

Table 2. Selected geometric parameters (Å, °)

Ca1—O1 <sup>i</sup>	2.419 (3)	Ca2—O3 <sup>iv</sup>	2.333 (3)
Ca1—O2	2.423 (3)	Ca2—O4 <sup>v</sup>	2.390 (4)
Ca1—O3	2.649 (4)	Ca2—O5 <sup>vi</sup>	2.290 (3)
Ca1—O4	2.282 (4)	B1—O1	1.416 (6)
Ca1—O4 <sup>ii</sup>	2.470 (4)	B1—O4 <sup>ii</sup>	1.361 (6)
Ca1—O5	2.434 (3)	B1—O5	1.349 (6)
Ca1—O5 <sup>iii</sup>	2.362 (3)	B2—O1	1.420 (6)
Ca2—O2	2.409 (4)	B2—O2 <sup>vii</sup>	1.368 (6)
Ca2—O2 <sup>iii</sup>	2.413 (3)	B2—O3 <sup>viii</sup>	1.353 (6)
Ca2—O3	2.415 (4)		
O1 <sup>i</sup> —Ca1—O2	84.0 (1)	O2—Ca2—O3	88.1 (1)
O1 <sup>i</sup> —Ca1—O3	53.7 (1)	O2—Ca2—O4 <sup>v</sup>	112.7 (1)
O1 <sup>i</sup> —Ca1—O4	124.1 (1)	O2—Ca2—O5 <sup>vi</sup>	166.8 (1)
O1 <sup>i</sup> —Ca1—O4 <sup>ii</sup>	110.6 (1)	O3—Ca2—O3 <sup>iv</sup>	92.1 (1)
O1 <sup>i</sup> —Ca1—O5	154.8 (1)	O3—Ca2—O4 <sup>v</sup>	157.9 (1)
O1 <sup>i</sup> —Ca1—O5 <sup>iii</sup>	80.8 (1)	O3—Ca2—O5 <sup>vi</sup>	86.0 (1)
O2—Ca1—O3	82.6 (1)	O4 <sup>v</sup> —Ca2—O5 <sup>vi</sup>	75.1 (1)
O2—Ca1—O4	92.6 (1)	B1—O1—B2	138.0 (4)
O2—Ca1—O5	89.0 (1)	O1—B1—O4 <sup>ii</sup>	114.5 (4)
O3—Ca1—O4	174.8 (1)	O1—B1—O5	123.6 (4)
O3—Ca1—O5	101.4 (1)	O4 <sup>ii</sup> —B1—O5	121.7 (4)
O4—Ca1—O4 <sup>ii</sup>	113.0 (1)	O1—B2—O2 <sup>vii</sup>	121.4 (4)
O4—Ca1—O5	80.3 (1)	O1—B2—O3 <sup>viii</sup>	111.8 (4)
O5—Ca1—O5 <sup>iii</sup>	114.7 (1)	O2 <sup>vii</sup> —B2—O3 <sup>viii</sup>	126.7 (4)
O2—Ca2—O2 <sup>iii</sup>	81.9 (1)		

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

The title structure was solved by direct methods [MULTAN83 (Main *et al.*, 1983) in *MolEN* (Fair, 1990)]. The positions of the Ca atoms were located by direct methods and those of the other atoms were located from successive difference Fourier syntheses. The structure was refined anisotropically using full-matrix least-squares techniques. The largest residual peak of  $1.15 \text{ e } \text{Å}^{-3}$  is  $0.93 \text{ Å}$  from the Ca2 atom. An extinction correction was applied to see if it reduced the difference density, but it did not help.

Data collection: *CONTROL* (Molecular Structure Corporation, 1988). Cell refinement: *CONTROL*. Data reduction: *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1204). Services for accessing these data are described at the back of the journal.

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## The double-anion salts $M_3[\text{ZnCl}_4]\text{NO}_3$ ( $M = \text{K}^+$ and $\text{NH}_4^+$ )

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## Abstract

The title compounds, tripotassium tetrachlorozincate nitrate,  $\text{K}_3[\text{ZnCl}_4]\text{NO}_3$ , and triammonium tetrachlorozincate nitrate,  $(\text{NH}_4)_3[\text{ZnCl}_4]\text{NO}_3$ , are newly discovered double-anion salts containing  $\text{ZnCl}_4^{2-}$  and  $\text{NO}_3^-$  ions. The compounds are isomorphous and contain minimally distorted anions. Hydrogen bonds to both Cl and O atoms in the ammonium compound have negligible distorting influence on anion geometries and appear only to orient the  $\text{NH}_4^+$  cations.

## Comment

Zompa & Haidar (1996) reported the structure of the tetrachlorocadmiate salt of a binucleating ligand, tetrahydrogen 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane, which forms a doubly positive 1:1 cationic complex with zinc ions in aqueous solution. Subsequent X-ray studies of a salt of the 1:1 zinc complex with this ligand (Zompa, 1999) showed that the counter-ion was the trichloro(nitrato)zincate(II) ion,  $[\text{ZnCl}_3(\text{NO}_3)]^{2-}$ , a previously unreported species in which the nitrate ion is bound to zinc through a single O atom. As a result of this discovery, we have been pursuing studies to determine if salts of  $[\text{ZnCl}_3(\text{NO}_3)]^{2-}$  can be produced with simpler cations, and if so, to determine

the minimal structure and size requirements for such formation. Attempts to produce small-cation salts of formula  $M_2[\text{ZnCl}_3(\text{NO}_3)]$ , where  $M = \text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$ , have not been successful. However, as a result of these investigations, we have prepared and characterized previously unreported double-anion salts with the formula  $M_3[\text{ZnCl}_4]\text{NO}_3$ , where  $M = \text{NH}_4^+$  and  $\text{K}^+$ . Inasmuch as this stoichiometry does not rule out the possible presence of  $[\text{ZnCl}_3(\text{NO}_3)]^{2-}$  ions, X-ray structure studies were undertaken to determine the composition of the zinc complex ions in these compounds.

The potassium, (1), and ammonium, (2), salts are isomorphous. The crystals do not contain  $[\text{ZnCl}_3(\text{NO}_3)]^{2-}$  and  $\text{Cl}^-$  ions, but instead are composed of equal numbers of  $\text{ZnCl}_4^{2-}$  and  $\text{NO}_3^-$  ions. The structure consists of rows of nitrate ions parallel to  $a$ , surrounded by cylinders of cations, which in turn are surrounded by concentric cylinders of tetrachlorozincate ions. In both compounds, the length of one symmetry-related pair of Zn—Cl bonds is shorter than the other two by 0.03–0.04 Å. Nonetheless, the tetrachlorozincate ions are more nearly tetrahedral in these compounds than has been reported for  $(\text{NH}_4)_2\text{ZnCl}_4$  (Mikhail, 1980) and  $\text{K}_2\text{ZnCl}_4$  (Mikhail & Peters, 1979). The nitrate-ion parameters are comparable to those found for room-temperature phases  $\text{NH}_4\text{NO}_3$ , (IV) (Choi *et al.*, 1972; Lucas *et al.*, 1979), and  $\text{KNO}_3$ , (II) (Nimmo & Lucas, 1973; Holden & Dickinson, 1975).

The ammonium compound, (2), shows evidence of hydrogen bonding to Cl atoms of  $\text{ZnCl}_4^{2-}$  and O atoms of  $\text{NO}_3^-$ . The close isomorphism with the potassium compound, (1), suggests that hydrogen bonds have little distorting influence on either complex ion, and merely serve to orient the ammonium ions. This contrasts with  $(\text{NH}_4)_2\text{ZnCl}_4$ , for which hydrogen bonding has been cited as contributing to distortion from tetrahedral geometry about the Zn atom and the reported irregularity in Zn—Cl distances (Mikhail, 1980).

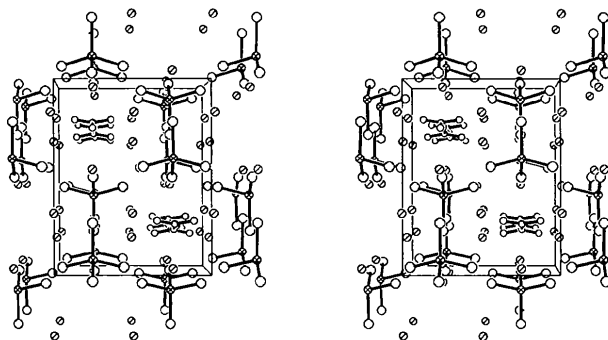


Fig. 1. Stereoview of the crystal packing of  $\text{K}_3[\text{ZnCl}_4]\text{NO}_3$  down  $a$ . K atoms are slashed, Zn crossed, N partially striped, Cl stippled and O clear. In the plane of the figure, the  $c$  axis is vertical and the  $b$  axis is horizontal.

## Experimental

The title compounds were prepared from aqueous solutions with the molar ratio  $\text{ZnCl}_2:2\text{MCl}: \text{MNO}_3$  ( $M = \text{NH}_4^+$ ,  $\text{K}^+$ ) and were characterized by elemental analysis for Zn, N, Cl, and H or K. Both solutions showed a pronounced tendency to supersaturate, requiring nucleation by seed crystals or chilling to 285 K. Following nucleation, suitable specimens were obtained by allowing overnight equilibration with the mother liquor or by slow evaporation for a limited time. The potassium salt was dried at 348 K in a vacuum oven. The ammonium salt sublimed under these conditions and was therefore dried over Drierite in a desiccator. The crystals were only mildly hygroscopic and required no special protection during X-ray measurements.

### Compound (1)

#### Crystal data

$\text{K}_3[\text{ZnCl}_4]\text{NO}_3$   
 $M_r = 386.48$   
 Orthorhombic  
*Pnma*  
 $a = 9.256(3) \text{ \AA}$   
 $b = 9.726(3) \text{ \AA}$   
 $c = 12.073(3) \text{ \AA}$   
 $V = 1086.9(6) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 2.362 \text{ Mg m}^{-3}$   
 $D_m = 2.3(1) \text{ Mg m}^{-3}$   
 $D_m$  measured by flotation

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 24 reflections  
 $\theta = 15.9\text{--}22.2^\circ$   
 $\mu = 4.357 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Block  
 $0.5 \times 0.5 \times 0.4 \text{ mm}$   
 Colorless

#### Data collection

Syntex  $P2_1$  diffractometer  
 $\theta$ – $2\theta$  scans  
 Absorption correction:  
 $\psi$  scan (Sheldrick, 1990)  
 $T_{\min} = 0.482$ ,  $T_{\max} = 0.558$   
 1840 measured reflections  
 1840 independent reflections  
 1840 reflections with  
 $I > 0$

$\theta_{\max} = 31.12^\circ$   
 $h = 0 \rightarrow 13$   
 $k = 0 \rightarrow 14$   
 $l = 0 \rightarrow 17$   
 3 standard reflections  
 every 75 reflections  
 intensity decay: none

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.089$   
 $S = 1.208$   
 1840 reflections  
 64 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 1.0236P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.010$   
 $\Delta\rho_{\max} = 0.679 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -1.156 \text{ e \AA}^{-3}$   
 (0.79 Å from Zn)  
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (1)

	$U_{eq} = (1/3)\sum_j U^{jj} a^j a^j \cdot \mathbf{a}_j$			
	$x$	$y$	$z$	$U_{eq}$
Zn	0.82026 (6)	1/4	0.40800 (4)	0.02303 (13)
Cl1	1.03376 (13)	1/4	0.50010 (11)	0.0411 (3)
Cl2	0.87384 (15)	1/4	0.22381 (10)	0.0365 (3)
Cl3	0.69273 (10)	0.05970 (8)	0.44919 (7)	0.0366 (2)
N	0.6568 (4)	1/4	0.7294 (3)	0.0242 (7)

O1	0.7861 (4)	1/4	0.7584 (3)	0.0362 (8)
O2	0.5942 (3)	0.3614 (3)	0.7124 (2)	0.0359 (6)
K1	0.08386 (11)	3/4	0.03730 (8)	0.0280 (2)
K2	0.12267 (9)	0.49576 (8)	0.31771 (6)	0.03523 (18)

Table 2. Selected geometric parameters (Å, °) for (1)

Zn—Cl3	2.2509 (10)	N—O2	1.246 (3)
Zn—Cl1	2.2676 (14)	N—O1	1.247 (5)
Zn—Cl2	2.2784 (14)		
Cl3—Zn—Cl3 <sup>1</sup>	110.63 (6)	Cl1—Zn—Cl2	106.79 (6)
Cl3—Zn—Cl1	110.41 (4)	O2 <sup>1</sup> —N—O2	120.9 (4)
Cl3—Zn—Cl2	109.26 (3)	O2—N—O1	119.50 (18)

Symmetry code: (i)  $x, \frac{1}{2} - y, z$ .**Compound (2)***Crystal data*(NH<sub>4</sub>)<sub>3</sub>[ZnCl<sub>4</sub>]NO<sub>3</sub> $M_r = 323.31$ 

Orthorhombic

*Pnma* $a = 9.268 (3) \text{ \AA}$  $b = 10.042 (3) \text{ \AA}$  $c = 12.482 (3) \text{ \AA}$  $V = 1161.7 (6) \text{ \AA}^3$  $Z = 4$  $D_x = 1.849 \text{ Mg m}^{-3}$  $D_m = 1.8 (1) \text{ Mg m}^{-3}$  $D_m$  measured by flotationMo  $K\alpha$  radiation $\lambda = 0.71073 \text{ \AA}$ 

Cell parameters from 24 reflections

 $\theta = 16.3\text{--}21.6^\circ$  $\mu = 3.015 \text{ mm}^{-1}$  $T = 293 (2) \text{ K}$ 

Hexagonal prism

 $0.5 \times 0.5 \times 0.5 \text{ mm}$ 

Colorless

*Data collection*Syntex P2<sub>1</sub> diffractometer $\theta$ - $2\theta$  scans

Absorption correction:

 $\psi$  scan (Sheldrick, 1990) $T_{\min} = 0.523, T_{\max} = 0.645$ 

1962 measured reflections

1962 independent reflections

1962 reflections with

 $I > 0$  $\theta_{\max} = 31.06^\circ$  $h = 0 \rightarrow 13$  $k = 0 \rightarrow 14$  $l = 0 \rightarrow 18$ 

3 standard reflections

every 75 reflections

intensity decay: none

*Refinement*Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.043$  $wR(F^2) = 0.105$  $S = 1.090$ 

1962 reflections

83 parameters

Only coordinates of H atoms refined

 $w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.5098P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.093$  $\Delta\rho_{\max} = 0.509 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -0.808 \text{ e \AA}^{-3}$ 

Extinction correction: none

Scattering factors from

*International Tables for**Crystallography* (Vol. C)Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (2)

	$x$	$y$	$z$	$U_{\text{eq}}$
Zn	0.82143 (5)	1/4	0.40896 (3)	0.02825 (13)
Cl1	1.03141 (11)	1/4	0.50387 (9)	0.0444 (3)
Cl2	0.88055 (13)	1/4	0.23134 (7)	0.0426 (2)
Cl3	0.69644 (9)	0.06329 (7)	0.44482 (6)	0.04310 (19)
N	0.6591 (3)	1/4	0.7273 (2)	0.0265 (6)
O1	0.7858 (3)	1/4	0.7601 (3)	0.0521 (8)
O2	0.5980 (2)	0.3574 (2)	0.7072 (2)	0.0502 (6)
N1	0.0879 (4)	3/4	0.0313 (3)	0.0357 (7)
N2	0.1194 (4)	0.4942 (3)	0.3220 (2)	0.0441 (6)

Table 4. Selected geometric parameters (Å, °) for (2)

Zn—Cl3	2.2489 (9)	N—O2	1.243 (3)
Zn—Cl1	2.2783 (12)	N—O1	1.243 (4)
Zn—Cl2	2.2837 (11)		
Cl3—Zn—Cl3 <sup>1</sup>	112.96 (5)	Cl1—Zn—Cl2	107.45 (5)
Cl3—Zn—Cl1	109.66 (3)	O2 <sup>1</sup> —N—O2	120.3 (3)
Cl3—Zn—Cl2	108.47 (3)	O2—N—O1	119.76 (16)

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

For both compounds, data collection: *P3/PC* (Siemens, 1993); cell refinement: *P3/PC*; data reduction: *XDISK* in *P3/PC*; program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1211). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). **C55**, 8–11**Na<sub>2</sub>Mg(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, the Mg end-member of the bloedite-type of mineral**

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**Abstract**

The crystal structure of a natural sample of disodium magnesium bis(sulfate) tetrahydrate, Na<sub>2</sub>Mg(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, the Mg end-member of the bloedite-type of min-