INORGANIC COMPOUNDS

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Pentaamminenitrocobalt(III) Dichloride and Dibromide at 290 K and 150 K

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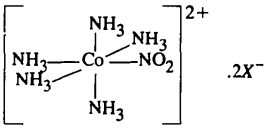
Abstract

The structures of $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(NO_2)(NH_3)_5]Br_2$ were refined at 290 K and at 150 K. For both compounds the same crystal was used for data collection at different temperatures. The data at 290 K are in good agreement with previously published results [Börtin (1968). *Acta Chem. Scand.* **22**, 2890–2898; Cotton & Edwards (1968). *Acta Cryst.* B**24**, 474–477; Kubota & Ohba (1992). *Acta Cryst.* B**48**, 627–632]. The structures at 150 K are anisotropically distorted compared with those at 290 K, but the space group and the general structural pattern remain the same.

Comment

A comparative study of the structures of the title compounds at 290 K and 150 K was part of a project studying the anisotropy of structural distortion of cobalt(III) nitroammine complexes induced by various means: cooling, increasing pressure, isomorphous substitution or homogeneous linkage isomerization. The present contribution reports the structural data for the title compounds at 290 K and 150 K, and the details of the



X = Cl, Br

data collection and data refinement procedures. A detailed comparison of the structures, the analysis of the anisotropy of structural distortion on cooling and its comparison with structural strain resulting from an increase in hydrostatic pressure or linkage isomerization is reported elsewhere (Boldyreva, Kivikoski & Howard, 1997).

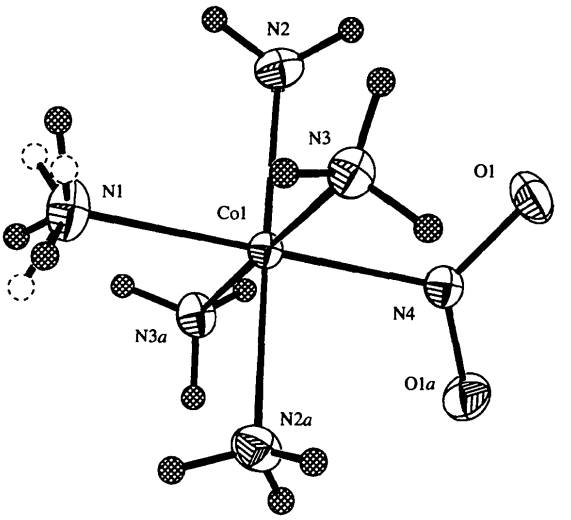


Fig. 1. A view of the $[Co(NO_2)(NH_3)_5]^{2+}$ cation in $[Co(NO_2)(NH_3)_5]Cl_2$ at 150 K showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level for non-H atoms; H atoms are drawn as small circles of arbitrary radii.

Experimental

The title compounds were synthesized from $[Co(CO_3)(NH_3)_5](NO_3)$ as described by Mäueler (1981). The crystals were grown at ambient temperature from aqueous solutions.

$[Co(NO_2)(NH_3)_5]Cl_2$ at 290 K

Crystal data

$[Co(NO_2)(NH_3)_5]Cl_2$
M_r = 261.01
Monoclinic
$C2/c$
a = 10.338 (2) Å
b = 8.687 (2) Å
c = 10.756 (2) Å
β = 95.05 (1)°
V = 962.2 (3) Å^3
Z = 4
D_x = 1.802 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 24.695–24.995°
μ = 2.31 mm^{-1}
T = 290 K
Distorted cuboctahedron
0.5 × 0.45 × 0.4 mm
Ruby

Data collection

Rigaku AFC-6*S* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.391, T_{max} = 0.538
2469 measured reflections
1163 independent reflections

1074 reflections with $I > 2\sigma(I)$
R_{int} = 0.02
θ_{max} = 27.97°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.048$
$S = 0.984$
1163 reflections
59 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0220P)^2 + 0.8015P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.005$
$\Delta\rho_{max} = 0.223$ e Å^{-3}
$\Delta\rho_{min} = -0.264$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0635 (17)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for $[Co(NO_2)(NH_3)_5]Cl_2$ at 290 K*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co1	0	0.28552 (3)	1/4	0.01892 (11)
Cl1	0.20751 (4)	0.01613 (5)	0.01368 (3)	0.03235 (12)
N3	0.01826 (14)	0.2880 (2)	0.43265 (11)	0.0302 (3)
N4	0	0.5071 (2)	1/4	0.0247 (3)
N2	0.18915 (13)	0.2874 (2)	0.24672 (14)	0.0340 (3)
N1	0	0.0566 (2)	1/4	0.0351 (4)
O1	−0.07315 (13)	0.57829 (15)	0.31376 (12)	0.0429 (3)

Table 2. *Selected geometric parameters (Å, °) for $[Co(NO_2)(NH_3)_5]Cl_2$ at 290 K*

Co1—N4	1.925 (2)	Co1—N1	1.989 (2)
Co1—N3	1.9571 (12)	N4—O1	1.2312 (15)
Co1—N2^i	1.9590 (14)		
O1—N4—O1^i	119.7 (2)	O1—N4—Co1	120.15 (9)

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

$[Co(NO_2)(NH_3)_5]Cl_2$ at 150 K

Crystal data

$[Co(NO_2)(NH_3)_5]Cl_2$
$M_r = 261.01$
Monoclinic
$C2/c$
$a = 10.215$ (3) Å
$b = 8.697$ (4) Å
$c = 10.748$ (3) Å
$\beta = 95.41$ (2)°
$V = 950.7$ (6) Å^3
$Z = 4$
$D_x = 1.824$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 24.775$–$24.99°$
$\mu = 2.34$ mm^{-1}
$T = 150$ K
Distorted cuboctahedron
0.5 × 0.45 × 0.4 mm
Ruby

Data collection

Rigaku AFC-6*S* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.387$, $T_{max} = 0.534$
2446 measured reflections
1152 independent reflections
1077 reflections with $I > 2\sigma(I)$
$R_{int} = 0.02$
$\theta_{max} = 28.00°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.038$
$S = 1.106$
1152 reflections
59 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0126P)^2 + 0.6359P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.251$ e Å^{-3}
$\Delta\rho_{min} = -0.286$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0579 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for $[Co(NO_2)(NH_3)_5]Cl_2$ at 150 K*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co1	0	0.28784 (2)	1/4	0.01144 (9)
Cl1	0.20713 (3)	0.01902 (3)	0.01504 (3)	0.01878 (9)
O1	−0.07355 (10)	0.57980 (11)	0.31472 (9)	0.0250 (2)
N3	0.02304 (11)	0.28945 (12)	0.43304 (9)	0.0178 (2)
N4	0	0.5085 (2)	1/4	0.0155 (3)
N2	−0.19115 (11)	0.29091 (13)	0.25606 (11)	0.0208 (2)
N1	0	0.0596 (2)	1/4	0.0236 (3)

Table 4. *Selected geometric parameters (Å, °) for $[Co(NO_2)(NH_3)_5]Cl_2$ at 150 K*

Co1—N4	1.919 (2)	Co1—N1	1.985 (2)
Co1—N3	1.9592 (11)	O1—N4	1.2376 (12)
Co1—N2	1.9600 (12)		
O1—N4—O1^i	119.8 (2)	O1—N4—Co1	120.08 (8)

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

$[Co(NO_2)(NH_3)_5]Br_2$ at 290 K

Crystal data

$[Co(NO_2)(NH_3)_5]Br_2$
$M_r = 349.93$
Monoclinic
$C2/c$
$a = 10.680$ (3) Å
$b = 8.838$ (4) Å
$c = 10.990$ (3) Å
$\beta = 94.70$ (2)°
$V = 1033.9$ (6) Å^3
$Z = 4$
$D_x = 2.248$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 21.145$–$23.925°$
$\mu = 9.36$ mm^{-1}
$T = 290$ K
Distorted cuboctahedron
0.5 × 0.45 × 0.4 mm
Ruby

Data collection

Rigaku AFC-6*S* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.045$, $T_{max} = 0.120$
2648 measured reflections
1249 independent reflections
981 reflections with $I > 2\sigma(I)$
$R_{int} = 0.02$
$\theta_{max} = 28.02°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 12$
$l = -15 \rightarrow 15$
3 standard reflections every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.052$
$S = 1.036$
1249 reflections
59 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 0.0603P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.375$ e Å^{-3}
$\Delta\rho_{min} = -0.454$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0095 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [Co(NO$_2$)(NH$_3$)$_5$]Br$_2$ at 290 K*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co1	0	0.28837 (5)	1/4	0.02081 (14)
Br1	0.20769 (3)	0.01538 (3)	0.01036 (3)	0.03177 (11)
N4	0	0.5067 (4)	1/4	0.0271 (7)
N3	0.0134 (2)	0.2930 (3)	0.4295 (2)	0.0299 (5)
N2	0.1841 (2)	0.2880 (3)	0.2501 (2)	0.0318 (5)
O1	−0.0715 (2)	0.5759 (3)	0.3125 (2)	0.0490 (6)
N1	0	0.0632 (4)	1/4	0.0323 (8)

Table 6. *Selected geometric parameters (Å, °) for [Co(NO$_2$)(NH$_3$)$_5$]Br$_2$ at 290 K*

Co1—N4	1.930 (3)	Co1—N1	1.990 (4)
Co1—N2	1.966 (2)	N4—O1^i	1.231 (3)
Co1—N3^i	1.967 (2)		
O1^i—N4—O1	120.4 (3)	O1—N4—Co1	119.8 (2)

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

[Co(NO$_2$)(NH$_3$)$_5$]Br$_2$ at 150 K

Crystal data

[Co(NO$_2$)(NH$_3$)$_5$]Br$_2$
$M_r = 349.93$
Monoclinic
$C2/c$
$a = 10.575$ (2) Å
$b = 8.815$ (5) Å
$c = 10.970$ (2) Å
$\beta = 94.97$ (2)°
$V = 1018.8$ (6) Å^3
$Z = 4$
$D_x = 2.282$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 23.99$–$24.9°$
$\mu = 9.50$ mm^{-1}
$T = 150$ K
Distorted cuboctahedron
0.5 × 0.45 × 0.4 mm
Ruby

Data collection

Rigaku AFC-6*S* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.044$, $T_{max} = 0.118$
2605 measured reflections
1230 independent reflections
1034 reflections with $I > 2\sigma(I)$
$R_{int} = 0.02$
$\theta_{max} = 28.01°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.049$
$S = 1.100$
1230 reflections
59 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0188P)^2 + 0.6873P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.522$ e Å^{-3}
$\Delta\rho_{min} = -0.393$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0075 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [Co(NO$_2$)(NH$_3$)$_5$]Br$_2$ at 150 K*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co1	0	0.29000 (5)	1/4	0.01327 (12)
Br1	0.20719 (2)	0.01728 (3)	0.01109 (2)	0.01923 (10)
N4	0	0.5084 (3)	1/4	0.0181 (6)
N3	0.0154 (2)	0.2948 (2)	0.4299 (2)	0.0194 (4)
O1	−0.0727 (2)	0.5786 (2)	0.3126 (2)	0.0298 (5)
N2	0.1852 (2)	0.2894 (3)	0.2484 (2)	0.0214 (5)
N1	0	0.0643 (4)	1/4	0.0218 (7)

Table 8. *Selected geometric parameters (Å, °) for [Co(NO$_2$)(NH$_3$)$_5$]Br$_2$ at 150 K*

Co1—N4	1.925 (3)	Co1—N1	1.990 (3)
Co1—N2	1.960 (2)	N4—O1	1.240 (2)
Co1—N3	1.966 (2)		
O1^i—N4—O1	120.1 (3)	O1^i—N4—Co1	120.0 (2)

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

Since lattice parameters of cobalt(III) nitroammine complexes are known to vary slightly from crystal to crystal of the same compound, comparative studies at the two temperatures were carried out using the same crystal without removing the crystal from the diffractometer. All experiments were carried out in the dark to prevent possible photochemical linkage isomerization. The temperature was maintained and controlled using a Cryosystem (Oxford Cryosystems) open-flow gas cryostat (Cosier & Glazer, 1986).

In order to improve the statistics, the reflections were deliberately collected in a reciprocal volume double the minimum required by crystal symmetry, and equivalent reflections were merged.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989); software used to prepare material for publication: *SHELXL*93.

The study was carried out at the Chemistry Department (Crystallography Group) of Durham University, where EB and JK were spending some research time

as guests of JAKH. The authors gratefully acknowledge financial support from the Royal Society (EB), the Academy of Finland and the British Council (JK).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1068). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

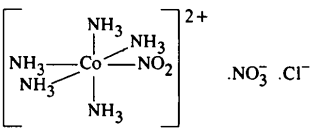
References

Boldyreva, E. V., Kivikoski, J. & Howard, J. A. K. (1997). *Acta Cryst.* B53. In the press.
Börtin, O. (1968). *Acta Chem. Scand.* **22**, 2890–2898.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Cotton, F. A. & Edwards, W. T. (1968). *Acta Cryst.* B**24**, 474–477.
Kubota, M. & Ohba, S. (1992). *Acta Cryst.* B**48**, 627–632.
Mäueler, G. (1981). *Prax. Naturwiss. Chem. Köln*, **3**, 81–86.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1989). *SHELXTL-Plus*. Release 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

group at the two temperatures was shown to be *Pnam*, not $Pna2_1$ as reported previously. Large anisotropic structural distortion was observed on cooling, but the space group and the general structural pattern remain the same.

Comment

A comparative study of the structure of the title compound at 290 K and 150 K was part of a project studying the anisotropy of structural distortion of cobalt(III) nitroammine complexes induced by various means: cooling, increasing pressure, isomorphous substitution or homogeneous linkage isomerization. This paper reports the structural data for the title compound at 290 K and 150 K, and the details of the data collection and data



refinement procedures. A detailed comparison of the structures, the analysis of the anisotropy of structural distortion on cooling and its comparison with structural strain resulting from an increase in hydrostatic pressure or linkage isomerization is reported elsewhere (Boldyreva, Kivikoski & Howard, 1997).

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Pentaamminenitrocobalt(III) Chloride Nitrate at 290 K and 150 K

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Abstract

The structure of the title compound, $[Co(NO_2)(NH_3)_5]$-$Cl(NO_3)$, was determined at 290 K and 150 K using the same crystal. The general structural pattern was shown to be similar to that previously reported by Podberezskaya, Virovets & Boldyreva [*Russ. J. Struct. Chem.* (1991), **32**, 89–95] for 290 K, but the space

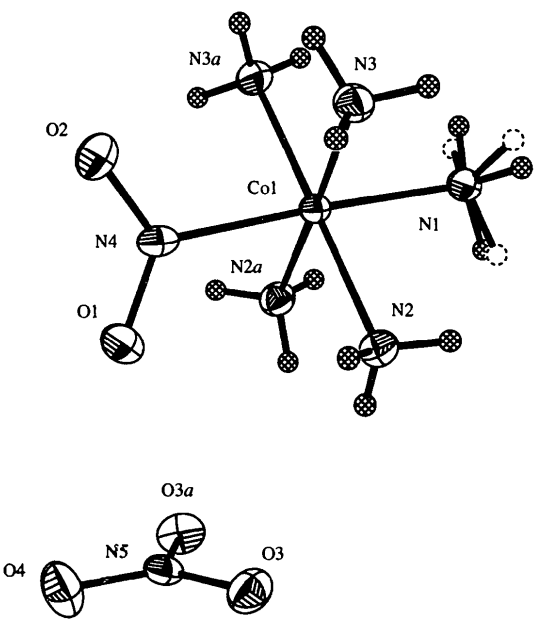

Fig. 1. A view of the $[Co(NO_2)(NH_3)_5]^{2+}$ cation and the $(NO_3)^-$ anion at 150 K showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level for the non-H atoms; H atoms are drawn as small circles of arbitrary radii.