C48	−0.2383 (8)	0.5001 (9)	−0.1576 (5)	0.071 (4)
C49	−0.1775 (8)	0.4354 (8)	−0.1476 (5)	0.067 (4)
C50	−0.1302 (8)	0.4139 (8)	−0.0935 (5)	0.063 (4)
N51	−0.3007 (6)	0.5044 (6)	0.0392 (4)	0.058 (3)
C52	−0.2599 (8)	0.4992 (8)	0.0945 (5)	0.069 (4)
C53	−0.2880 (9)	0.4352 (9)	0.1245 (5)	0.079 (4)
C54	−0.355 (1)	0.3821 (9)	0.1024 (6)	0.090 (5)
C55	−0.3985 (9)	0.3867 (9)	0.0478 (6)	0.084 (5)
C56	−0.3687 (8)	0.4482 (9)	0.0165 (5)	0.063 (4)
C57	−0.4118 (8)	0.4534 (9)	−0.0413 (6)	0.072 (4)
C58	−0.4529 (8)	0.4548 (8)	−0.0879 (6)	0.067 (4)
C59	−0.5042 (8)	0.4538 (8)	−0.1432 (5)	0.064 (4)
C60	−0.5854 (9)	0.4154 (8)	−0.1636 (5)	0.073 (4)
C61	−0.6213 (8)	0.4269 (8)	−0.2206 (5)	0.069 (4)
C62	−0.5674 (8)	0.4743 (8)	−0.2435 (5)	0.061 (4)
C63	−0.5792 (8)	0.4947 (8)	−0.2976 (6)	0.063 (4)
C64	−0.5831 (8)	0.5125 (8)	−0.3424 (5)	0.062 (4)
C65	−0.5803 (8)	0.5359 (8)	−0.3966 (5)	0.064 (4)
N66	−0.5160 (6)	0.5940 (6)	−0.4007 (4)	0.061 (3)
C67	−0.5101 (8)	0.6182 (8)	−0.4492 (5)	0.063 (4)
C68	−0.5700 (9)	0.5827 (9)	−0.4979 (5)	0.077 (4)
C69	−0.6325 (9)	0.5253 (9)	−0.4939 (6)	0.089 (5)
C70	−0.6416 (9)	0.4996 (9)	−0.4440 (6)	0.085 (5)
N71	−0.1846 (8)	0.6448 (8)	0.3676 (5)	0.086 (4)
O72	−0.1080 (5)	0.6055 (5)	0.3940 (3)	0.070 (3)
O73	−0.1976 (5)	0.6455 (5)	0.3173 (3)	0.074 (3)
O74	−0.2314 (7)	0.6748 (7)	0.3928 (4)	0.114 (4)
N76	−0.1810 (8)	0.4253 (8)	0.2880 (5)	0.086 (4)
O77	−0.1423 (5)	0.4837 (6)	0.2661 (3)	0.072 (3)
O78	−0.1630 (6)	0.4325 (6)	0.3391 (4)	0.095 (3)
O79	−0.2373 (6)	0.3756 (6)	0.2620 (4)	0.089 (3)
N81	−0.3764 (9)	0.7180 (9)	−0.0267 (5)	0.094 (4)
O82	−0.3529 (6)	0.6628 (6)	−0.0562 (4)	0.088 (3)
O83	−0.3306 (6)	0.7123 (7)	0.0216 (4)	0.113 (4)
O84	−0.4342 (7)	0.7708 (7)	−0.0453 (4)	0.109 (4)
N86	−0.1001 (7)	0.6874 (7)	0.0373 (5)	0.070 (3)
O87	−0.1400 (5)	0.6307 (5)	0.0593 (3)	0.065 (2)
O88	−0.1390 (6)	0.6997 (5)	−0.0128 (4)	0.082 (3)
O89	−0.0343 (6)	0.7266 (6)	0.0627 (3)	0.084 (3)
N91	0.7159 (8)	0.7441 (9)	0.6706 (5)	0.092 (4)
O92	0.6414 (6)	0.7231 (5)	0.6316 (3)	0.076 (3)
O93	0.7240 (6)	0.7056 (6)	0.7126 (4)	0.105 (4)
O94	0.7607 (7)	0.8004 (7)	0.6568 (4)	0.115 (4)
N96	0.6764 (8)	0.4859 (9)	0.6834 (5)	0.097 (4)
O97	0.6367 (5)	0.5321 (6)	0.7129 (3)	0.081 (3)
O98	0.6692 (6)	0.5161 (6)	0.6372 (4)	0.097 (3)
O99	0.7171 (7)	0.4209 (8)	0.7006 (4)	0.128 (4)

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

Co1—N26	2.05 (1)	Co2—O83	2.37 (1)
Co1—N31	2.072 (8)	Co2—O87	2.020 (7)
Co1—O72	2.024 (9)	Co2—O88	2.373 (9)
Co1—O73	2.396 (8)	Co3—N11	2.09 (1)
Co1—O77	2.039 (8)	Co3—$N66^{i}$	2.055 (9)
Co1—O78	2.37 (1)	Co3—O92	2.002 (9)
Co2—N46	2.06 (1)	Co3—O93	2.425 (9)
Co2—N51	2.07 (1)	Co3—O97	1.991 (8)
Co2—O82	2.059 (8)	Co3—O98	2.53 (1)
N26—Co1—N31	106.3 (4)	N51—Co2—O88	154.3 (3)
N26—Co1—O72	115.4 (4)	O82—Co2—O83	55.1 (4)
N26—Co1—O73	90.1 (3)	O82—Co2—O87	135.4 (3)
N26—Co1—O77	95.9 (4)	O82—Co2—O88	93.2 (3)
N26—Co1—O78	153.4 (3)	O83—Co2—O87	89.2 (3)
N31—Co1—O72	95.7 (4)	O83—Co2—O88	89.7 (3)
N31—Co1—O73	152.7 (4)	O87—Co2—O88	57.3 (3)
N31—Co1—O77	113.5 (3)	N11—Co3—$N66^{i}$	113.9 (4)
N31—Co1—O78	86.9 (3)	N11—Co3—O92	106.3 (4)
O72—Co1—O73	57.2 (3)	N11—Co3—O93	85.7 (4)
O72—Co1—O77	129.2 (3)	N11—Co3—O97	101.8 (4)
O72—Co1—O78	85.3 (4)	N11—Co3—O98	157.0 (3)
O73—Co1—O77	85.6 (3)	$N66^{i}$—Co3—O92	97.6 (4)
O73—Co1—O78	87.7 (3)	$N66^{i}$—Co3—O93	151.9 (4)
O77—Co1—O78	57.5 (4)	$N66^{i}$—Co3—O97	110.0 (4)
N46—Co2—N51	104.6 (4)	$N66^{i}$—Co3—O98	80.9 (4)
N46—Co2—O82	95.9 (4)	O92—Co3—O93	56.2 (3)
N46—Co2—O83	150.3 (3)	O92—Co3—O97	127.8 (4)
N46—Co2—O87	112.4 (4)	O92—Co3—O98	88.0 (4)
N46—Co2—O88	85.8 (4)	O93—Co3—O97	83.7 (3)
N51—Co2—O82	108.7 (4)	O93—Co3—O98	87.7 (3)
N51—Co2—O83	92.0 (4)	O97—Co3—O98	55.6 (4)
N51—Co2—O87	97.0 (4)		

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

Only Co and S atoms were refined anisotropically; all the other non-H atoms were refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal ADDREF SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *Xtal SIMPEL*. Program(s) used to refine structure: *Xtal CRYLSQ*. Molecular graphics: *PLUTON* (Spek, 1992). Software used to prepare material for publication: *Xtal BONDLA CIFIO*.

The authors are indebted to Mr S. Gorter for his assistance in the collection and processing of the diffraction data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1163). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 61–63

Neodymium Hexacyanocobaltate(III) Tetrahydrate

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(Received 20 April 1995; accepted 24 July 1995)

Abstract

Neodymium hexacyanocobaltate(III) tetrahydrate, $NdCo(CN)_6.4H_2O$, crystallizes in the orthorhombic space group *Cmcm*. The structure consists of octahedrally coordinated Co atoms and eight-coordinate Nd atoms linked by non-linear cyanide bridges, which produce an undulation throughout the polymeric array. Two water molecules are coordinated to the Nd atoms and

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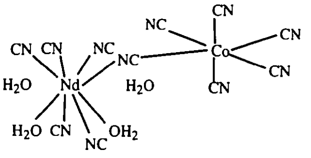
two are zeolitic in nature, occupying cavities in the polymeric array within hydrogen-bonding distance of the coordinated water molecules.

Comment

Initial studies of the lanthanide cobalt hexacyanides by James & Willand (1916) reported that the microscopic crystals belonged to the hexagonal system. Bonet & Pâris (1975) characterized the $LnCo(CN)_6$ compounds and assigned these phases to the hexagonal $LaFe(CN)_6.5H_2O$ structure ($P6_3/m$) even though they were tetrahydrates. An investigation by Hulliger, Landolt & Vetsch (1976) reported that the larger lanthanide cobalt hexacyanides (Ln = La, Ce and Pr) form hexagonal structures similar to that of the $LaFe(CN)_6.5H_2O$ complex, which was later confirmed for La and Pr by Mullica, Milligan & Kouba (1979), and Mullica & Sappenfield (1991). However, the smaller rare earth elements (Ln = Sm–Lu) crystallize in an orthorhombic modification as seen in $SmCo(CN)_6.3H_2O$ (Mullica & Sappenfield, 1989). Both phases may be present in the cobalt hexacyanides of Ce, Pr and Nd. A gradual transformation from the hexagonal pentahydrate to the orthorhombic tetrahydrate by the loss of one water molecule occurs upon standing. The structural investigation of the title compound, (I), was initiated to further our interest in the structure and morphology of the cobalt hexacyanides.



(I)

The Co atom is octahedrally coordinated by six cyano C atoms. The Nd atom is eightfold coordinated by six cyano N and two water O atoms arranged as a square antiprism. Four symmetry-related N1 atoms form one square face [deviation from the mean plane is 0.00 (1) Å] of the square antiprism while two symmetry related N2 and O1 atoms form the opposing square face, which is planar to within 0.01 (1) Å. The dihedral angle between the planes is 0.00 (1)°. The octahedral cobalt and the eight-coordinate Nd atoms are linked by non-linear cyanide bridges [Nd—N—C = 166.4 (2) and 148.6 (2)° and Co—C—N = 178.3 (2) and 179.6 (3)°]. The non-linear bridging produces an undulation throughout the polymeric array. The zeolitic water molecules occupy cavities in the polymeric structure within hydrogen-bonding distance [O···O = 2.805 (3) Å] of the coordinated water molecules (O1). The IR spectrum displays a very strong and broad ν-OH band at 3376 cm^{-1}. The zeolitic property of O2 and its location within the structure can be attributed to the hydrogen bonding.

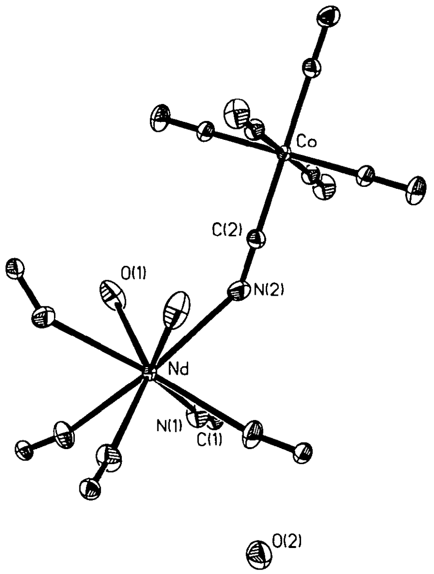


Fig. 1. A perspective view of $NdCo(CN)_6.4H_2O$ displaying the square-antiprism arrangement about the Nd atom and the octahedral geometry around the Co atom. Displacement ellipsoids are shown at 50% probability.

Experimental

The title compound was synthesized by the mixing of aqueous solutions of 0.2 *M* $NdCl_3$ (pH 4) and 0.1 *M* $K_3Co(CN)_6$. Starting materials were of reagent grade quality and were used without further purification. The mixture was filtered and stored in the dark. Clear light-purple single crystals formed after 2–5 days. The crystal density D_m was measured by flotation in bromoform and bromobenzene.

Crystal data

$NdCo(CN)_6.4H_2O$
$M_r = 431.34$
Orthorhombic
Cmcm
$a = 7.4251\ (8)$ Å
$b = 12.790\ (3)$ Å
$c = 13.723\ (2)$ Å
$V = 1303.2\ (4)$ Å^3
$Z = 4$
$D_x = 2.20$ Mg m^{-3}
$D_m = 2.15\ (2)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 5.94$–$33.16°$
$\mu = 5.244$ mm^{-1}
$T = 292$ K
Clear prism
0.34 × 0.19 × 0.07 mm
Light purple

Data collection

Enraf–Nonius CAD-4*F* diffractometer
ω–2θ scans
Absorption correction: combination of ψ scans and spherical (Enraf–Nonius, 1985)
$T_{min} = 0.308$, $T_{max} = 0.495$
2527 measured reflections
1569 independent reflections

1502 observed reflections [$F > 4\sigma(F)$]
$R_{int} = 0.037$
$\theta_{max} = 35.00°$
$h = -3 \rightarrow 11$
$k = -6 \rightarrow 20$
$l = -6 \rightarrow 22$
3 standard reflections
frequency: 120.0 min
intensity decay: 1.5%

Refinement

Refinement on *F*
$R = 0.022$
$wR = 0.038$
$S = 1.301$
1502 reflections
52 parameters
No H atoms located
$w = 1/[\sigma^2(F) + 0.0003F^2]$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 2.00$ e Å^{-3}
$\Delta\rho_{\min} = -1.24$ e Å^{-3}

Extinction correction: *SHELXTL-Plus* (Sheldrick, 1989)
Extinction coefficient: 0.0030 (1)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

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

	x	y	z	$U_{\rm eq}$
Nd	0	0.32466 (1)	1/4	0.0106 (1)
Co	0	0	0	0.0103 (2)
C1	0.3195 (2)	0.4548 (1)	0.0870 (1)	0.0169 (6)
C2	0	0.1337 (2)	0.0579 (2)	0.017 (1)
N1	0.2064 (3)	0.4266 (2)	0.1382 (1)	0.0267 (8)
N2	0	0.2148 (2)	0.0938 (2)	0.027 (1)
O1	0.2649 (4)	0.2132 (3)	1/4	0.036 (2)
O2	0	0.6544 (2)	0.0997 (2)	0.035 (2)

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

Co—C1$^{\rm i}$	1.886 (2)	Nd—O1	2.429 (3)
Co—C2	1.885 (3)	C1—N1	1.153 (3)
Nd—N1	2.531 (2)	C2—N2	1.149 (4)
Nd—N2	2.563 (3)		
N1—Nd—N1$^{\rm ii}$	74.7 (1)	C1$^{\rm i}$—Co—C1$^{\rm vii}$	90.6 (1)
N1—Nd—N1$^{\rm iii}$	117.9 (1)	C1$^{\rm i}$—Co—C1$^{\rm viii}$	180.0 (1)
N1—Nd—N1$^{\rm iv}$	74.5 (1)	C1$^{\rm i}$—Co—C2$^{\rm ix}$	89.4 (1)
N1—Nd—N2	77.0 (1)	C1$^{\rm i}$—Co—C2	90.6 (1)
N1—Nd—N2$^{\rm v}$	142.2 (1)	C2—Co—C2$^{\rm ix}$	180.0 (1)
N1—Nd—O1	79.2 (1)	Co$^{\rm x}$—C1—N1	178.3 (2)
N1—Nd—O1$^{\rm iii}$	142.4 (1)	Co—C2—N2	179.6 (3)
N2—Nd—N2$^{\rm v}$	113.5 (1)	Nd—N1—C1	166.4 (2)
N2—Nd—O1	71.2 (1)	Nd—N2—C2	148.6 (2)
O1—Nd—O1$^{\rm iii}$	108.2 (1)	O2$^{\rm xi}$—O1—O2$^{\rm xii}$	94.7 (1)
C1$^{\rm i}$—Co—C1$^{\rm vi}$	89.4 (1)	O1$^{\rm xiii}$—O2—O1$^{\rm xiv}$	77.0 (1)

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

A conoscopic rotational examination using two crossed polarizers on a Zeiss Photomicroscope II confirmed the optical quality and biaxial nature of the crystal. A Mattson FTIR spectrometer using the KBr pressed pellet method was employed to obtain pertinent spectral data. The water molecules of hydration [3.9 (1) water molecules per formula unit] were verified by a thermal gravimetric analysis (Perkin-Elmer TGS-1). Excess maximum and minimum density in the difference Fourier is in the area of the heavy lanthanide atom. The structure was checked for additional symmetry by the *MISSYM* program (Le Page, 1987, 1988; Gabe, Le Page, Charland, Lee & White, 1989).

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1988). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Enraf-Nonius, 1985). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1989). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus XP*. Software used to prepare material for publication: *CIFGEN* (local program).

The authors acknowledge the financial support of The Robert A. Welch Foundation (grant AA-0668) and Baylor University.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 63–66

Anhydrous *trans*-(Aniline)chlorobis(dimethylglyoximato)cobalt(III)

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(*Received 14 November 1994; accepted 17 July 1995*)

Abstract

The crystal structure of anhydrous *trans*-(aniline)-chlorobis[dimethylglyoximato(1−)]cobalt(III), [CoCl($C_4H_7N_2O_2$)$_2$(C_6H_7N)], has been determined. The Co ion shows distorted octahedral coordination with the N atoms of the dimethylglyoximato ligands in the equatorial sites and the N atom of aniline and the Cl atom in the apical sites. From the values of the Co—N distances and the N—Co—N angles it is deduced that both equa-

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Acta Crystallographica Section C
ISSN 0108-2701 ©1996