Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

$Na_3Co(NO_2)_6$ at 293 and 10 K

Brian N. Figgis* and Alexandre N. Sobolev

Chemistry Department, University of Western Australia, 35 Stirling Highway, Crawley WA 6009, Australia
Correspondence e-mail: bnf@crystal.uwa.edu.au

Received 6 April 2001
Accepted 14 May 2001

The crystal structure of trisodium hexanitrocobaltate(III) has been determined by X-ray diffraction at 293 and 10 K. It contains the slightly distorted octahedral $Co(NO_2)_6^{3-}$ anion. The accurate and extensive data sets collected should be suitable for charge–density analysis studies.

Comment

$Na_3Co(NO_2)_6$ is a classical transition metal coordination complex and the high site symmetry of the almost octahedral $Co(NO_2)_6^{3-}$ ion present in the trigonal space group makes it an attractive candidate for charge–density studies. Unit-cell parameters of the compound were reported by Okaya *et al.* (1957) and the structure was determined at ambient temperature by powder methods (Gromilov *et al.*, 1992). Here, we report, from X-ray diffraction, a much more accurate room-temperature structure and at 10 K, an accurate extensive data set that should be suitable for such charge–density analysis.

The crystal structure was solved on an X-ray data set collected at room temperature in the space group $R\bar{3}m$, and refined on F^2 to $R = 0.033$ using anisotropic displacement parameters. In that space group, the NO_2 group is situated on a crystal mirror plane. Close inspection of the displacement parameters of atoms which lie on the mirror plane (*e.g.* atom O1 has $U_{11} = U_{22} = 0.076$ and $U_{33} = 0.021$ Å^{-2}) led us to the conclusion that the crystal is a merohedral twin, in which the reciprocal lattices coincide exactly. If the twinning population ratio is 50:50, the $\bar{3}m$ Laue symmetry is retained for given Bragg peak positions. Accordingly, we refined the structure in both the 293 and the 10 K cases in space group $R\bar{3}$, using the twin option of *SHELXL*97 (Sheldrick, 1997), and we obtained distinctly better results, $R = 0.0197$, than without the twinning option. At 10 K, the R factors without and with the twinning option were 0.0784 and 0.0213, respectively.

The environments of the sodium cations and the anion are shown in Fig. 1. In the $Co(NO_2)_6^{3-}$ anion, the CoN_6 unit is almost octahedral. The angle between N atoms related by the threefold rotation axis and subtended at the Co atom is 86.9°, contrasting with the ideal octahedral value of 90°. The Na^+ ions are situated on two crystallographically non-equivalent threefold axes. Atom Na1 is surrounded by six O atoms which form a distorted octahedron with Na—O distances typical for this type of polyhedron. The coordination sphere of Na2 is more complicated, with 12 O atoms surrounding the sodium in a distorted dodecahedron. Table 1 lists important bond lengths and angles.

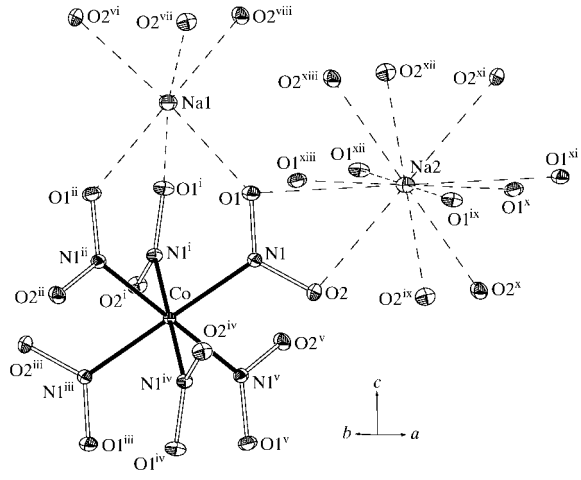

Figure 1
The environments of the atoms in $Na_3Co(NO_2)_6$ at 10 K. Displacement ellipsoids are shown at the 50% probability level.

Experimental

$Na_3Co(NO_2)_6$ (Univar, analytical reagent) was recrystallized by very slow evaporation of an aqueous solution.

Compound (I) at 293 K

Crystal data

$Na_3Co(NO_2)_6$
$M_r = 403.96$
Trigonal, $R\bar{3}$
$a = 7.806$ (1) Å
$c = 14.867$ (2) Å
$V = 784.5$ (2) Å^3
$Z = 3$
$D_x = 2.565$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 reflections
$\theta = 22.0$–$22.0°$
$\mu = 1.86$ mm^{-1}
$T = 293$ (2) K
Prism, dark red
0.38 × 0.26 × 0.25 mm

Data collection

Huber 512 goniometer diffractometer
ω–2θ scans
Absorption correction: *GAUSSIAN* in *Xtal*3.7 (Hall *et al.*, 2000)
$T_{min} = 0.620$, $T_{max} = 0.673$
3068 measured reflections
518 independent reflections
518 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 30.1°$
$h = -11 \rightarrow 11$
$k = -10 \rightarrow 10$
$l = -21 \rightarrow 21$
3 standard reflections every 100 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.055$
$S = 1.10$
518 reflections
36 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 0.9654P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0096 (13)

Compound (I) at 10 K

Crystal data

$Na_3Co(NO_2)_6$
M_r = 403.96
Trigonal, $R\overline{3}$
a = 7.7724 (4) Å
c = 14.763 (2) Å
V = 772.4 (1) Å^3
Z = 3
D_x = 2.606 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 29.8–40.1°
μ = 1.89 mm^{-1}
T = 10.5 (1) K
Prism, dark red
0.38 × 0.26 × 0.25 mm

Data collection

Huber 512 goniometer diffractometer
ω–2θ scans
Absorption correction: *GAUSSIAN* in *Xtal*3.7 (Hall *et al.*, 2000)
T_{min} = 0.591, T_{max} = 0.673
10695 measured reflections
1819 independent reflections
1819 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 50.1°
$h = -16 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = -31 \rightarrow 31$
3 standard reflections
every 100 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.061
S = 1.07
1819 reflections
36 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0390P)^2 + 0.4843P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −1.39 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0083 (11)

The room-temperature and very low temperature data sets were collected on a locally assembled Huber 512 goniometer equipped with a Displex 202D cryogenic refrigerator (Henriksen *et al.*, 1986; Larsen, 1995). A full sphere of data was collected. Lists of calculated and observed structure factors are given in the supplementary material. For the 10 K X-ray data collection, correction for the absorption by the beryllium shields was performed using the *PROFIT* (Streltsov & Zavodnik, 1989) program.

For both compounds, data collection: local diffractometer control software; cell refinement: local diffractometer control software; data reduction: *PROFIT* (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

BNF and ANS are grateful to the Australian Research Council for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1013). Services for accessing these data are described at the back of the journal.

Table 1
Bond lengths (Å) and angles (°) in the $Co(NO_2)_6^{3-}$ anion, and the geometry of the Na^+ cation and O-atom interactions.

Bond ($X1-X2$)	293 K	10.5 K	Symmetry transformations ($X2$)
Co—N	1.966 (2)	1.9679 (4)	0, i, ii, iii, iv, v
N—O1	1.226 (2)	1.2326 (7)	0
N—O2	1.238 (3)	1.2395 (6)	0
Na1—O1	2.322 (2)	2.3098 (6)	0, i, ii
Na1—O2	2.338 (2)	2.3141 (5)	vi, vii, vii
Na2—O1	2.873 (2)	2.8637 (5)	0, ix, x, xi, xii, xiii
Na2—O2	2.653 (2)	2.6291 (5)	0, ix, x, xi, xii, xiii
Na1—Na2	3.513 (1)	3.4811 (7)	vi
Angle ($X1-X2-X3$)			Symmetry transformations ($X1$,$X3$)
O1—N—O2	117.9 (2)	118.51 (5)	0,0
O1—N—Co	123.0 (1)	122.73 (4)	0,0
O2—N—Co	119.1 (1)	118.73 (4)	0,0
N—O1—Na1	133.7 (1)	132.61 (4)	0,0
N—O1—Na2	93.3 (1)	92.24 (3)	0,0
Na1—O1—Na2	130.95 (6)	130.97 (2)	0,0
N—O2—Na2	103.97 (9)	103.73 (3)	0,0
N—Co—N	180.0	180.0	0,iii; i,iv; ii,v
N—Co—N	86.91 (5)	86.94 (2)	0,iv; 0,v; i,iii; i,v; ii,iii; ii,iv
N—Co—N	93.09 (5)	93.06 (2)	0,ii; 0,xii; i,ii; iii,iv; iii,v; iv,v
O1—Na1—O1	76.26 (6)	76.95 (2)	0,ii; 0,xii; i,ii
O1—Na1—O2	104.00 (7)	104.74 (2)	0,viii; i,vi; ii,vii
O1—Na1—O2	174.26 (7)	173.21 (2)	0,vi; i,vii; ii,viii
O1—Na1—O2	98.18 (6)	96.93 (2)	0,vii; i,viii; ii,vi
O2—Na1—O2	81.67 (5)	81.69 (2)	viii,vi; viii,vii; vi,vii
O1—Na2—O1	119.585 (6)	119.664 (2)	0,ix; 0,x; ix,x; xi,xiii; xii,xi; xii,xiii
O1—Na2—O1	180.0	180.0	0,xi; x,xiii; xii,ix
O1—Na2—O1	60.415 (6)	60.336 (2)	0,xii; 0,xiii; ix,xi; ix,xiii; x,xi; xii,x
O2—Na2—O1	104.17 (8)	103.28 (2)	0,x; ix,0; x,ix; xi,xiii; xii,xi; xiii,xii
O2—Na2—O1	108.73 (7)	110.10 (2)	0,ix; ix,x; x,0; xi,xii; xii,xiii; xiii,xi
O2—Na2—O1	135.31 (4)	134.74 (1)	0,xi; ix,xii; x,xiii; xi,0; xii,ix; xiii,x
O2—Na2—O1	44.69 (4)	45.26 (1)	0,0; ix,ix; x,x; xi,xi; xii,xii; xiii,xiii
O2—Na2—O1	71.27 (7)	69.90 (2)	0,xii; ix,xiii; x,xi; xi,ix; xii,x; xiii,0
O2—Na2—O1	75.83 (8)	76.72 (2)	0,xiii; ix,xi; x,xii; xi,x; xii,0; xiii,ix
O2—Na2—O2	109.62 (4)	109.71 (2)	0,xii; 0,xiii; ix,xi; ix,xiii; x,xi; xii,x
O2—Na2—O2	180.0	180.0	0,xi; x,xiii; xii,ix
O2—Na2—O2	70.38 (4)	70.29 (2)	0,ix; 0,x; i,xi; ix,x; xi,xiii; xii,xiii

Symmetry codes: (i) $-y, x-y, z$; (ii) $-x+y, -x, z$; (iii) $-x, -y, -z$; (iv) $y, -x+y, -z$; (v) $x-y, x, -z$; (vi) $-\frac{1}{3}+x, \frac{1}{3}+y, \frac{1}{3}+z$; (vii) $-\frac{1}{3}-y, -\frac{2}{3}+x-y, \frac{1}{3}+z$; (viii) $\frac{2}{3}-x+y, \frac{1}{3}-x, \frac{1}{3}+z$; (ix) $-y, -1+x-y, z$; (x) $1-x+y, -x, z$; (xi) $\frac{2}{3}-x, -\frac{2}{3}-y, \frac{1}{3}-z$; (xii) $\frac{2}{3}+y, \frac{1}{3}-x+y, \frac{1}{3}-z$; (xiii) $-\frac{1}{3}+x-y, -\frac{2}{3}+x, \frac{1}{3}-z$.

References

Bruker (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Gromilov, S. A., Alekseev, V. I., Badina, I. A. & Khrapenko, S. P. (1992). *Russ. J. Inorg. Chem.* **37**, 306–309.
Hall, S. R., du Boulay, D. J. & Olthof-Hazekamp, R. (2000). Editors. *Xtal*3.7 *System of Crystallographic Programs*. University of Western Australia, Perth: Lamb.
Henriksen, K., Larsen, F. K. & Rasmussen, S. E. (1986). *J. Appl. Cryst.* **19**, 390–394.
Larsen, F. K. (1995). *Acta Cryst.* B**51**, 468–482.
Okaya, Y., Pepinsky, R., Tekeuchi, Y., Kuroya, H., Shimada, A., Gallitelli, P., Stemple, N. & Beevers, A. (1957). *Acta Cryst.* **10**, 798–801.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Streltsov, V. A. & Zavodnik, V. E. (1989). *Sov. Phys. Crystallogr.* **34**, 824–828.