metal-organic compounds

Two novel glycine metal halogenides: *catena*-poly[[[diaquanickel(II)]-di-μ-glycine] dibromide] and *catena*-poly[[[tetraaquamagnesium(II)]-μ-glycine] dichloride]

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In *catena*-poly[[[diaquanickel(II)]-di-μ-glycine] dibromide], {[Ni(C$_2$H$_5$NO$_2$)$_2$(H$_2$O)$_2$]Br$_2$}$_n$, (I), the Ni atom is located on an inversion centre. In *catena*-poly[[[tetraaquamagnesium(II)]-μ-glycine] dichloride], {[Mg(C$_2$H$_5$NO$_2$)(H$_2$O)$_4$]Cl$_2$}$_n$, (II), the Mg atom and the non-H atoms of the glycine molecule are located on a mirror plane. All other atoms are located on general positions. The atomic arrangements of both compounds are characterized by [MO_6] octahedra (M = Ni or Mg) connected by glycine molecules, with the halogenide ions in the interstices. In (I), four of the coordinating O atoms are from glycine and two are from water molecules, building layers of octahedra and organic molecules. In (II), two of the coordinating O atoms are from glycine and four are from water molecules. The octahedra and organic molecules form chains.

Comment

For glycine complexes of divalent metal halogenides, 15 structurally characterized compounds are known, which crystallize in 13 different structural types (Table 1). In the course of our studies of compounds of glycine and inorganic salts, we have found two new examples, namely bis-(glycine) nickel(II) dibromide dihydrate, (I), and glycine magnesium(II) dichloride tetrahydrate, (II).

The main features of both structures are the coordination polyhedra of the metal cations. These are slightly distorted octahedra in which all ligands are O atoms. In compound (I), the Ni^{II} atom is located on a centre of symmetry. Four of the ligand atoms (O1, O2 and their equivalents) belong to the carboxylate groups of the glycine molecules and the remaining two to water molecules. The Ni—O distances range from 2.033 (2) to 2.086 (2) Å, with the shortest to the water molecules (Table 2). In compound (II), the octahedra display

mirror symmetry, and the ligands are four O atoms from water molecules and two carboxylate O atoms (O1 and O2). The Mg—O distances range from 2.016 (1) to 2.062 (1) Å, but here those to the water molecules are the longest (Table 4). All these distances are in good agreement with usual values for Mg—O and Ni—O ionic bonds (Shannon, 1976). The observed coordination of metal cations solely with oxygen is not common to all the glycine complexes in Table 1; the halogen atoms can also form part of the coordination sphere, as in glycine manganese(II) dichloride dihydrate (Clegg *et al.*, 1987), where two adjacent vertices of the strongly distorted octahedral [MnO$_4$Cl$_2$] unit are Cl atoms.

(I) (II)
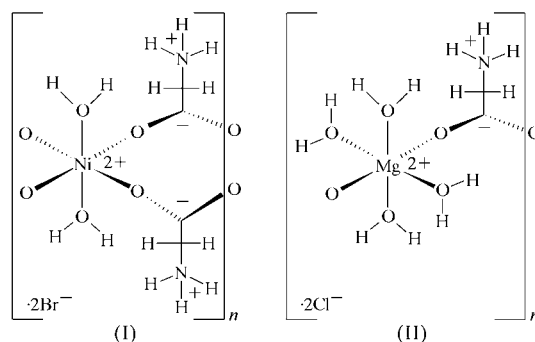
In both compounds, the glycine molecules exist in the zwitterionic form, NH$_3$$^+CH_2COO^-$, which is normal for compounds of amino acids with inorganic salts. However, there are also many examples in the literature of glycinium or glycinate compounds, *e.g.* lithium glycinate (Müller *et al.*, 1994) or glycinium chloride (Di Blasio *et al.*, 1977). In compound (I), the glycine ligands are nearly planar, the O1—
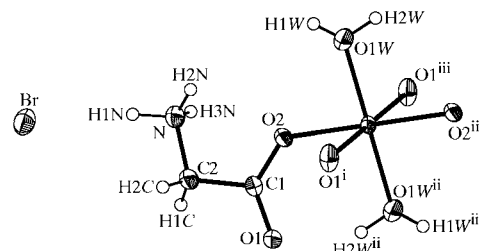
Figure 1
The connectivity in compound (I) (*ORTEP-3*; Farrugia, 1997), shown with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $-x, y + \frac{1}{2}, \frac{1}{2} - z$; (ii) $-x, -y, -z$; (iii) $x, \frac{1}{2} - y, z + \frac{1}{2}$.]
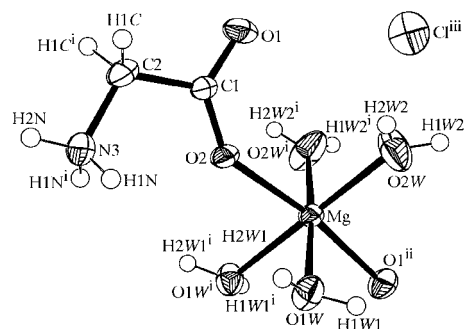
Figure 2
The connectivity in compound (II) (*ORTEP-3*; Farrugia, 1997), shown with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $x + \frac{1}{2}, y, \frac{1}{2} - z$; (iii) $x - \frac{1}{2}, y, \frac{1}{2} - z$.]

C1—C2—N torsion angle being −171.03 (1)°. Within the carboxylate groups, both C—O distances are similar [O1—C1 = 1.251 (3) Å and O2—C1 = 1.256 (3) Å], which is an expected consequence of delocalization of the electrons in the carboxylate group. The geometry of the glycine molecules in compound (II) is unusual. The molecules (atoms O1, O2, C1, C2, N) are located in a mirror plane. Although stereochemically possible, this symmetry seems to occur very rarely (other amino acid molecules cannot have symmetries other than 1). To the best of our knowledge, this is the first example of symmetry m for a glycine molecule (zwitterion) in a glycine

complex of an inorganic salt. Since all non-H atoms lie in the same plane, the O1—C1—C2—N torsion angle is 180°. Even the terminal H atoms of the amino group match this symmetry well. A refinement in the corresponding non-centrosymmetric space group resulted in the same positions, but with very large displacement parameters. Also, a check of this lower symmetry structure with the program *PLATON* (Spek, 2003) indicated a 100% probability of the higher symmetry, *i.e.* *Pnma*. The C—O distances in the carboxylate groups are 1.242 (1) (O1—C1) and 1.247 (1) Å (O2—C1).

The major structural differences between the two compounds correlate with the different stoichiometries. In compound (I), the ratio of organic molecules to cations is 2:1, while in compound (II) it is 1:1. Since in both compounds the glycine molecules act as bridging ligands, each octahedron in compound (I) is connected to four adjacent octahedra, and each octahedron in compound (II) to two adjacent octahedra. Consequently, this results in the formation of infinte layers in (I) and of infinite chains in (II). These ratios are also expressed in the degree of hydration, since the remaining apices of the octahedra are O atoms of water molecules. Neither structure contains non-coordinated water molecules. The [Ni(C2H5NO2)2(H2O)2] layers in (I) are oriented parallel to (100), with the glycine molecules essentially perpendicular to the layers and the amino groups facing away from the layers (Figs. 3 and 4). The [Mg(C2H5NO2)(H2O)4] chains in (II) are parallel to [100]. The glycine molecules are oriented nearly perpendicular to the polyhedra chain axis, alternating up and down in the [001] direction, thus giving the chains a zigzag appearance. The symmetry of the chains is 2/m, with the chain axis lying in the mirror plane (Fig. 5). Note that the terms 'layer' and 'chain' refer to the connectivity resulting from strong interactions, *i.e.* ionic or covalent bonds.

In both structures, the halogenide ions are located in the interstices between the glycine molecules. In compound (I), each Br⁻ anion accepts three hydrogen bonds from amino
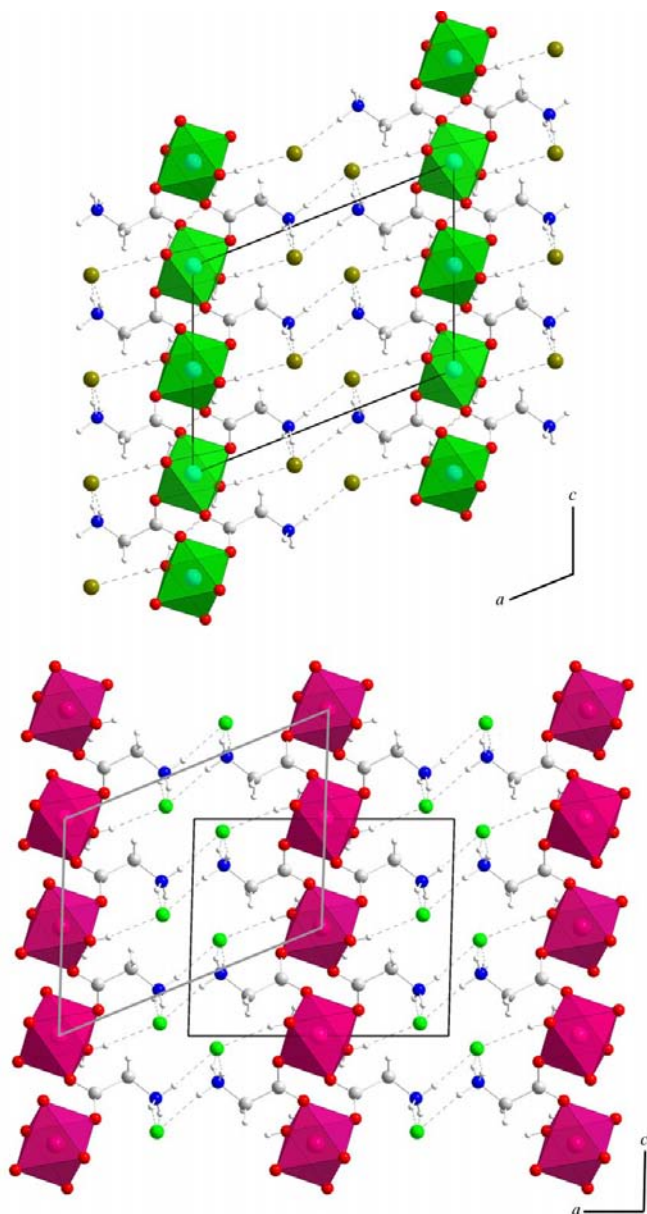
Figure 3
A packing diagram (*DIAMOND*; Bergerhoff *et al.*, 1996) for bis(glycine) nickel(II) dibromide dihydrate (top) compared with bis(glycine) cobalt dichloride dihydrate (bottom). Both structures are viewed along [010]. The layers are oriented vertically. For the purposes of comparison, the unit cell of the bromide structure is superimposed on the chloride structure (grey lines). To observe the difference between the two compounds notice the orientation of the octahedra.
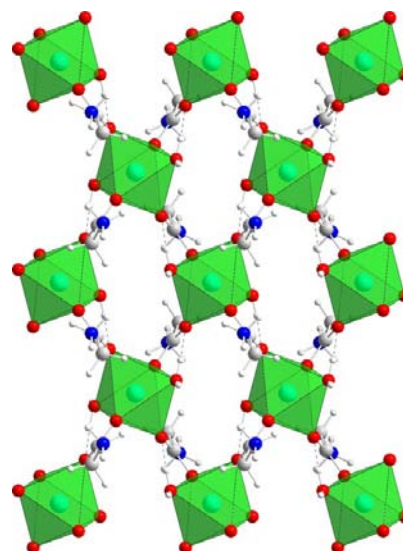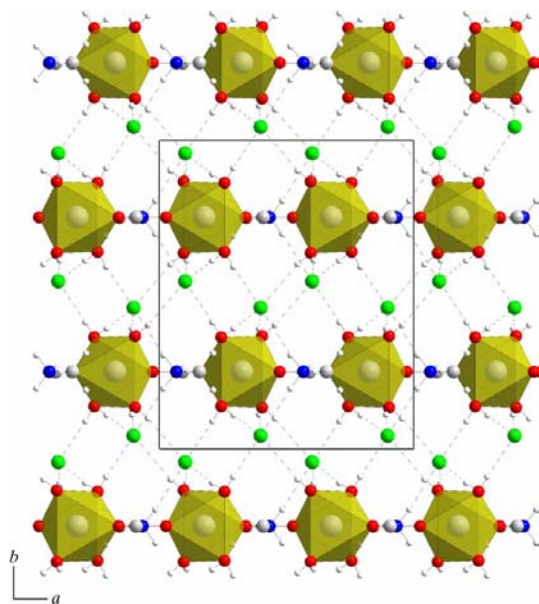

Figure 4
A view (*DIAMOND*; Bergerhoff *et al.*, 1996) of one layer in bis(glycine) nickel(II) dibromide dihydrate, parallel to (100).

Figure 5
A packing diagram (*DIAMOND*; Bergerhoff et al., 1996) for glycine magnesium(II) dichloride tetrahydrate, [MgCl$_2$(C$_2$H$_5$NO$_2$)]·4H$_2$O, viewed along [001]. The chains are oriented horizontally, with the glycine molecules facing away from and towards the viewer.

groups and one from a water molecule. One bond, namely N—H1N···Br, is an inter-layer bond, while the three other bonds exist within the layer. In addition, there is another intra-layer hydrogen bond, namely O1W—H2W···O1. In compound (II), the Cl$^-$ anions are located in the interstices between the chains and each anion accepts five hydrogen bonds, four from water molecules and one from an amino group. All four water molecules that act as donors are part of different octahedra. Details of the hydrogen bonds are given in Tables 3 and 5.

The 17 known glycine complexes of divalent metal halogenides are summarized in Table 1. An examination of the unit-cell parameters and symmetries of these compounds indicates that most of the structures differ from each other. The only group of isostructural compounds are the bis-(glycine) metal(II) dibromide dihydrates [metal(II) = Ni, Co, Mn or Mg]. Compound (I) belongs to this group. For the manganese compound (Głowiak & Ciunik, 1978), no H-atom positions were determined, and thus no definitive comparison with the hydrogen-bonding systems in compound (I) can be made. (The authors mention only three hydrogen bonds which are in agreement with the bonds of the title compounds, but no information about the remaining two hydrogen bonds is given.)

It is interesting to note a structural similarity between compound (I) and bis(glycine) cobalt dichloride dihydrate (Stenzel & Fleck, 2004). Both compounds possess a glycine–metal ratio of 2:1. In both structures the coordination polyhedra and their connection *via* glycine molecules, as well as the location and intra-layer bonding of the halogenide ions, are nearly identical. When examining diagrams of both structures viewed along the monoclinic axis, they appear to be identical (Fig. 3). However, in the bromide compound, the

[Ni(C$_2$H$_5$NO$_2$)$_2$(H$_2$O)$_2$] layers are mutually shifted by $\frac{1}{2}$ along the *c* axis compared with the [Co(C$_2$H$_5$NO$_2$)$_2$(H$_2$O)$_2$] layers of the chloride compound. This can be seen in Fig. 3 when comparing the orientation of the octahedra (note the positions of the apical water molecules: they face alternately 'left' and 'right'). A view of one layer is given in Fig. 4. This structural relation is also expressed in the unit-cell parameters: the lengths of the *b* and *c* axes are similar (see Table 1), as are the distances between the layers ($a \times \sin \beta$), and, consequently, the unit-cell volumes V [$a \times \sin \beta$ = 10.970 (Br) or 10.564 Å (Cl), and V = 577.9 (2) (Br) or 559.4 (2) Å^3 (Cl)].

In contrast with the large number (more than 30%) of non-centrosymmetric crystals among structurally characterized glycine compounds [Cambridge Structural Database (Version 5.26, November 2004 release; Allen, 2002) and the present compounds], only three out of 17 glycine metal halogenides crystallize non-centrosymmetrically. Groups of spherical symmetry, such as halogenide anions, apparently promote the formation of centrosymmetric crystals. A paper reviewing these structures and discussing the correlation between composition and symmetry of compounds of glycine with inorganic compounds is in preparation (Fleck, unpublished).

Experimental

Aqueous solutions of glycine and NiBr$_2$ in a 1:0.83 molar ratio for (I), and of glycine and MgCl$_2$ in a 1:0.71 molar ratio for (II), were slowly evaporated at a temperature of approximately 295 K. Over a period of several weeks, small green tabular crystals up to 0.2 mm in length of compound (I) and colourless elongated crystals up to 0.3 mm in length of compound (II) were formed.

Compound (I)

Crystal data

[Ni(C$_2$H$_5$NO$_2$)$_2$(H$_2$O)$_2$]Br$_2$	D_x = 2.326 Mg m^{-3}
M_r = 404.70	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1569
a = 11.805 (2) Å	reflections
b = 6.021 (1) Å	θ = 4.1–30.0°
c = 8.749 (2) Å	μ = 8.60 mm^{-1}
β = 111.63 (3)°	T = 293 (2) K
V = 578.1 (2) Å^3	Prism, green
Z = 2	0.15 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer	1593 independent reflections
	1363 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.026
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)	θ_{max} = 30.0°
	h = −15 → 16
	k = −8 → 8
T_{min} = 0.310, T_{max} = 0.423	l = −12 → 9
3883 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0083P)^2 + 0.67P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.026	
$wR(F^2)$ = 0.055	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.08	$(\Delta/\sigma)_{max}$ = 0.001
1593 reflections	$\Delta\rho_{max}$ = 0.78 e Å^{-3}
99 parameters	$\Delta\rho_{min}$ = −0.76 e Å^{-3}
All H-atom parameters refined	Extinction correction: *SHELXL97* (Sheldrick, 1997)
	Extinction coefficient: 0.0065 (8)

Table 1
A comparison of the stoichiometries, symmetries and unit-cell parameters of glycine divalent metal halogenides (Å, °).

Compound	a	b	c	α	β	γ	Space group	Reference
Glycine $MgCl_2 \cdot 4H_2O$	10.59	12.90	7.71	90	90	90	$Pnma$	(a)
Glycine $CaCl_2$	14.77	19.57	9.07	90	90	90	$Pb2_1a$	(b)
Glycine $BaCl_2 \cdot H_2O$	8.31	14.84	9.32	90	90	90	$Pbcn$	(c)
Glycine $SrCl_2 \cdot 3H_2O$	16.42	9.35	8.26	90	90	90	$Pbcn$	(c)
Glycine $MnCl_2$	4.97	7.92	6.98	107.4	115.9	87.0	$P\bar{1}$	(c)
Glycine $MnCl_2 \cdot 2H_2O$	8.40	5.61	16.79	90	90.2	90	$P2_1/c$	(d)
Glycine $CoCl_2 \cdot 2H_2O$	6.38	15.88	7.75	90	97.6	90	$P2_1/n$	(d)
Glycine$_2$ $CoCl_2 \cdot 2H_2O$	10.57	5.99	8.84	90	91.6	90	$P2_1/c$	(e)
Glycine $NiCl_2$	8.21	5.48	8.31	90	91.0	90	$P2_1$	(f)
Glycine $ZnCl_2$	11.23	15.25	15.66	90	90	90	$Pbn2_1$	(g)
Glycine$_2$ $PtCl_2 \cdot 2H_2O$	5.36	7.05	8.44	85.7	75.9	71.7	$P\bar{1}$	(h)
Glycine$_3$ $CaBr_2$	9.15	14.84	20.31	90	90	90	$Pbc2_1$	(i)
Glycine$_2$ $MnBr_2 \cdot 2H_2O$	21.61	12.65	8.99	90	90	90	$Pbca$	(j)
Glycine$_2$ $MnBr_2 \cdot 2H_2O$	11.94	6.06	8.98	90	111.7	90	$P2_1/c$	(j)
Glycine$_2$ $CoBr_2 \cdot 2H_2O$	11.77	6.06	8.82	90	111.5	90	$P2_1/c$	(k)
Glycine$_2$ $MgBr_2 \cdot 2H_2O$	11.84	6.07	8.83	90	111.9	90	$P2_1/c$	(l)
Glycine$_2$ $NiBr_2 \cdot 2H_2O$	11.81	6.02	8.75	90	111.6	90	$P2_1/c$	(a)

References: (a) this work; (b) Ravikumar et al. (1986); (c) Narayanan & Venkataraman (1975); (d) Clegg et al. (1987); (e) Stenzel & Fleck (2004); (f) Fleck & Bohatý (2004); (g) Hariharan et al. (1989); (h) Davies et al. (1995); (i) Mohana Rao & Natarajan (1980); (j) Głowiak & Ciunik (1978); (k) Ravikumar et al. (1985); (l) Krishnakumar & Natarajan (1995).

Table 2
Selected geometric parameters (Å, °) for (I).

Ni—O1W	2.034 (2)	Ni—O1^{i}	2.0876 (18)
Ni—O2	2.0595 (16)		
O1W—Ni—O1W^{ii}	180.0 (2)	O1W^{ii}—Ni—O1^{i}	92.27 (9)
O1W—Ni—O2	90.28 (8)	O2—Ni—O1^{i}	86.31 (7)
O1W^{ii}—Ni—O2	89.72 (8)	O2^{ii}—Ni—O1^{i}	93.69 (7)
O2—Ni—O2^{ii}	180.00 (4)	O1^{i}—Ni—O1^{iii}	180.0
O1W—Ni—O1^{i}	87.73 (9)		

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

Table 3
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
N—H1N$\cdots$Br	0.94 (4)	2.46 (4)	3.384 (2)	168 (3)
N—H2N$\cdots$Br^{iv}	0.86 (4)	2.67 (4)	3.498 (2)	161 (3)
N—H3N$\cdots$Br^{v}	0.89 (4)	2.54 (4)	3.363 (3)	155 (3)
O1W—H1$W\cdots$Br^{iv}	0.76 (4)	2.51 (4)	3.275 (2)	175 (4)
O1W—H2$W\cdots$O1^{ii}	0.84 (5)	1.96 (5)	2.711 (3)	148 (4)
C2—H2$C\cdots$Br^{vi}	0.96 (4)	3.00 (5)	3.780 (3)	139 (3)

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

Compound (II)

Crystal data

$[Mg(C_2H_5NO_2)(H_2O)_4]Cl_2$
$M_r = 242.34$
Orthorhombic, $Pnma$
$a = 10.587$ (2) Å
$b = 12.899$ (3) Å
$c = 7.714$ (2) Å
$V = 1053.4$ (4) Å^3
$Z = 4$
$D_x = 1.528$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2396 reflections
$\theta = 4.1$–33.7°
$\mu = 0.67$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
$0.30 \times 0.15 \times 0.15$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)
$T_{min} = 0.824$, $T_{max} = 0.906$
3968 measured reflections

2163 independent reflections
1940 reflections with $I > 2\sigma(I)$
$R_{int} = 0.010$
$\theta_{max} = 33.8°$
$h = -16 \rightarrow 16$
$k = -20 \rightarrow 20$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.077$
$S = 1.04$
2163 reflections
92 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 0.26P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.068 (6)

Table 4
Selected geometric parameters (Å, °) for (II).

Mg—O1^{i}	2.0165 (10)	Mg—O2W	2.0624 (9)
Mg—O2	2.0420 (9)	Mg—O1W	2.1032 (8)
O1^{i}—Mg—O2	171.22 (4)	O2—Mg—O1W	86.23 (3)
O1^{i}—Mg—O2W	94.04 (4)	O2W^{ii}—Mg—O1W	176.59 (4)
O2—Mg—O2W	92.02 (4)	O2W—Mg—O1W	90.41 (5)
O2W^{ii}—Mg—O2W	92.58 (8)	O1W—Mg—O1W^{ii}	86.56 (5)
O1^{i}—Mg—O1W	87.38 (3)		

Symmetry codes: (i) $x+\frac{1}{2}, y, \frac{1}{2}-z$; (ii) $x, \frac{3}{2}-y, z$.

Table 5
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
N3—H1N$\cdots$Cl^{iii}	0.88 (2)	2.34 (2)	3.2167 (9)	173 (2)
N3—H2N$\cdots$O1W^{iv}	0.87 (3)	2.35 (2)	3.0579 (13)	139 (1)
O1W—H1$W1\cdots$Cl	0.86 (2)	2.30 (2)	3.1523 (9)	173 (2)
O1W—H2$W1\cdots$Cl^{iii}	0.84 (2)	2.30 (2)	3.1287 (9)	169 (2)
O2W—H1$W2\cdots$Cl^{v}	0.81 (2)	2.37 (2)	3.1649 (12)	170 (2)
O2W—H2$W2\cdots$Cl^{vi}	0.79 (2)	2.40 (2)	3.1593 (11)	161 (2)

Symmetry codes: (iii) $\frac{3}{2}-x, 1-y, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, y, -z-\frac{1}{2}$; (v) $\frac{3}{2}-x, 1-y, z+\frac{1}{2}$; (vi) $x-\frac{1}{2}, y, \frac{1}{2}-z$.

For both compounds, data collection: COLLECT (Bruker–Nonius, 2003); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Version 2.1; Bergerhoff et al., 1996); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1726). Services for accessing these data are described at the back of the journal.

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