg atoms both show octahedral coordination, with a mean Cr—O distance of 1.966 Å and a mean Mg—O distance of 2.066 Å. Dirubidium copper(II) dioxalate dihydrate [diaquabis(μ-oxalato)copper(II)dirubidium(I)], [$Rb_2Cu(C_2O_4)_2(H_2O)_2$], (III), is also layered and is isotypic with the previously described K_2- and $(NH_4)_2Cu^{II}(C_2O_4)_2\cdot 2H_2O$ compounds. The two non-equivalent Cu atoms lie on inversion centres and are both (4+2)-coordinated. Hydrogen bonds are medium-strong to weak in the three compounds. The oxalate groups are slightly non-planar only in the Cs–Mg compound, (II), and are more distinctly non-planar in the K–Cu compound, (III).

Comment

As part of recent work on the crystal chemistry and topology of, firstly, complex metal oxalates (Fleck & Kolitsch, 2004) and, secondly, bismuth(III) oxalates (Kolitsch, 2003), the three title compounds, rubidium chromium(III) dioxalate dihydrate, (I), dicaesium magnesium dioxalate tetrahydrate, (II), and dirubidium copper dioxalate dihydrate, (III), have been prepared from aqueous solutions at room temperature and their crystal structures determined from single-crystal X-ray data collected at 293 K. Two of the three oxalates, *viz.* (I) and (II), represent novel structure types.

Compound (I) has a layered atomic arrangement with space-group symmetry $C2/m$. The asymmetric unit contains one unique Rb atom, one unique C atom, three O atoms and one H atom. Layers of Rb atoms parallel to the (001) plane are connected to parallel layers of $CrO_4(H_2O)_2$ octahedra *via* tetradentate bridging oxalate groups approximately along [$\bar{1}$02] (Figs. 1 and 2). The layered character of the structure explains the tabular (001) habit of the crystals. The Rb atoms are coordinated to eight O3 atoms in a very narrow distance range (Table 1), with a mean Rb—O distance of 3.017 Å. The RbO_8 polyhedron may be described as a rather distorted tetragonal prism. The $CrO_4(H_2O)_2$ octahedron consists of four O atoms from tetradentate oxalate groups and two apical *trans* water molecules (O*W*2). The $CrO_4(H_2O)_2$ octahedron is only slightly distorted (Table 1) and has a mean Cr—O distance of 1.966 Å; the bonds to the water molecules are slightly longer by comparison. In the only other Rb–Cr^{III} oxalate known, *viz.* $Rb_3Cr^{III}(C_2O_4)_3\cdot 3H_2O$ (Van Niekerk & Schoening, 1952*a*; Merrachi *et al.*, 1987), which is isotypic with its K analogue (Van Niekerk & Schoening, 1952*b*; Taylor, 1978), the Cr atom also has an octahedral coordination.

The mean Rb—O and mean Cr—O distances are close to expected values, although the Cr—O distance is slightly shorter than the average distance in oxidic Cr compounds (1.999 Å; Baur, 1981). This may be explained by the influence of the strong oxalate C—O bonds, which force the Cr atom to keep its four coordinated oxalate O atoms at a close distance. The oxalate group is planar and shows expected bond lengths (Table 1). The single hydrogen bond in (I) is medium strong, with an O*W*2$\cdots$O1 distance of 2.6514 (13) Å (Table 2 and Fig. 1). It is directed approximately along [492] and [4$\bar{9}$2] to the O1 ligands of adjacent $CrO_4(H_2O)_2$ octahedra, and thus provides a strong linkage within the 'octahedral' layer.

Compound (I) is not isostructural with $KCr^{III}(C_2O_4)_2\cdot 3H_2O$, which has space group $P2/c$ and one more water molecule per formula unit (Van Niekerk & Schoening, 1951), although $CrO_4(H_2O)_2$ octahedra exist in both compounds. The Cr—O*W* bonds in the K–Cr compound are longer than the Cr—O bonds, as is found in (I).

Compound (II) represents a second new structure type, which also has a layered character, although the layering is less distinct. The compound crystallizes in space group $C2/c$. The asymmetric unit contains one unique Cs atom, one Mg atom, two C atoms, six O atoms and four H atoms. Only the Mg atom is located on a special position, $(0, y, \frac{1}{4})$. Slightly distorted $MgO_4(H_2O)_2$ octahedra are located in layers parallel to (10$\bar{1}$), the layers being separated by somewhat corrugated layers of Cs atoms (Figs. 3 and 4). The $MgO_4(H_2O)_2$ octahedron consists of two *cis* water molecules (O*W*5) and four *cis* O atoms from bidentate oxalate groups. The unusual *cis* arrangements of the different ligands are probably responsible for the slight distortion of the $MgO_4(H_2O)_2$ octahedron (Table 3 and Fig. 4). The average Mg—O bond length is 2.066 Å, which is slightly shorter than the average distance in oxidic Mg compounds (2.085 Å; Baur, 1981). The Cs atom has a geometrically irregular but otherwise clearly defined coordination sphere involving nine O atoms (mean Cs—O = 3.303 Å), two of which belong to water molecules (Table 3). Atom O*W*6 is only bonded to Cs, while the less strongly bonded atom O*W*5 is shared with the Mg atom. The oxalate group is nearly planar and has expected bond geometries (Table 3). Hydrogen bonding in (II) is provided by water molecules O*W*5 and O*W*6 bonded to the Mg and Cs atoms. The four hydrogen bonds are medium-strong to weak, with O$\cdots$O distances ranging between 2.684 (2) and 2.760 (2) Å (Table 4). The three strongest bonds are all directed along vectors approximately in the $(10\bar{1})$ plane, *i.e.* the plane of the layers in the structure.

Compound (III) (space group $P\bar{1}$) is isotypic with both the K analogue, $K_2Cu^{II}(C_2O_4)_2\cdot 2H_2O$ (Viswamitra, 1962*a*; Weichert & Löhn, 1974), and the NH_4 analogue, $(NH_4)_2Cu^{II}(C_2O_4)_2\cdot 2H_2O$ (Viswamitra, 1962*b*). It should be mentioned that the structure of the present Rb compound is based on a standard (reduced) unit cell, whereas the previous structure models of the two above-mentioned analogues were described using a non-standard unit cell. Compound (III) is metrically pseudo-monoclinic, with a *C*-centred cell and cell parameters $a = 10.53$, $b = 14.51$ and $c = 7.00$ Å, and $\alpha = 90.2$, $\beta = 103.4$ and $\gamma = 90.2°$.

The atomic arrangement in (III) (Figs. 5 and 6) is based on layers of CuO_6 polyhedra separated by layers of Rb atoms, similar to the situation in compounds (I) and (II). Oxalate groups provide the necessary linkage between these units. The two non-equivalent Rb atoms are each surrounded by eight O atoms (mean Rb—O = 3.031 Å for atom Rb1 and 3.045 Å for atom Rb2; Table 5). The Rb–O polyhedra are highly irregular. Atom Cu1 has a (4+2)-coordination in which all six bonds are to oxalate O atoms. In contrast, atom Cu2 has a (less pronounced) (4+2)-coordination in which the two long bonds are to atoms O*W*9 of one of the two non-equivalent water molecules (Table 5, and Figs. 5 and 6); atom O*W*10 of the other water molecule is bonded to Rb1 only. The two CuO_6 polyhedra can both be described as elongated octahedra with only weak angular distortions (Table 5). The two non-equivalent oxalate groups play different roles. The first tetradentate group links adjacent $Cu1O_6$ and $Cu2O_6$ polyhedra in the (001)

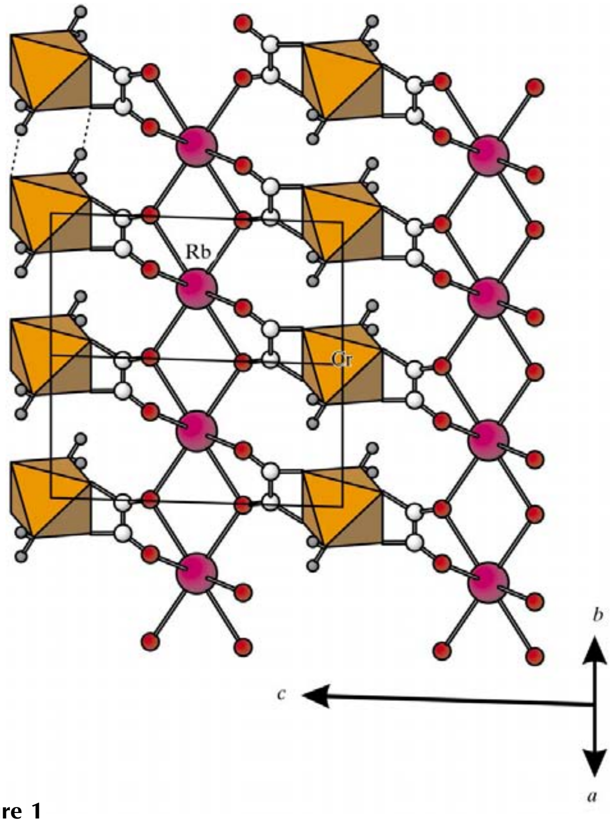

Figure 1
The layered structure of (I) projected along [110]. Oxalate groups provide a linkage between (001) layers of $CrO_4(H_2O)_2$ octahedra and parallel layers of eight-coordinated Rb atoms (large spheres). The single medium-strong hydrogen bond strengthening the octahedral layer is shown as a dashed line in the top left-hand part of the figure. The unit cell is outlined.

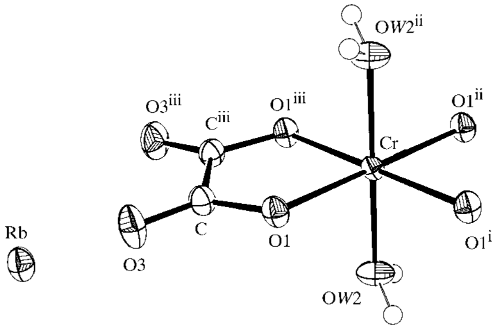

Figure 2
The connectivity in (I), shown with displacement ellipsoids at the 50% probability level [symmetry codes: (i) $1 - x, y, -z$; (ii) $1 - x, 1 - y, -z$; (iii) $x, 1 - y, z$].

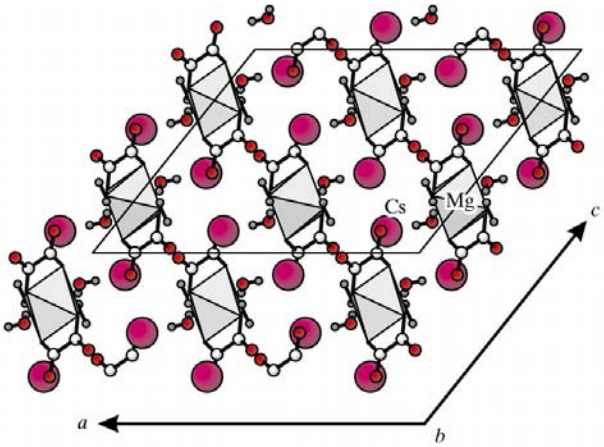

Figure 3
The layered structure of (II) projected along [010]. Layers of $MgO_4(H_2O)_2$ octahedra parallel to $(10\bar{1})$ are separated by corrugated layers of nine-coordinate Cs atoms (large spheres). Oxalate groups link these units together in different directions. The unit cell is outlined.

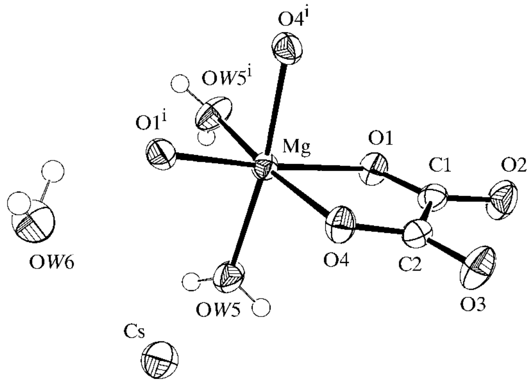

Figure 4
The connectivity in (II), shown with displacement ellipsoids at the 50% probability level [symmetry code: (i) $-x, y, \frac{1}{2} - z$].

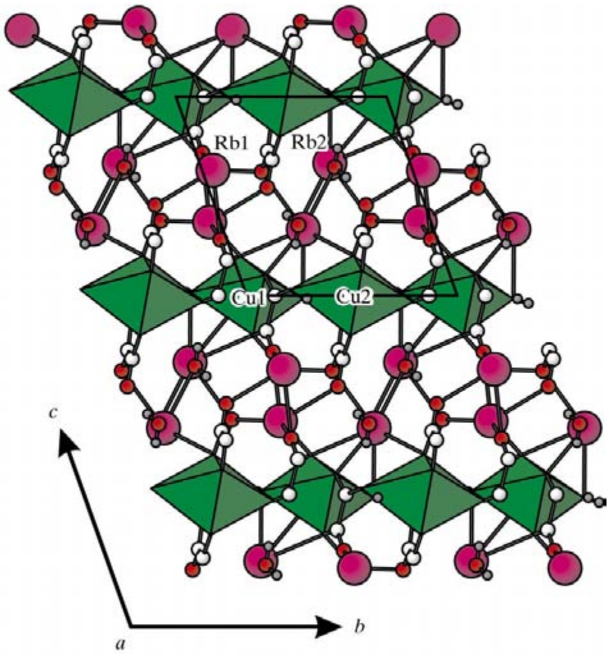

Figure 5
The layered structure of (III) projected along [100]. Layers of CuO_6 polyhedra parallel to (001) are separated by layers of eight-coordinated Rb atoms (large spheres). Oxalate groups link these units together in different directions (see *Comment* text). Only the stronger Rb—O bonds (those less than 3.1 Å) are shown. The unit cell is outlined.

plane *via* the single bridge O3—C1—O5 (three of the four O ligands are shared with the two Cu atoms, while the fourth O ligand is shared with the Rb2 atom). The second equally tetradentate group provides a connection approximately along [114] between the $Cu1O_6$ polyhedra and the two RbO_8 polyhedra. Both oxalate groups are slightly non-planar [maximum deviation for the group containing atoms C1 and C2 is 7.62 (19)°, and that for the group containing atoms C3 and C4 is 3.7 (2)°], whereas in the K analogue (Weichert & Löhn, 1974), only one of the two groups is non-planar (maximum deviation = 9°). The reported structure data for the NH_4 analogue (Viswamitra, 1962*b*) are of too low precision to allow any comment on the non-planarity of the oxalate groups. Hydrogen bonding in (III) is weak, with all O···O distances greater than 2.793 (3) Å (Table 6).

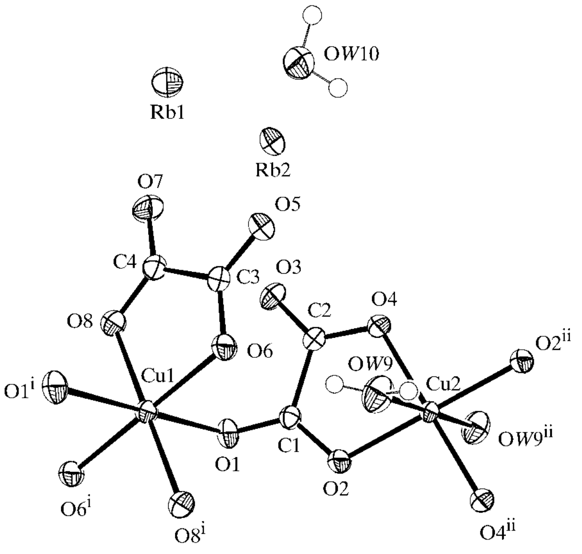

Figure 6
The connectivity in (III), shown with displacement ellipsoids at the 50% probability level [symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, 1-y, -z$].

Experimental

All three title compounds crystallized from slowly evaporated aqueous solutions at room temperature. Compound (I) formed dark-pink indistinctly tabular (001) crystals, arranged to form clusters of radiating individuals. The crystals grew from a solution containing dissolved Rb_2CO_3, $Cr(NO_3)_3\cdot9H_2O$ and oxalic acid dihydrate (pH = 4). No other compound crystallized from the solution. Compound (II) grew from a solution containing dissolved $CsCO_3$, magnesium hydroxide carbonate, minor CsF and oxalic acid dihydrate (pH = 4). The colourless thick tabular crystal used for the structural study was distinctly monoclinic, but the large majority of the other crystals showed a hexagonal (or pseudo-hexagonal) tabular habit, with flat bipyramidal faces and re-entrant angles between adjacent crystal faces bordering the plane of flattening. The appearance of these crystals is similar to that of snow crystals and they may be twins [the $MgO_4(H_2O)_2$ octahedra in Fig. 2 show a pseudo-hexagonal arrangement] or possibly a dimorph. No other compound crystallized from the solution. Compound (III) crystallized as block-shaped to isometric blue pleochroitic individuals from a solution containing dissolved Rb_2CO_3, copper hydroxide carbonate, $CuCl_2$, nitric acid and oxalic acid dihydrate (pH = 8). The blue crystals formed thick crusts which were covered by smaller amounts of blue–green indistinct opaque platelets of an uninvestigated compound.

Compound (I)

Crystal data

$[RbCr(C_2O_4)_2(H_2O)_2]$
$M_r = 349.54$
Monoclinic, $C2/m$
$a = 6.639$ (1) Å
$b = 7.313$ (1) Å
$c = 10.078$ (2) Å
$\beta = 92.46$ (3)°
$V = 488.85$ (14) Å^3
$Z = 2$

$D_x = 2.375$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 752 reflections
$\theta = 2.0$–$30.0°$
$\mu = 6.16$ mm^{-1}
$T = 293$ (2) K
Plate, pink
$0.20 \times 0.18 \times 0.03$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.372$, $T_{\max} = 0.837$
1410 measured reflections

759 independent reflections
708 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.012$
$\theta_{\max} = 30.1°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.060$
$S = 1.12$
759 reflections
47 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.23P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.96$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.022 (2)

Table 1
Selected geometric parameters (Å, °) for (I).

Rb—O3^{i}	2.9906 (13)	O1—C	1.3047 (17)
Rb—O3^{ii}	3.0426 (14)	O3—C	1.2093 (17)
Cr—O1^{iii}	1.9583 (10)	C—C^{iii}	1.559 (3)
Cr—O*W*2	1.9816 (15)		
O3—C—O1	125.31 (14)	O1—C—C^{iii}	113.47 (8)
O3—C—C^{iii}	121.21 (9)		

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (ii) $-x, y, 1-z$; (iii) $x, 1-y, z$.

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O*W*2—H$\cdots$O1^{i}	0.80 (2)	1.88 (2)	2.6514 (13)	160 (2)

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

Compound (II)

Crystal data

$[Cs_2Mg(C_2O_4)_2(H_2O)_4]$
$M_r = 538.23$
Monoclinic, $C2/c$
$a = 17.045\ (3)$ Å
$b = 7.368\ (1)$ Å
$c = 13.588\ (3)$ Å
$\beta = 128.61\ (3)°$
$V = 1333.5\ (7)$ Å^3
$Z = 4$
$D_x = 2.681$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2059 reflections
$\theta = 2.0$–$30.0°$
$\mu = 5.57$ mm^{-1}
$T = 293\ (2)$ K
Fragment, colourless
0.14 × 0.13 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.482$, $T_{\max} = 0.573$
3719 measured reflections
1935 independent reflections
1773 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.009$
$\theta_{\max} = 30.0°$
$h = -23 \rightarrow 23$
$k = -10 \rightarrow 10$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.040$
$S = 1.10$
1935 reflections
104 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.009P)^2 + 2.37P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.68$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00120 (11)

Table 3
Selected geometric parameters (Å, °) for (II).

Cs—O2^{i}	3.104 (2)	Mg—O*W*5^{iii}	2.0439 (17)
Cs—O3^{ii}	3.1486 (16)	Mg—O4^{iii}	2.0748 (16)
Cs—O*W*6	3.155 (2)	Mg—O1^{iii}	2.0778 (16)
Cs—O1^{iii}	3.2962 (16)	C1—O2	1.240 (2)
Cs—O1^{iv}	3.3338 (15)	C1—O1	1.263 (2)
Cs—O2^{v}	3.339 (2)	C1—C2	1.558 (3)
Cs—O*W*5	3.3694 (19)	C2—O3	1.231 (2)
Cs—O3^{v}	3.4514 (18)	C2—O4	1.267 (2)
Cs—O4	3.5309 (15)		
O2—C1—O1	126.41 (19)	O3—C2—O4	125.94 (18)
O2—C1—C2	117.79 (17)	O3—C2—C1	119.39 (17)
O1—C1—C2	115.78 (16)	O4—C2—C1	114.65 (16)

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

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O*W*5—H1$\cdots$O*W*6^{i}	0.82 (4)	1.88 (4)	2.684 (2)	166 (3)
O*W*5—H2$\cdots$O3^{ii}	0.78 (4)	1.96 (4)	2.735 (3)	170 (3)
O*W*6—H3$\cdots$O2^{iii}	0.84 (3)	1.89 (3)	2.729 (2)	174 (3)
O*W*6—H4$\cdots$O4^{iv}	0.74 (3)	2.02 (3)	2.760 (2)	174 (3)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (iii) $-x, y, \frac{1}{2}-z$; (iv) $-x, -y, -z$.

Compound (III)

Crystal data

$[Rb_2Cu(C_2O_4)_2(H_2O)_2]$
$M_r = 446.55$
Triclinic, $P\overline{1}$
$a = 7.000\ (1)$ Å
$b = 8.949\ (2)$ Å
$c = 8.982\ (2)$ Å
$\alpha = 108.05\ (3)°$
$\beta = 97.69\ (3)°$
$\gamma = 97.99\ (3)°$
$V = 520.34\ (22)$ Å^3
$Z = 2$
$D_x = 2.850$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2903 reflections
$\theta = 2.0$–$30.0°$
$\mu = 11.44$ mm^{-1}
$T = 293\ (2)$ K
Fragment, blue
0.12 × 0.07 × 0.07 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.305$, $T_{\max} = 0.449$
5809 measured reflections
3011 independent reflections
2641 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 30.0°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.059$
$S = 1.06$
3011 reflections
174 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 0.24P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.71$ e Å^{-3}
$\Delta\rho_{\min} = -0.80$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0221 (10)

Table 5
Selected geometric parameters (Å, °) for (III).

Rb1—O*W*10	2.953 (2)	Rb2—O7	2.964 (2)
Rb1—O*W*10^{i}	2.954 (2)	Rb2—O4^{iv}	2.9901 (17)
Rb1—O2^{ii}	2.9575 (18)	Rb2—O*W*9^{iv}	3.109 (2)
Rb1—O5	3.0304 (19)	Rb2—O2^{ii}	3.2414 (17)
Rb1—O8^{iii}	3.0450 (18)	Rb2—O7^{v}	3.285 (2)
Rb1—O4^{iv}	3.054 (2)	Rb2—O5	3.536 (2)
Rb1—O*W*9^{ii}	3.073 (2)	Cu1—O6^{vi}	1.9429 (17)
Rb1—O7	3.181 (2)	Cu1—O8	1.9444 (16)
Rb1—O5^{i}	3.533 (2)	Cu1—O1^{vi}	2.6512 (19)
Rb2—O3^{v}	2.9024 (17)	Cu2—O4	1.9363 (15)
Rb2—O5^{iv}	2.912 (2)	Cu2—O2	1.9487 (16)
Rb2—O3	2.9586 (19)	Cu2—O*W*9	2.508 (2)
O6^{vi}—Cu1—O6	180.00 (9)	O4—Cu2—O4^{vii}	180.00 (10)
O6^{vi}—Cu1—O8	94.73 (7)	O4—Cu2—O2	85.75 (7)
O6—Cu1—O8	85.27 (7)	O4^{vii}—Cu2—O2	94.25 (7)
O8—Cu1—O8^{vi}	180.00 (9)	O2—Cu2—O2^{vii}	180.0
O6^{vi}—Cu1—O1^{vi}	90.62 (7)	O4—Cu2—O*W*9	88.69 (7)
O6—Cu1—O1^{vi}	89.38 (7)	O4^{vii}—Cu2—O*W*9	91.31 (7)
O8—Cu1—O1^{vi}	92.83 (7)	O2—Cu2—O*W*9	85.22 (7)
O8^{vi}—Cu1—O1^{vi}	87.17 (7)	O2^{vii}—Cu2—O*W*9	94.78 (7)

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $x, y, 1+z$; (iii) $-x, -y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $-x, 1-y, 1-z$; (vi) $-x, -y, -z$; (vii) $1-x, 1-y, -z$.

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
OW9—H3···O6	0.79 (5)	2.08 (5)	2.824 (3)	156 (4)
OW9—H4···O1^{i}	0.86 (4)	2.08 (4)	2.843 (3)	147 (4)
OW10—H1···O7^{i}	0.76 (4)	2.05 (4)	2.793 (3)	166 (4)
OW10—H2···O1^{ii}	0.82 (4)	1.99 (4)	2.817 (3)	177 (4)

Symmetry codes: (i) $1+x, y, z$; (ii) $1+x, y, 1+z$.

The H atoms in all three compounds were freely refined; see Tables 2, 4 and 6 for the refined O—H distances.

For all three title compounds, data collection: *COLLECT* (Nonius, 2002); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Financial support from the Austrian Science Foundation (FWF; grant No. P15220-N06) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1664). Services for accessing these data are described at the back of the journal.

References

Baur, W. H. (1981). *Structure and Bonding in Crystals*, Vol. II, edited by M. O'Keeffe & A. Navrotsky, pp. 31–52. New York: Academic Press.
Dowty, E. (1999). *ATOMS*. Version 5.0.4 for Windows and Macintosh. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Fleck, M. & Kolitsch, U. (2004). In preparation.
Kolitsch, U. (2003). *Acta Cryst.* C**59**, m501–m504.
Merrachi, E. H., Mentzen, B. F. & Chassagneux, F. (1987). *Rev. Chim. Miner.* **24**, 427–445. (In French.)
Nonius (2002). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Taylor, D. (1978). *Aust. J. Chem.* **31**, 1455–1462.
Van Niekerk, J. N. & Schoening, F. R. L. (1951). *Acta Cryst.* **4**, 35–41.
Van Niekerk, J. N. & Schoening, F. R. L. (1952*a*). *Acta Cryst.* **5**, 475–476.
Van Niekerk, J. N. & Schoening, F. R. L. (1952*b*). *Acta Cryst.* **5**, 196–202.
Viswamitra, M. A. (1962*a*). *Z. Kristallogr.* **117**, 437–449.
Viswamitra, M. A. (1962*b*). *J. Chem. Phys.* **37**, 1408–1414.
Weichert, T. & Löhn, J. (1974). *Z. Kristallogr.* **139**, 223–235. (In German.)