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.

Acta Cryst. (1997). C**53**, 526-528

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

Elena V. Boldyreva,[a] Jussi Kivikoski[b] and J. A. K. Howard[b]

[a]*Institute of Solid State Chemistry, Russian Academy of Sciences, Kutateladze 18, Novosibirsk 128, 630128 Russia, and* [b]*Department of Chemistry, Durham University, Science Laboratories, South Road, DH1 3LE Durham, England. E-mail: elena@solid.nsk.su*

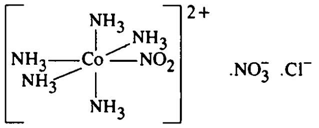
(*Received 18 October 1996; accepted 13 November 1996*)

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 group at the two temperatures was shown to be *Pnam*, not *Pna*2$_1$ 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).



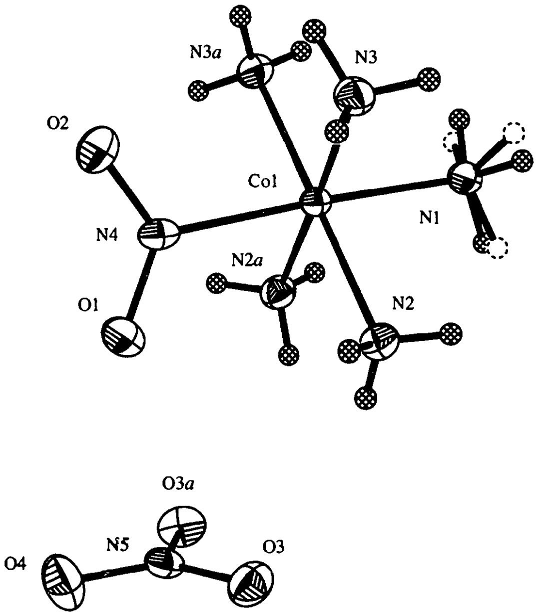


Fig. 1. A view of the [Co(NO$_2$)(NH$_3$)$_5$]$^{2+}$ cation and the (NO$_3$)$^-$ anion at 150 K showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level for the non-H atoms; H atoms are drawn as small circles of arbitrary radii.

Experimental

The crystals of the title compound were grown at ambient temperature from an aqueous solution containing equimolar quantities of $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(NO_2)(NH_3)_5](NO_3)_2$, as described in Gmelin (1964). $[Co(NO_2)(NH_3)_5]Cl_2$ and $[Co(NO_2)(NH_3)_5](NO_3)_2$ were synthesized from $[Co(CO_3)(NH_3)_5](NO_3)$ as described by Mäueler (1981).

$[Co(NO_2)(NH_3)_5]Cl(NO_3)$ at 290 K

Crystal data

$[Co(NO_2)(NH_3)_5]Cl(NO_3)$
$M_r = 287.57$
Orthorhombic
Pnam
$a = 14.814\ (3)$ Å
$b = 9.623\ (2)$ Å
$c = 7.309\ (2)$ Å
$V = 1041.9\ (6)$ Å^3
$Z = 4$
$D_x = 1.833$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 16.955–23.615°$
$\mu = 1.92$ mm^{-1}
$T = 290$ K
Elongated prism
$0.5 \times 0.3 \times 0.2$ mm
Ruby

Data collection

Rigaku AFC-6*S* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: 36 ψ scans of 6 reflections (North, Phillips & Mathews, 1968)
$T_{\min} = 0.553$, $T_{\max} = 0.681$
2762 measured reflections
1353 independent reflections
1050 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.02$
$\theta_{\max} = 28.01°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 13$
$l = -10 \rightarrow 10$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.067$
$S = 0.993$
1353 reflections
83 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 0.3911P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.058$
$\Delta\rho_{\max} = 0.339$ e Å^{-3}
$\Delta\rho_{\min} = -0.290$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0061 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) at 290 K*

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

	x	y	z	$U_{\rm eq}$
Co1	0.13299 (2)	0.20415 (4)	−1/4	0.02056 (12)
Cl1	0.15198 (5)	−0.01892 (8)	1/4	0.0308 (2)
N1	0.12397 (15)	0.4104 (2)	−1/4	0.0277 (5)
N2	0.22559 (10)	0.2183 (2)	−0.0576 (2)	0.0296 (4)
N4	0.14679 (15)	0.0016 (3)	−1/4	0.0261 (5)
N3	0.03941 (11)	0.1861 (2)	−0.0622 (3)	0.0309 (4)
O2	0.0802 (2)	−0.0705 (2)	−1/4	0.0447 (6)
O1	0.22340 (15)	−0.0456 (2)	−1/4	0.0445 (6)
N5	0.4111 (2)	−0.0010 (3)	−1/4	0.0300 (5)
O4	0.4122 (2)	−0.1289 (3)	−1/4	0.0569 (7)
O3	0.41064 (11)	0.0644 (2)	−0.1024 (2)	0.0463 (4)

Table 2. *Selected geometric parameters (Å, °) at 290 K*

Co1—N3	1.959 (2)	N4—O2	1.206 (3)
Co1—N4	1.960 (3)	N4—O1	1.222 (3)
Co1—N2	1.969 (2)	N5—O4	1.231 (3)
Co1—N1	1.989 (3)	N5—O3	1.249 (2)
O2—N4—O1	123.1 (3)	O4—N5—O3	120.24 (13)
O1—N4—Co1	117.8 (2)	O3—N5—O3^{i}	119.5 (3)

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

$[Co(NO_2)(NH_3)_5]Cl(NO_3)$ at 150 K

Crystal data

$[Co(NO_2)(NH_3)_5]Cl(NO_3)$
$M_r = 287.57$
Orthorhombic
Pnam
$a = 14.726\ (5)$ Å
$b = 9.646\ (7)$ Å
$c = 7.219\ (3)$ Å
$V = 1025.4\ (8)$ Å^3
$Z = 4$
$D_x = 1.863$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 20.42–23.945°$
$\mu = 1.95$ mm^{-1}
$T = 150$ K
Elongated prism
$0.5 \times 0.3 \times 0.2$ mm
Ruby

Data collection

Rigaku AFC-6*S* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: 36 ψ scans of 6 reflections (North, Phillips & Mathews, 1968)
$T_{\min} = 0.544$, $T_{\max} = 0.677$
2723 measured reflections
1335 independent reflections
1091 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.02$
$\theta_{\max} = 27.99°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 13$
$l = -10 \rightarrow 10$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.062$
$S = 1.042$
1333 reflections
83 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0260P)^2 + 0.5638P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.425$ e Å^{-3}
$\Delta\rho_{\min} = -0.350$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0060 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) at 150 K*

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

	x	y	z	$U_{\rm eq}$
Co1	0.13352 (2)	0.20341 (3)	−1/4	0.01327 (11)
Cl1	0.15142 (4)	−0.02121 (6)	1/4	0.0195 (2)
N1	0.12440 (14)	0.4092 (2)	−1/4	0.0184 (4)
N4	0.14829 (14)	0.0015 (2)	−1/4	0.0163 (4)
N2	0.22605 (10)	0.21811 (15)	−0.0541 (2)	0.0192 (3)
O1	0.22563 (13)	−0.0450 (2)	−1/4	0.0276 (5)
N3	0.03976 (10)	0.1849 (2)	−0.0592 (2)	0.0203 (3)
O2	0.08081 (13)	−0.0713 (2)	−1/4	0.0284 (5)
N5	0.41219 (14)	0.0025 (2)	−1/4	0.0193 (5)
O4	0.4150 (2)	−0.1255 (2)	−1/4	0.0365 (5)
O3	0.41137 (9)	0.06827 (15)	−0.0999 (2)	0.0276 (3)

Table 4. *Selected geometric parameters (Å, °) at 150 K*

Co1—N3	1.958 (2)	N4—O2	1.217 (3)
Co1—N4	1.960 (2)	N4—O1	1.224 (3)
Co1—N2	1.9691 (15)	N5—O4	1.235 (3)
Co1—N1	1.989 (2)	N5—O3	1.256 (2)
O2—N4—O1	123.3 (2)	O4—N5—O3	120.35 (11)
O2—N4—Co1	118.9 (2)	O3—N5—O3^{i}	119.3 (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 both 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 structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989); software used to prepare material for publication: *SHELXL93*.

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: SK1070). 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.* B**53**. In the press.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Gmelin (1964). *Handbuch der Anorganischen Chemie, Kobalt, Teil B - Ergänzungsband, Lieferung* 2, N. 58, p. 414. Weinheim: Verlag Chemie.

Mäueler, G. (1981). *Prax. Naturwiss. Chem. Köln*, **3**, 81–86.

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.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Podberezskaya, N. V., Virovets, A. V. & Boldyreva, E. V. (1991). *Russ. J. Struct. Chem.* **32**, 89–95.

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.

Acta Cryst. (1997). C**53**, 528–530

Electrochemically Lithiated Vanadium Oxide, $Li_2V_6O_{13}$

ÖRJAN BERGSTRÖM, TORBJÖRN GUSTAFSSON AND JOHN O. THOMAS

Institute of Chemistry, Uppsala University, Box 531, S-751 21 Uppsala, Sweden. E-mail: orjan.bergstrom@kemi.uu.se

(*Received 10 September 1996; accepted 9 December 1996*)

Abstract

Single crystals of V_6O_{13} were grown by chemical vapour transport and then electrochemically lithiated. The title compound, dilithium hexavanadium tridecaoxide, was the first phase formed during electrochemical lithiation at 2.65 V *versus* Li/Li$^+$. The $Li_2V_6O_{13}$ structure can be described as layers of VO_6 octahedra stacked perpendicular to the *c* direction. Lithiation causes a 7.6% expansion along the *c* axis. The lithium ions occupy positions with fivefold square-pyramidal oxygen coordination between the layers.

Comment

The title compound is the first lithiated phase obtained during discharge of a lithium battery containing the well known lithium intercalation host compound V_6O_{13}. An essential basis for understanding the relationship between structure and electrochemical properties in modern lithium-battery electrodes is a precise knowledge of the crystal structures of the various lithiated phases formed during cycling. Earlier work on lithiated V_6O_{13} has used X-ray and neutron diffraction techniques on powder samples: phases $Li_xV_6O_{13}$ for *x* between 0.5 and 1.0 (Lampe-Önnerud, Nordblad & Thomas, 1996; West, Zachau-Christiansen, Jacobsen & Atlung, 1985) have been reported as the first lithiated phase. Powder diffraction techniques seem inadequate in revealing the subtleties of the lithiation process. In this single-crystal X-ray study on an electrochemically lithiated sample we are able to determine the detailed lithiated structure.

The structure of V_6O_{13} can be described as layers of VO_6 octahedra parallel to the *ab* plane. There are two types of layers in the structure: one containing V1 centred around $z = 0$ and one containing V2 and V3