of the refined site occupation factor was used as the site occupation factor of the new atomic positions.

An unusual electron density peak of 1.7 e Å^{-3} was seen near (1.05 Å) Ru(1) which may be due, in part, to errors in the Ru(1) absorption correction.

The X-ray diffraction and crystallographic computing system was purchased from funds provided by the US National Science Foundation grant CHE-8513273.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71187 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1057]

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catena-Poly[{aqua(cyanoacetato-κ*O*)(*N*,*N*-dimethylformamide-κ*O*)neodymium}-di-μ-cyanoacetato-κ*O*,κ*O'*:κ*O'*] Monohydrate

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Abstract

The structure consists of polymeric neutral chains composed of aquatris(cyanoacetato)(dimethylformamide)-neodymium units and water of hydration. The neodymium environment consists of seven carboxylate O atoms, one dimethyl formamide O atom and one water O atom. There are no Nd—N bonds.

Comment

It was suggested recently (Vaidya, Deshpande, Jain & Jain, 1988) that the cyanoacetate anion can act as both an O- and an N-donor ligand towards lanthanide cations. Therefore, we decided to study the crystal structure of a lanthanide cyanoacetate in order to investigate the coordination properties of the anion. We could not obtain crystals of neodymium tris(cyanoacetate) from a pure water solution. Crystals of the title compound were obtained by adding a few drops of dimethylformamide (DMF) to an aqueous solution of neodymium cyanoacetate and then allowing the mixture to evaporate for a few days at ambient temperature.

The neodymium coordination environment consists of nine O atoms, of which seven are carboxylate O atoms, one a DMF O atom, and one a water O atom. All distances are within the previously observed range. The coordination figure is rather irregular. The best-fitted tricapped trigonal prism had Δ [defined as $\Sigma d_i^2/9$ where d_i is the distance between *i*th atom and the relevant vertex of the ideal least-squares-fitted polyhedron (Drew, 1977)] equal to 0.240 Å^2. For the best capped-square antiprism, Δ was 0.233 Å^2. The cyanoacetate ions are either bridging bidentate *O*,*O'*:*O* or unidentate *O* ligands. The cyano groups are either involved in hydrogen bonds (N3), or in van der

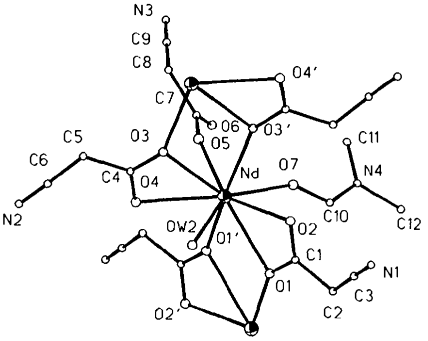

Fig. 1. Fragment of the polymeric chain.

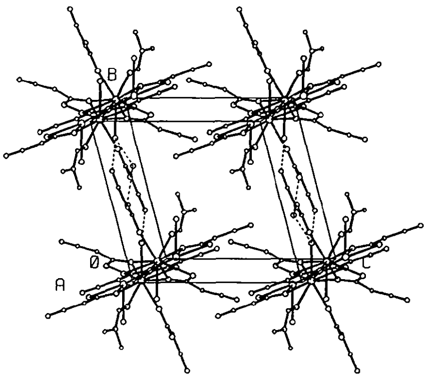

Fig. 2. View of the unit cell. The dashed lines represent the hydrogen bonds.

Waals interactions only (N1 and N2). Two peaks (of 2.6 and 2.3 e Å^{-3} at 2.37 and 2.13 Å from C5 and C2, respectively) on the final $\Delta\rho$ map may indicate some kind of disorder, perhaps of the relevant cyano groups; this was not, however, included in the model.

The crystal is composed of one-dimensional polymeric chains running along the [100] direction. These, together with water of crystallization, are tied through hydrogen bonds to form (001) planes which in turn are held together *via* van der Waals interactions. An *ORTEP* (Johnson, 1976) view of the neodymium coordination is shown in Fig. 1, and the unit-cell content is presented in Fig. 2.

Experimental

Crystal data

$[Nd(C_3H_2NO_2)_3(C_3H_7NO)(H_2O)].H_2O$
$M_r = 505.53$
Triclinic
$P\bar{1}$
$a = 8.377$ (6) Å
$b = 10.848$ (9) Å
$c = 11.043$ (9) Å
$\alpha = 104.68$ (7)°
$\beta = 102.31$ (6)°
$\gamma = 97.01$ (6)°
$V = 932$ (2) Å^3
$Z = 2$

$D_x = 1.802$ (3) Mg m^{-3}
$D_m = 1.79$ Mg m^{-3}
Density measured by flotation in $CHCl_3/CHBr_3$
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 13 reflections
$\theta = 5.5$–11°
$\mu = 2.86$ mm^{-1}
$T = 289$ (1) K
Plate
0.4 × 0.15 × 0.03 mm
Pink-violet

Data collection

Syntex $P2_1$ computer-controlled four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2134 measured reflections
2015 independent reflections
1956 observed reflections [$F > 6\sigma(F)$]

$R_{\rm int} = 0.0194$
$\theta_{\rm max} = 22.5°$
$h = 0 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 11$
2 standard reflections monitored every 50 reflections
intensity variation: 5.5%

Refinement

Refinement on F
Final $R = 0.0529$
$wR = 0.0501$
1838 reflections
237 parameters
Only H-atom U's refined
Calculated weights $w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\rm max} = 0.018$
$\Delta\rho_{\rm max} = 2.61$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.35$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Syntex (1973) *P*2$_1$ software. Data reduction: locally modified *XTL/XTLE* programs (Syntex, 1976). Program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *SHELX*76. Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: locally modified *XTL/XTLE* programs.

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

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

	x	y	z	$U_{\rm eq}$
Nd	0.25242 (10)	0.02399 (8)	0.00185 (8)	0.0189 (3)
O1	0.5239 (11)	−0.0506 (9)	0.1028 (9)	0.029 (4)
O2	0.3270 (12)	−0.0547 (9)	0.2078 (10)	0.035 (4)
O3	−0.0503 (11)	−0.0767 (9)	−0.1259 (9)	0.026 (4)
O4	0.1285 (13)	−0.0732 (10)	−0.2482 (9)	0.038 (4)
O5	0.1525 (14)	0.1888 (10)	−0.0805 (10)	0.046 (5)
O6	0.2727 (15)	0.3805 (12)	−0.0838 (13)	0.060 (6)
C1	0.4703 (18)	−0.0704 (13)	0.1974 (14)	0.027 (6)
C2	0.5871 (20)	−0.1084 (18)	0.3007 (15)	0.046 (8)
C3	0.5051 (21)	−0.1526 (17)	0.3881 (16)	0.045 (8)
C4	−0.0144 (18)	−0.0952 (14)	−0.2354 (14)	0.027 (6)
C5	−0.1584 (24)	−0.1531 (22)	−0.3534 (16)	0.078 (10)
C6	−0.1061 (23)	−0.1904 (20)	−0.4720 (17)	0.061 (9)
C7	0.1502 (21)	0.2969 (17)	−0.1005 (14)	0.032 (7)
C8	−0.0256 (19)	0.3187 (14)	−0.1586 (15)	0.033 (6)
C9	−0.0250 (20)	0.4440 (20)	−0.1797 (16)	0.046 (8)
N1	0.4406 (23)	−0.1881 (17)	0.4587 (16)	0.074 (9)
N2	−0.0750 (24)	−0.2212 (21)	−0.5676 (19)	0.097 (10)
N3	−0.0270 (21)	0.5452 (16)	−0.1928 (16)	0.068 (8)
N4	0.6027 (19)	0.3805 (13)	0.3188 (13)	0.050 (6)
O7	0.4195 (14)	0.2143 (10)	0.1687 (10)	0.044 (5)
C10	0.5518 (23)	0.2570 (19)	0.2550 (17)	0.047 (8)
C11	0.5208 (28)	0.4823 (20)	0.2902 (21)	0.076 (11)
C12	0.7681 (27)	0.4192 (24)	0.4216 (21)	0.094 (11)
O*W*1	0.3987 (15)	0.6402 (10)	0.0406 (12)	0.059 (6)
O*W*2	0.2144 (13)	−0.2155 (9)	−0.0666 (9)	0.039 (4)

Table 2. *Geometric parameters* (Å, °)

Nd—O1	2.626 (10)	Nd—O4	2.617 (9)
Nd—O1$^{\rm i}$	2.427 (10)	Nd—O5	2.364 (11)
Nd—O2	2.608 (10)	Nd—O7	2.426 (11)
Nd—O3	2.575 (10)	Nd—O*W*2	2.474 (10)
Nd—O3$^{\rm ii}$	2.429 (10)		
O1—Nd—O1$^{\rm i}$	65.5 (4)	O5—Nd—O3$^{\rm ii}$	79.5 (4)
O2—Nd—O1$^{\rm i}$	115.4 (4)	O5—Nd—O3	75.4 (4)
O2—Nd—O1	50.0 (4)	O5—Nd—O4	71.8 (4)
O3$^{\rm ii}$—Nd—O1$^{\rm i}$	160.6 (4)	O7—Nd—O1$^{\rm i}$	83.7 (4)
O3$^{\rm ii}$—Nd—O1	120.7 (4)	O7—Nd—O1	74.5 (4)
O3$^{\rm ii}$—Nd—O2	72.0 (4)	O7—Nd—O2	75.6 (4)
O3—Nd—O1$^{\rm i}$	122.7 (4)	O7—Nd—O3$^{\rm ii}$	80.9 (4)
O3—Nd—O1	138.9 (4)	O7—Nd—O3	141.9 (4)
O3—Nd—O2	110.0 (4)	O7—Nd—O4	143.6 (4)
O3—Nd—O3$^{\rm ii}$	66.4 (4)	O7—Nd—O5	80.1 (4)
O4—Nd—O1$^{\rm i}$	72.0 (4)	O*W*2—Nd—O1$^{\rm i}$	93.3 (4)
O4—Nd—O1	116.6 (4)	O*W*2—Nd—O1	69.8 (4)
O4—Nd—O2	139.3 (4)	O*W*2—Nd—O2	71.4 (4)
O4—Nd—O3$^{\rm ii}$	115.2 (4)	O*W*2—Nd—O3$^{\rm ii}$	106.1 (4)
O4—Nd—O3	50.7 (4)	O*W*2—Nd—O3	69.6 (4)
O5—Nd—O1$^{\rm i}$	86.3 (4)	O*W*2—Nd—O4	68.1 (4)
O5—Nd—O1	143.6 (4)	O*W*2—Nd—O5	137.9 (4)
O5—Nd—O2	144.9 (4)	O*W*2—Nd—O7	141.8 (4)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $-x, -y, -z$.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71191 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1058]

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Structure of a $V_2Cu_2S_4$ Cubane-Like Cluster $(Et_4N)_2[V_2Cu_2S_4(S_2CNMe_2)_2(SPh)_2]$

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Abstract

The title compound, bis(tetraethylammonium) bis-(*N*,*N*-dimethyldithiocarbamato)-$1\kappa^2S,S';2\kappa^2S,S'$-bis(phenylthiolato)-$3\kappa S,4\kappa S$-tetra-$\mu_3$-sulfido-$1{:}2{:}3\kappa^3S;1{:}2{:}4\kappa^3S;1{:}3{:}4\kappa^3S;2{:}3{:}4\kappa^3S$-*tetrahedro*-dicopperdivanadium, is a cubane-like cluster containing a $V_2Cu_2(\mu_3\text{-}S)_4$ distorted-cubic core. Each V atom is chelated by a dimethyldithiocarbamate group and each Cu atom is bonded to a phenylthiolate group.

Comment

Heterometallic thiocubane clusters have attracted attention due to their relevance and importance to a wide variety of chemical, industrial and biological systems. Among the V-containing heteronuclear thiocubanes only a few complexes, with VFe_3S_4 (Kovacs & Holm, 1987) and $V_2Fe_2S_4$ (Rauchfuss, Weatherill, Wilson & Zebrowski, 1983) cores, have been structurally characterized. We have recently reported $V_2Cu_2S_4$ and $V_2Ag_2S_4$ cubane clusters and determined the structures of $(Et_4N)_2[V_2M_2S_4(OC_4H_8NCS_2)_2(PhS)_2]$ (M = Cu, Ag; Yang, Liu, Huang, Kang & Lu, 1992). Here, we report the crystal structure of a compound containing a $V_2Cu_2S_4$ cubic core which was obtained from an assembly reaction system including $(NH_4)_3VS_4$, CuCl, $Me_2NCSSNa$ and C_6H_5SNa in the molar ratio 1:3:4:4 in dimethylformamide (DMF). This compound was crystallized from $DMF/CH_3CN/(CH_3)_2CO$ solution to give single black crystals used for X-ray diffraction.

The title compound contains well separated tetraethylammonium cations and $[V_2Cu_2S_4(S_2CNMe_2)_2(SPh)_2]^{2-}$ anions. There is a distorted cubic $V_2Cu_2S_4$ core in the anion. A crystallographically imposed C_2 axis passes through the centers of both the V—S(1)—V′—S(1′) and Cu—S(2)—Cu′—S(2′) units. Each V atom is chelated by a dimethyldithiocarbamate group and coordinated by three μ_3-S atoms in a distorted square pyramidal site which is out of the equatorial plane toward the apical S(2) atom. Each Cu atom is coordinated by three μ_3-S atoms and a terminal phenylthiolate group in a distorted tetrahedral site. The metal bond distances of 2.803 (5) Å for V···V and 2.762 (2) to 2.791 (3) Å for V···Cu, which indicate direct intermetallic contacts, are comparable to those in other V–S dimers (Duraj, Andras & Kibala, 1990: Halbert, Hutchings, Rhodes & Stiefel, 1986) and V–Cu–S clusters (Müller, Schimanski & Bögge, 1987; Scattergood, Bonney, Slater, Garner & Clegg, 1987). In comparison with $[V_2Cu_2S_4(S_2CNC_4H_8O)_2(SPh)_2]^{2-}$, the anion of the title complex shows the same structural features of the core with similar bond distances and angles. The non-H atoms in the dimethyldithiocarbamate group are coplanar. The C(20)—N(20) bond distance of 1.28 (2) Å indicates a C=N double bond, strongly indicating that the dimethyldithiocarbamate group coordinates to a V atom in the form $(Me)_2N^+{=}C(S^-)_2$ rather than $(Me)_2N{—}C(S_2)^-$. The four C atoms in the tetraethylammonium cation, C(31), C(33), C(35) and C(37), are disordered and have the occupancies given in Table 1.

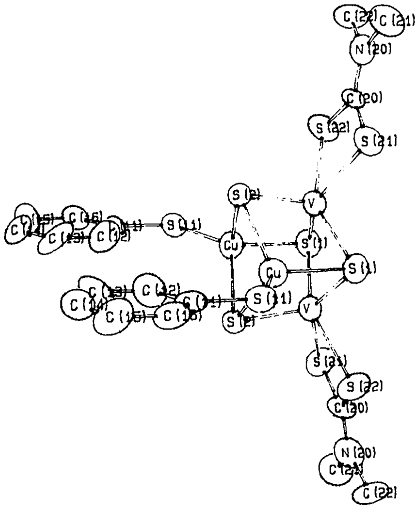

Fig. 1. Structure and atomic labelling of the $[V_2Cu_2S_4(S_2CNMe_2)_2(SPh)_2]^{2-}$ anion.