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Calcium octaammine dichloride

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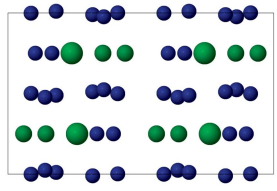
The redetermination of the crystal structure of calcium octaammine chloride, or octaamminecalcium dichloride, $[Ca(NH_3)_8]Cl_2$, based on synchrotron X-ray diffraction powder data, revealed a more reasonable model in terms of N···N distances in comparison with the previous model [Westman *et al.* (1981). *Acta Chem. Scand. Ser. A*, **35**, 467–472].

3D view



Structure description

The reaction of $CaCl_2$ with NH_3 is promising for the energy efficiency improvement of automobiles and factories and is one form of thermal energy storage (TES) technology (Klerke *et al.*, 2008). A detailed knowledge of the crystal structure of $[Ca(NH_3)_8]Cl_2$ is necessary for understanding the reaction mechanism associated with the uptake of ammonia from $CaCl_2$. In the current study, we developed *in situ* XRD equipment and redetermined the crystal structure of $[Ca(NH_3)_8]Cl_2$. The main difference from the structure model reported in the previous study (powder X-ray diffraction data; Westman *et al.*, 1981) is the position of one N atom which had an unrealistically short N···N distances of 2.13 Å. Whereas this N atom was modelled in the previous study to be on a general position of space group *Pnma* (Wyckoff site 8*d*), it is now modelled to be split over two positions located on a mirror plane (Wyckoff site 4*c*), leaving to more reasonable N···N distances > 3.1 Å. The current structure model is supported by isotypism with $[Sr(NH_3)_8]Cl_2$ (Lysgaard *et al.*, 2012), $[Ca(NH_3)_8]Br_2$ and $[Ca(NH_3)_8]I_2$ (Woidy *et al.*, 2014). The coordination polyhedra around the alkaline earth ions are twofold-capped trigonal-prisms (Fig. 1; Table 1). Although no H-atom positions could be determined in the current synchrotron powder study, N···Cl contacts in the range 3.45–3.70 Å are evidence for hydrogen bonding between the complex cations and the chloride anions.

Table 1
Selected bond lengths (Å).

Ca1—N4	2.601 (4)	Ca1—N2	2.702 (7)
Ca1—N3	2.616 (4)	Ca1—N1	3.078 (7)
Ca1—N5	2.646 (4)		

Synthesis and crystallization

A quartz glass capillary cell was developed for the *in situ* X-ray powder diffraction (XRD) under NH_3 gas pressure. The outside and inside diameters were 1.5875 mm (1/16 inch) and 1.0 mm, respectively. Carbon fiber was mixed with $CaCl_2$ powder to prevent breaking of the capillary by expansion of $CaCl_2$ powder during NH_3 adsorption. $[Ca(NH_3)_8]Cl_2$ was synthesized *in situ* in the capillary under 518 kPa of NH_3 gas pressure. The XRD experiments were performed at BL5S2 at Aichi Synchrotron Radiation Center in Aichi province, Japan.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal structure was modelled in the same space group (*Pnma*) as in the previous work by Westman *et al.* (1981). The coordinations of all atoms were estimated by application of direct methods for structure solution by using the *EXPO2014* software (Altomare *et al.*, 2013). Wyckoff positions of atoms Ca1, Cl1, Cl2 (on sites 4*c* with mirror symmetry), and N3, N4 and N5 (on general positions 8*d*) are the same as those reported in the previous study. In contrast to the previous model, sites N1 and N2 were modelled to be located on mirror planes, instead of as one atom on a general position. Mixing carbon fiber with $CaCl_2$ deteriorates the analytical accuracy by the overlap between diffraction peaks. Therefore, several parameters were constrained during the refinement as follows: (i) anisotropic displacement parameters of Cl2 were constrained to be the same as that of the Cl1 site; (ii) H atoms of the NH_3 molecules were not positioned; (iii) isotropic displacement parameters were used for all N atoms. The Rietveld refinement (Fig. 2) was performed with the *RIETAN-FP* program (Izumi & Momma, 2007) using a split pseudo-Voigt profile function (Toraya, 1990).

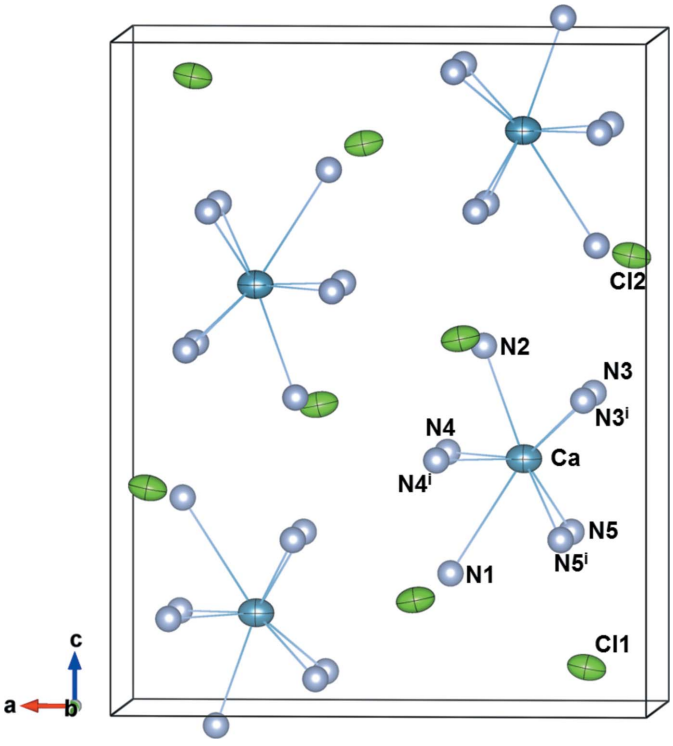


Figure 1
The crystal structure of $[Ca(NH_3)_8]Cl_2$, viewed approximately along [010]. The blue and green ellipsoids represent Ca and Cl atoms, respectively, at the 50% probability level. Grey spheres indicate N atoms (arbitrary radius) of the NH_3 molecules. [Symmetry code (i) $x, -y+\frac{1}{2}, z$.]

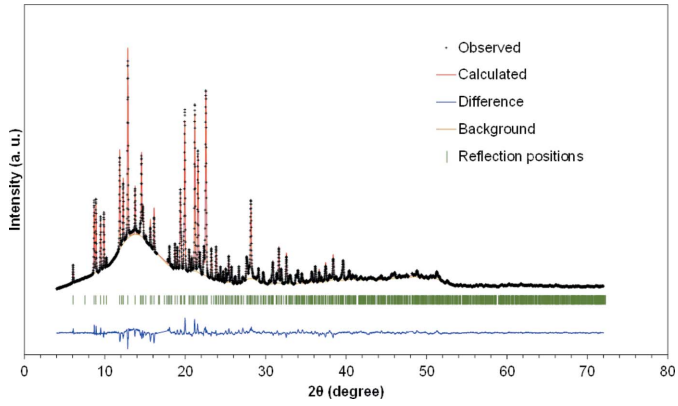


Figure 2
Rietveld refinement of $[Ca(NH_3)_8]Cl_2$. 2θ ranges 16.50–17.80 and 47.48–48.18° are excluded because diffuse diffraction peaks of mixed carbon fiber appeared.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ca(NH_3)_8]Cl_2$
M_r	247.23
Crystal system, space group	Orthorhombic, *Pnma*
Temperature (K)	301
a, *b*, *c* (Å)	12.0924 (2), 7.3293 (1), 15.1975 (2)
V (Å^3)	1346.94 (3)
Z	4
Radiation type	Synchrotron, λ = 0.9995754 Å
Specimen shape, size (mm)	Cylinder, 0.5 × 0.5
Data collection	
Diffractometer	BL5S2 Debye-Scherrer Camera
Specimen mounting	Quartz capillary.
Data collection mode	Transmission
Scan method	Stationary detector
Refinement	
R factors and goodness of fit	R_p = 0.021, R_{wp} = 0.028, R_{exp} = 0.024, R_{Bragg} = 0.039, $R(F)$ = 0.030, χ^2 = 1.407
No. of parameters	43
H-atom treatment	H-atom parameters not refined

Computer programs: local data-collection software, *EXPO2014* (Altomare *et al.*, 2013), *VESTA* (Momma & Izumi, 2011), *RIETAN-FP* (Izumi & Momma, 2007) and *publCIF* (Westrip, 2010).

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References

Altomare, A., Cuocci, C., Giacovazzo, C., Moliterni, A., Rizzi, R., Corriero, N. & Falcicchio, A. (2013). *J. Appl. Cryst.* **46**, 1231–1235.
Izumi, F. & Momma, K. (2007). *Solid State Phenom.* **130**, 15–20.
Klerke, A., Christensen, C. H., Nørskov, J. K. & Vegge, T. (2008). *J. Mater. Chem.* **18**, 2304–2310.
Lysgaard, S., Ammitzbøll, A. L., Johnsen, R. E., Norby, P., Quaade, U. J. & Vegge, T. (2012). *Int. J. Hydrogen Energy*, **37**, 18927–18936.
Momma, K. & Izumi, F. (2011). *J. Appl. Cryst.* **44**, 1272–1276.
Toraya, H. (1990). *J. Appl. Cryst.* **23**, 485–491.
Westman, S., Werner, P.-E., Schuler, T. & Raldow, W. (1981). *Acta Chem. Scand. Ser. A*, **35**, 467–472.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Woidy, P., Karttunen, A. J., Müller, T. G. & Kraus, F. (2014). *Z. Naturforsch. Teil B*, **69**, 1141–1148.

full crystallographic data

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Calcium octaammine dichloride

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Octaamminecalcium dichloride

Crystal data

$[Ca(NH_3)_8]Cl_2$
M_r = 247.23
Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
a = 12.0924 (2) Å
b = 7.3293 (1) Å
c = 15.1975 (2) Å
V = 1346.94 (3) Å^3
Z = 4
F(000) = 440.00
D_x = 1.100 Mg m^{-3}
Synchrotron radiation, λ = 0.9995754 Å
T = 301 K
Particle morphology: powder
white
cylinder, 0.5 × 0.5 mm
Specimen preparation: Prepared at 301 K and 518 kPa

Data collection

BL5S2 Debye-Scherrer Camera diffractometer
Radiation source: synchrotron
Specimen mounting: Quartz capillary.
Data collection mode: transmission
Scan method: Stationary detector

Refinement

Least-squares matrix: full
R_p = 0.021
R_{wp} = 0.028
R_{exp} = 0.024
R_{Bragg} = 0.039
$R(F)$ = 0.030
$R(F^2)$ = 0.02947
7419 data points
Excluded region(s): 2θ ranges of 16.5 to 17.8 and 47.78 to 48.18 degrees were excluded because the diffraction of the carbon fiber appeared.
Profile function: split pseudo-Voigt function
43 parameters
0 restraints
9 constraints
H-atom parameters not refined
Weighting scheme based on measured s.u.'s $1/y_i$
$(\Delta/\sigma)_{max}$ < 0.001
Background function: RIETAN-FP composite background function number 3.

Special details

Experimental. The powder mounted in the quartz capillary that was filled by the NH_3 gas, 518 kPa (abs).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ca1	0.2599 (2)	0.25	0.3651 (2)	0.053 (2)
Cl1	0.1428 (3)	0.25	0.0556 (2)	0.067 (2)
Cl2	0.0589 (2)	0.25	0.6675 (2)	0.067 (2)

N1	0.3970 (5)	0.25	0.1944 (5)	0.029 (2)*
N2	0.3347 (6)	0.25	0.5326 (5)	0.029 (2)*
N3	0.1395 (3)	0.0237 (6)	0.4574 (3)	0.021 (1)*
N4	0.4130 (4)	0.0009 (6)	0.3684 (3)	0.021 (1)*
N5	0.1813 (3)	0.0106 (6)	0.2507 (3)	0.021 (1)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.068 (3)	0.050 (2)	0.042 (2)	0	−0.000 (2)	0
Cl1	0.079 (2)	0.086 (2)	0.036 (2)	0	0.009 (2)	0
Cl2	0.079 (2)	0.086 (2)	0.036 (2)	0	0.009 (2)	0

Geometric parameters (Å, º)

Ca1—N4	2.601 (4)	Ca1—N5	2.646 (4)
Ca1—N4^{i}	2.601 (4)	Ca1—N5^{i}	2.646 (4)
Ca1—N3	2.616 (4)	Ca1—N2	2.702 (7)
Ca1—N3^{i}	2.616 (4)	Ca1—N1	3.078 (7)
N4—Ca1—N4^{i}	89.2 (2)	N3—Ca1—N5	74.4 (1)
N4—Ca1—N3	86.6 (1)	N3—Ca1—N5^{i}	125.0 (2)
N4—Ca1—N3^{i}	146.2 (2)	N3—Ca1—N2	71.4 (2)
N4—Ca1—N5	78.6 (1)	N3—Ca1—N1	138.8 (1)
N4—Ca1—N5^{i}	137.2 (2)	N3^{i}—Ca1—N5	125.0 (2)
N4—Ca1—N2	75.1 (2)	N3^{i}—Ca1—N5^{i}	74.4 (1)
N4—Ca1—N1	68.5 (1)	N3^{i}—Ca1—N2	71.4 (2)
N4^{i}—Ca1—N3	146.2 (2)	N3^{i}—Ca1—N1	138.8 (1)
N4^{i}—Ca1—N3^{i}	86.6 (1)	N5—Ca1—N5^{i}	83.1 (2)
N4^{i}—Ca1—N5	137.2 (2)	N5—Ca1—N2	137.7 (1)
N4^{i}—Ca1—N5^{i}	78.6 (1)	N5—Ca1—N1	68.9 (1)
N4^{i}—Ca1—N2	75.1 (2)	N5^{i}—Ca1—N2	137.7 (1)
N4^{i}—Ca1—N1	68.5 (1)	N5^{i}—Ca1—N1	68.9 (1)
N3—Ca1—N3^{i}	78.7 (2)	N2—Ca1—N1	127.8 (2)

Symmetry code: (i) x, $-y+1/2$, z.