Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1202). Services for accessing these data are described at the back of the journal.

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Pentaamminenitrocobalt(III) Dichloride at Pressures of 0.24, 0.52, 1.25, 1.91 and 3.38 GPa

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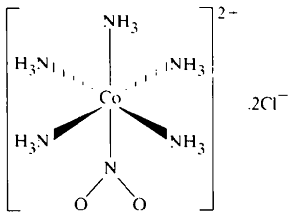
Abstract

The structure of $[Co(NO_2)(NH_3)_5]Cl_2$ has been refined anisotropically from data collected at 0.24, 0.52, 1.25, 1.91 and 3.38 GPa in a diamond anvil cell (DAC). For comparison, the structure of the same crystal in the same DAC was also refined at ambient pressure. The structures at high pressures are anisotropically distorted compared with that at ambient pressure determined in this work and by Börtin [*Acta Chem. Scand.* (1968), **22**, 2890–2898], Kubota & Ohba [*Acta Cryst.* (1992), B**48**, 627–632] and Boldyreva *et al.* [*Acta Cryst.* (1997*c*), C**53**, 523–526], but the space group and the general structural pattern remain the same.

Comment

A comparative study of the structures of the title compound at ambient pressure and at high pressures formed part of a project on the study of the anisotropy of structural distortion of Co^{III}–nitroammine complexes induced by various means, *i.e.* cooling (Boldyreva *et al.*, 1997*a*,*b*,*c*,*d*), increasing pressure (Boldyreva *et al.*, 1994, 1996; Boldyreva, Naumov & Ahsbahs, 1997, 1998*b*; Boldyreva, Kuz'mina & Ahsbahs, 1997), isomorphous substitution and homogeneous linkage isomerization (Boldyreva, 1994, 1996; Boldyreva *et al.*, 1993; Masciocchi *et al.*, 1994).

The present contribution reports on the structural data for the title compound, (I), at ambient pressure, 0.24, 0.52, 1.25, 1.91 and 3.38 GPa, as well as providing details of the data collection and data refinement procedures. A detailed comparison of the structures,



(I)

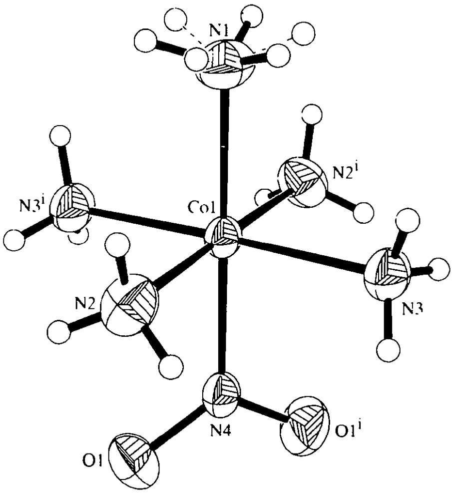


Fig. 1. View of the $[Co(NO_2)(NH_3)_5]^{2+}$ cation showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels as at ambient pressure; H atoms are drawn as small circles of arbitrary radii.

as well as an analysis of the anisotropy of structural distortion with increasing pressure and its comparison with the structural strain on cooling (Boldyreva *et al.*, 1997*b*,*c*), will be published elsewhere (Boldyreva *et al.*, 1998*a*). [The results were initially reported at the German Seminar on High Pressure Crystallography Techniques, Rauischholzhausen (1996), at the Russian National Conference on the Application of X-rays, Synchrotron Radiation, Neutrons and Electrons for Studies of Materials, Dubna (1997), at the 13th Seminar on Intermolecular Interactions and Conformations of Molecules, Tver' (1997), and at the ECM-97, Lisbon (1997).]

Experimental

The title compound was synthesized from $[Co(CO_3)(NH_3)_5](NO_3)$ according to Mäueler (1981). The crystals were grown at ambient temperature from aqueous solution.

(I) at ambient pressure

Crystal data

$[Co(NO_2)(NH_3)_5]Cl_2$
$M_r = 261.01$
Monoclinic
$C2/c$
$a = 10.326\ (1)$ Å
$b = 8.670\ (1)$ Å
$c = 10.720\ (1)$ Å
$\beta = 94.93\ (1)^\circ$
$V = 956.2\ (2)$ Å^3
$Z = 4$
$D_x = 1.813$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections in 8 positions each
$\theta = 3.52$–10.27°
$\mu = 2.325$ mm^{-1}
$T = 293\ (2)$ K
Round plate
$0.20 \times 0.20 \times 0.11$ mm
Ruby

Data collection

Stoe four-circle diffractometer
ω scans
Absorption correction: none
2626 measured reflections
1150 independent reflections
589 reflections with $I > 2\sigma(I)$

$R_{int} = 0.032$
$\theta_{max} = 35.99^\circ$
$h = -15 \rightarrow 15$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$
2 standard reflections frequency: 180 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.046$
$S = 0.600$
1150 reflections
58 parameters
All H atoms refined
$w = 1/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.227$ e Å^{-3}
$\Delta\rho_{min} = -0.245$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I) at ambient pressure*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co1	0	0.28534 (5)	1/4	0.02025 (13)
Cl1	0.20740 (6)	0.01547 (7)	0.01333 (6)	0.0339 (2)
N1	0	0.0577 (3)	1/4	0.0373 (9)
N2	0.1887 (2)	0.2873 (2)	0.2467 (2)	0.0355 (6)
N3	0.0176 (2)	0.2884 (2)	0.4325 (2)	0.0313 (5)
N4	0	0.5068 (3)	1/4	0.0241 (8)
O1	0.0737 (2)	0.5787 (2)	0.1869 (2)	0.0467 (6)

Table 2. *Selected geometric parameters (Å, °) for (I) at ambient pressure*

Co1—N1	1.974 (3)	Co1—N4	1.920 (3)
Co1—N2	1.952 (2)	N4—O1	1.231 (2)
Co1—N3	1.949 (2)		
O1—N4—O1^i	119.1 (4)	O1—N4—Co1	120.5 (2)

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

(I) at 0.24 GPa

Crystal data

$[Co(NO_2)(NH_3)_5]Cl_2$
$M_r = 261.01$
Monoclinic
$C2/c$
$a = 10.314\ (1)$ Å
$b = 8.587\ (1)$ Å
$c = 10.710\ (1)$ Å
$\beta = 94.95\ (1)^\circ$
$V = 944.9\ (2)$ Å^3
$Z = 4$
$D_x = 1.835$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections in 8 positions each
$\theta = 3.52$–10.34°
$\mu = 2.353$ mm^{-1}
$T = 293\ (2)$ K
Round plate
$0.20 \times 0.20 \times 0.11$ mm
Ruby

Data collection

Stoe four-circle diffractometer
ω scans
Absorption correction: none
2558 measured reflections
1145 independent reflections
647 reflections with $I > 2\sigma(I)$

$R_{int} = 0.033$
$\theta_{max} = 35.98^\circ$
$h = -15 \rightarrow 15$
$k = -11 \rightarrow 11$
$l = -16 \rightarrow 16$
2 standard reflections frequency: 300 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.047$
$S = 0.759$
1145 reflections
58 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0087P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.256$ e Å^{-3}
$\Delta\rho_{min} = -0.250$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for (I) at 0.24 GPa*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co1	0	0.28537 (6)	1/4	0.02074 (14)
Cl1	0.20813 (6)	0.01609 (8)	0.01270 (6)	0.0335 (2)
N1	0	0.0555 (3)	1/4	0.0354 (9)
N2	0.1892 (2)	0.2873 (2)	0.2473 (2)	0.0356 (6)
N3	0.0168 (2)	0.2877 (2)	0.4324 (2)	0.0320 (6)
N4	0	0.5089 (4)	1/4	0.0257 (8)
O1	0.0735 (2)	0.5811 (3)	0.1871 (2)	0.0464 (6)

Table 4. *Selected geometric parameters* (Å, °) *for (I) at 0.24 GPa*

Co1—N1	1.974 (3)	Co1—N4	1.919 (3)
Co1—N2	1.954 (2)	N4—O1	1.225 (2)
Co1—N3	1.947 (2)		
O1—N4—O1^i	119.2 (4)	O1—N4—Co1	120.4 (2)

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

(I) at 0.52 GPa

Crystal data

$[Co(NO_2)(NH_3)_5]Cl_2$
$M_r = 261.01$
Monoclinic
$C2/c$
$a = 10.312$ (1) Å
$b = 8.457$ (1) Å
$c = 10.683$ (1) Å
$\beta = 94.935$ (9)°
$V = 928.2$ (2) Å^3
$Z = 4$
$D_x = 1.868$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 12 reflections in 8 positions each
$\theta = 3.57–10.34°$
$\mu = 2.395$ mm^{-1}
$T = 293$ (2) K
Round plate
0.20 × 0.20 × 0.11 mm
Ruby

Data collection

Stoe four-circle diffractometer
ω scans
Absorption correction: none
2979 measured reflections
1116 independent reflections
644 reflections with $I > 2\sigma(I)$

$R_{int} = 0.034$
$\theta_{max} = 36°$
$h = -15 \rightarrow 15$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$
2 standard reflections
frequency: 300 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.050$
$S = 0.785$
1116 reflections
58 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.013P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.286$ e Å^{-3}
$\Delta\rho_{min} = -0.269$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for (I) at 0.52 GPa*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co1	0	0.28516 (6)	1/4	0.02026 (15)
Cl1	0.20902 (6)	0.01694 (8)	0.01184 (5)	0.0321 (2)
N1	0	0.0515 (4)	1/4	0.0349 (9)
N2	0.1890 (2)	0.2867 (3)	0.2480 (2)	0.0348 (6)
N3	0.0166 (2)	0.2877 (2)	0.4326 (2)	0.0298 (6)
N4	0	0.5124 (4)	1/4	0.0238 (8)
O1	0.0739 (2)	0.5857 (3)	0.1872 (2)	0.0441 (6)

Table 6. *Selected geometric parameters* (Å, °) *for (I) at 0.52 GPa*

Co1—N1	1.976 (3)	Co1—N4	1.922 (3)
Co1—N2	1.951 (2)	N4—O1	1.226 (2)
Co1—N3	1.944 (2)		
O1—N4—O1^i	119.3 (4)	O1—N4—Co1	120.4 (2)

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

(I) at 1.25 GPa

Crystal data

$[Co(NO_2)(NH_3)_5]Cl_2$
$M_r = 261.01$
Monoclinic
$C2/c$
$a = 10.400$ (1) Å
$b = 8.089$ (1) Å
$c = 10.658$ (1) Å
$\beta = 94.804$ (9)°
$V = 893.5$ (2) Å^3
$Z = 4$
$D_x = 1.940$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections in 8 positions each
$\theta = 3.64–10.39°$
$\mu = 2.488$ mm^{-1}
$T = 293$ (2) K
Round plate
0.20 × 0.20 × 0.11 mm
Ruby

Data collection

Stoe four-circle diffractometer
ω scans
Absorption correction: none
2540 measured reflections
1077 independent reflections
600 reflections with $I > 2\sigma(I)$

$R_{int} = 0.038$
$\theta_{max} = 35.98°$
$h = -15 \rightarrow 15$
$k = -10 \rightarrow 10$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 180 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.046$
$S = 0.659$
1077 reflections
58 parameters
All H atoms refined
$w = 1/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.287$ e Å^{-3}
$\Delta\rho_{min} = -0.248$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I) at 1.25 GPa*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co1	0	0.28451 (6)	1/4	0.01791 (14)
Cl1	0.21129 (5)	0.01714 (8)	0.00986 (5)	0.0282 (2)
N1	0	0.0401 (4)	1/4	0.0336 (9)
N2	0.1871 (2)	0.2864 (3)	0.2496 (2)	0.0291 (6)
N3	0.0140 (2)	0.2887 (3)	0.4330 (2)	0.0261 (5)
N4	0	0.5215 (4)	1/4	0.0197 (7)
O1	0.0750 (2)	0.5981 (3)	0.18814 (15)	0.0370 (6)

Table 8. *Selected geometric parameters (Å, °) for (I) at 1.25 GPa*

Co1—N1	1.977 (3)	Co1—N4	1.917 (3)
Co1—N2	1.946 (2)	N4—O1	1.230 (2)
Co1—N3	1.944 (2)		
O1—N4—O1^i	119.5 (3)	O1—N4—Co1	120.2 (2)

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

(I) at 1.91 GPa

Crystal data

[Co(NO$_2$)(NH$_3$)$_5$]Cl$_2$

M_r = 261.01

Monoclinic

$C2/c$

a = 10.443 (1) Å

b = 7.857 (1) Å

c = 10.601 (1) Å

β = 94.57 (1)°

V = 867.1 (2) Å^3

Z = 4

D_x = 1.999 Mg m^{-3}

D_m not measured

Mo $K\alpha$ radiation

λ = 0.71073 Å

Cell parameters from 14 reflections in 8 positions each

θ = 3.70–10.43°

μ = 2.564 mm^{-1}

T = 293 (2) K

Round plate

0.20 × 0.20 × 0.11 mm

Ruby

Data collection

Stoe four-circle diffractometer

ω scans

Absorption correction: none

2337 measured reflections

1039 independent reflections

607 reflections with $I > 2\sigma(I)$

R_{int} = 0.039

θ_{max} = 36.01°

$h = -15 \rightarrow 15$

$k = -10 \rightarrow 10$

$l = -15 \rightarrow 15$

3 standard reflections frequency: 180 min intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)]$ = 0.025

$wR(F^2)$ = 0.049

S = 0.700

1039 reflections

58 parameters

All H atoms refined

$w = 1/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = -0.003$

$\Delta\rho_{max}$ = 0.263 e Å^{-3}

$\Delta\rho_{min}$ = −0.350 e Å^{-3}

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 9. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I) at 1.91 GPa*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co1	0	0.28409 (7)	1/4	0.01600 (14)
Cl1	0.21281 (5)	0.01635 (8)	0.00823 (6)	0.0255 (2)
N1	0	0.0322 (4)	1/4	0.0298 (8)
N2	0.1862 (2)	0.2855 (3)	0.2506 (2)	0.0261 (6)
N3	0.0121 (2)	0.2894 (3)	0.4335 (2)	0.0238 (5)
N4	0	0.5278 (4)	1/4	0.0181 (7)
O1	0.0765 (2)	0.6079 (3)	0.1893 (2)	0.0340 (6)

Table 10. *Selected geometric parameters (Å, °) for (I) at 1.91 GPa*

Co1—N1	1.979 (3)	Co1—N4	1.915 (3)
Co1—N2	1.944 (2)	N4—O1	1.237 (2)
Co1—N3	1.940 (2)		
O1—N4—O1^i	118.9 (4)	O1—N4—Co1	120.6 (2)

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

(I) at 3.38 GPa

Crystal data

[Co(NO$_2$)(NH$_3$)$_5$]Cl$_2$

M_r = 261.01

Monoclinic

$C2/c$

a = 10.457 (1) Å

b = 7.619 (1) Å

c = 10.477 (1) Å

β = 94.126 (10)°

V = 832.6 (2) Å^3

Z = 4

D_x = 2.082 Mg m^{-3}

D_m not measured

Mo $K\alpha$ radiation

λ = 0.71073 Å

Cell parameters from 14 reflections in 8 positions each

θ = 3.77–10.50°

μ = 2.670 mm^{-1}

T = 293 (2) K

Round plate

0.20 × 0.20 × 0.11 mm

Ruby

Data collection

Stoe four-circle diffractometer

ω scans

Absorption correction: none

2221 measured reflections

991 independent reflections

619 reflections with $I > 2\sigma(I)$

R_{int} = 0.032

θ_{max} = 35.94°

$h = -15 \rightarrow 15$

$k = -9 \rightarrow 9$

$l = -15 \rightarrow 15$

3 standard reflections frequency: 180 min intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)]$ = 0.024

$wR(F^2)$ = 0.049

S = 0.710

991 reflections

58 parameters

All H atoms refined

$w = 1/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = -0.018$

$\Delta\rho_{max}$ = 0.273 e Å^{-3}

$\Delta\rho_{min}$ = −0.248 e Å^{-3}

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 11. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I) at 3.38 GPa*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co1	0	0.28369 (6)	1/4	0.01377 (13)
Cl1	0.21430 (5)	0.01493 (8)	0.00649 (5)	0.0224 (2)
N1	0	0.0246 (4)	1/4	0.0264 (8)
N2	0.1849 (2)	0.2838 (3)	0.2512 (2)	0.0228 (5)
N3	0.0096 (2)	0.2892 (3)	0.4349 (2)	0.0195 (5)
N4	0	0.5337 (4)	1/4	0.0158 (7)
O1	0.0787 (2)	0.6176 (3)	0.1913 (2)	0.0315 (5)

Table 12. *Selected geometric parameters (Å, °) for (I) at 3.38 GPa*

Co1—N1	1.974 (3)	Co1—N4	1.905 (3)
Co1—N2	1.932 (2)	N4—O1	1.240 (2)
Co1—N3	1.933 (2)		
O1—N4—O1^i	117.9 (3)	O1—N4—Co1	121.0 (2)

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

The pressure was created in a Merrill–Bassett diamond anvil cell (DAC) (Merrill & Bassett, 1974) of the four-screw type suggested by Mao & Bell (1980); the cell has been described by Ahsbahs *et al.* (1993). A methanol–ethanol–water (16:3:1) mixture was used as the pressure-transmitting medium (Piermarini *et al.*, 1973). The ruby fluorescence method (Barnet *et al.*, 1973; Piermarini *et al.*, 1975) could not be applied for pressure measurement since the title compound was sensitive to laser light and the single crystals would be destroyed during such a pressure-measurement procedure. A single crystal of $AlPO_4$ was used as an internal standard for pressure measurements. At first, two single crystals (one of $AlPO_4$ and the second of the title compound) were loaded in the DAC simultaneously and the changes in the lattice parameters of both crystals were measured as the pressure was increased. The pressure values were estimated from the previously published dependence of the lattice parameters of $AlPO_4$ on pressure (Sowa *et al.*, 1990). After that the crystal of $AlPO_4$ was removed from the DAC and in further experiments the values of pressure were estimated from the changes in the lattice parameters of the title compound. Preliminary rough estimates of pressure were made by observing the change in colour of nickel dimethylglyoxime (Zahner & Drickamer, 1960; Davis, 1968). A special gearing described by Turk (1989) was applied for a very smooth pressure change in the DAC. A special procedure was applied for lattice-parameter measurements (Hazen & Finger, 1982; Kutoglu, 1995, 1997), with each reflection measured in eight positions. This allowed precision in the measurement of lattice parameters as good as 0.0006 Å and 0.005° to be obtained, an order of magnitude better than the previous measurements on a powder sample of the title compound (Boldyreva *et al.*, 1994).

To increase the ratio of signal to background, a crystal as large as 200 µm in diameter and 110 µm thick was selected for the single-crystal study. The crystal was oriented in the DAC in such a way that the 111 reflection was parallel to the DAC axis, so that all the crystallographic directions were measured with comparable errors. The crystal was glued to one of the diamond culets with vaseline (the vaseline was initially cooked in a methanol–ethanol mixture in order to remove all components that would be soluble in the pressure-transmitting liquid). The crystal was centred at the diffractometer visually in two directions. Centring in the third direction (direction of the primary beam coinciding with the direction of the DAC axis) was performed according to the method of Ahsbahs; the centre of the gasket hole was centred by a 2θ scan of the primary beam at ω equal to plus and minus 30°, and in a second step described by Sowa (1994), the high-pressure cell was shifted parallel to its axis corresponding to the thickness of the gasket and the crystal.

The diameter of the diamond culets was 0.6 mm. The diameter of the hole in the gasket was 0.5 mm (an absolute limit for the given size of the diamond culets). The size of the hole allowed the collection of diffraction data in the angle ranges ω and $(2\theta-\omega)$ up to 40°. The hole was drilled into the gasket by a spark-erosion technique (Ahsbahs, 1984). Very hard steel (220.0250/R/1) was used as a gasket material. To minimize the shadowing by the gasket (Ahsbahs, 1987), the thickness of the gasket was optimized. The thickness of the gasket was 130 µm for data collection at ambient pressure. The high-pressure measurements started with the gasket thickness equal to 165 µm and ended with the thickness equal to 120 µm. The shadowing of the crystal, therefore, was slightly different at different pressures due to different thicknesses of the gasket.

To minimize the absorption of the X-rays by the DAC, the 'fixed-φ-method' (Finger & King, 1978; Kutoglu, 1997) was applied for data collection. The absorption of the X-rays by the empty DAC was measured experimentally and the results were used to correct the intensities of the reflections (Finger & King, 1978; Ahsbahs, 1987). Since the background was 2θ-dependent, ω scans were used for data collection (Ahsbahs, 1987). The Be background was entirely avoided by use of an edge-formed collimator in front of the counter, as described by Ahsbahs (1987). This allowed up to fourfold improvement of the signal-to-background ratio (Ahsbahs, 1987). To improve the signal-to-background ratio further, the size of the counter aperture in 2θ and χ was varied with 2θ range (being smaller in the lower 2θ range). The data were collected in the full reciprocal volume allowed by the shadow from the DAC [ω in the range -39 to 40°, χ in the range -86 to 96°, 2θ in the range 3 to 72°, $(2\theta-\omega)$ in the range -39 to 40° at φ equal to φ_0 and φ_0 + 180°; this gave about 30–40% of the total number of reflections that could be measured without the DAC]. The equivalent reflections were merged. In order to gain as good a signal-to-background ratio and as many observable reflections as possible, the data collection was very slow (3 s per point, 120 points per reflection, with 0.01° steps).

All the reflections were collected in a full-profile mode. The raw data were then processed with the help of the program *PROFILE* (Naumov & Boldyreva, 1997), allowing one to visualize the profiles of the reflections on the screen, to sort the reflections, to apply various corrections, to exclude erroneous data, to calculate the integral intensities of the reflections and to merge the equivalents.

Comparative studies at all the pressures were carried out for the same crystal in the same orientation in the DAC. All experiments were carried out in the dark or in red light to prevent possible photochemical reaction. The crystal remained unchanged after being stored in the DAC at high pressure for a year; it returned to the initial state after the DAC was unloaded back to ambient pressure. Hydrostatic compression of the same crystal in the second loading cycle resulted in the same changes in the lattice parameters and atomic coordinates as the first loading.

For all determinations, data collection: *MDIF*4 (Kutoglu, 1997); cell refinement: *CRYMIS* (Kutoglu, 1995); data reduction: *PROFILE* (Naumov & Boldyreva, 1997); program used to solve structure: *SHELXS*86 (Sheldrick, 1990); program used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ENVIRON* (Naumov & Boldyreva, 1998); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1022). Services for accessing these data are described at the back of the journal.

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$(NH_4)Zn_2(PO_4)(HPO_4)$

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Abstract

Ammonium dizinc phosphate hydrogenphosphate, a new ammonium zinc phosphate, consists of corrugated anionic layers of ZnO_4 and PO_4 tetrahedra, sharing vertices [d_{av}(Zn—O) = 1.948 (1), d_{av}(P—O) = 1.534 (1) Å and θ_{av}(Zn—O—P) = 136 (8)°]. Trigonally coordinated O atoms are present in these layers. Extra-layer NH_4^+ cations [d_{av}(N···O) = 2.993 (3) Å] complete the structure, which is isostructural with that of $KZn_2(PO_4)(HPO_4)$.