Related literature. The reinvestigation of $SmCo(CN)_6.4H_2O$ and $SmFe(CN)_6.4H_2O$ (Mullica & Sappenfield, 1989), which were originally thought to be in the monoclinic system ($P2_1/m$), has shown that these analogous compounds belong in the higher symmetry orthorhombic system, space group $Cmcm$, even though both data sets solved equally well in $P2_1/m$. The reinvestigation was motivated due to a private communication (Marsh, 1989a) which was followed by a publication (Marsh, 1989b). The bond lengths and angles as well as the geometric structural arrangement were virtually the same in both $Cmcm$ and $P2_1/m$. For this reason, the title compound, which is situated where a detectable discontinuity among tripositive lanthanide ions in a particular series is usually observed (at the 'gadolinium break'), was investigated. The crystallographic results for $GdFe(CN)_6.4H_2O$ were equivalent in $Cmcm$ ($R = 0.016$, $wR = 0.019$, $S = 1.61$) and in $P2_1/m$ ($R = 0.019$, $wR = 0.023$, $S = 1.92$). Hulliger, Landolt & Vetsch (1973), using magnetic and structural powder data, have correctly described the pseudo-hexagonal $LnT(CN)_6.4H_2O$ series (Ln = Sm,···Lu and $T = $ Fe and Co) as having orthorhombic symmetry. Recently, Gramlich, Petter & Hulliger (1990) have also shown that $ErFe(CN)_6.4H_2O$ and its analogs

belong in an orthorhombic system rather than in a monoclinic system. The work and conclusions of Hulliger, Landolt & Vetsch (1973) and those in this laboratory (Mullica & Sappenfield, 1989, and this paper) are now in direct agreement.

References

GRAMLICH, V., PETTER, W. & HULLIGER, F. (1990). *Acta Cryst.* C46, 724–726.
HULLIGER, F., LANDOLT, M. & VETSCH, H. (1973). *Proc. Tenth Rare-Earth Res. Conf.* Carefree, Arizonia. Vol. 80.
MARSH, R. E. (1989a). Private communication, March 1989.
MARSH, R. E. (1989b). *Acta Cryst.* C45, 127.
MULLICA, D. F. & SAPPENFIELD, E. L. (1989). *J. Solid State Chem.* 82, 168–171.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A24, 351–359.
PRANDTL, W. & MOHR, S. (1938). *Z. Anorg. Allg. Chem.* 236, 243–251.
SHELDRICK, G. M. (1989). *SHELXTL-PC.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
STOUT, G. H. & JENSEN, L. H. (1989). *X-ray Structure Determination*, 2nd ed., p. 393. New York: John Wiley.

Structure of the Second Polymorph of Niobium Pentachloride

BY F. ALBERT COTTON,* PIOTR A. KIBALA, MAREK MATUSZ AND ROBERT B. W. SANDOR

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843, USA

Abstract. (1) $NbCl_5$, $M_r = 270.17$, monoclinic, $P2_1/n$, $a = 7.785$ (2), $b = 10.201$ (2), $c = 8.074$ (2) Å, $\beta = 90.58$ (2)°, $V = 641.2$ (5) Å^3, $Z = 4$, $D_x = 2.80$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 37.70$ cm^{-1}, $F(000) = 504$, $T = 294$ K, $R = 0.017$ for 1101 observed reflections. Two $NbCl_5$ units form an edge-sharing bioctahedron. The Nb atoms are separated by 3.9881 (3) Å. The mean Nb—Cl_{bridge} distance is 2.567 (1) Å and the mean non-bridging equatorial and axial Nb—Cl bond lengths are 2.246 (2) and 2.292 (1) Å, respectively. The Nb—Cl_{bridge}—Nb angle is 101.93 (2)° and the Cl_{bridge}—Nb—Cl_{bridge} angle is 78.07 (2)°.

Experimental. A Pyrex tube evacuated to 2.67×10^{-2} Pa containing Nb (0.50 g, 5.4 mmol), S_2Cl_2 (0.43 mL, 5.4 mmol) and S (0.18 g, 5.4 mmol) was heated at 698 K for 48 h. Upon slow cooling several light yellow octahedral crystals of $NbCl_5$ formed on the walls of the tube. The quality of the crystals was confirmed by polarized light microscopy. An irregularly shaped crystal, $0.600 \times 0.40 \times 0.30$ mm, was sealed with epoxy cement in a glass capillary filled with degassed mineral oil under argon. Unit-cell dimensions were determined from least-squares analysis of 25 reflections with $20 < 2\theta < 30°$. Laue class and unit-cell dimensions were confirmed with axial photographs. Intensity data were collected to $\sin\theta/\lambda = 0.596$ Å^{-1} ($0 \le h \le 9$; $0 \le k \le 12$; $-9 \le l \le$

---

9) at variable scan speeds (3–20° min^{-1}), which depended on a pre-scan count with a skip option, using the moving-crystal/moving-counter technique, ω–2θ scans, on a Nicolet P3F equivalent diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Three standard reflections (400, 060 and 105) measured every 100 reflections displayed no significant change in intensity throughout the data collection ($<1.0\%$). 1308 reflections were measured, 1176 unique ($R_{int} = 0.015$) and 1101 with $F_o^2 > 3\sigma(F_o^2)$ considered observed. Data were corrected for Lorentz and polarization effects. Analytical absorption correction based on ψ scans (North, Phillips & Mathews, 1968) varied from 0.84 to 1.00.

Systematic absences indicated space group $P2_1/n$. The position of the Nb atom was determined from a Patterson map (SHELXS86, Sheldrick, 1986) and the remainder of the molecule was located and refined by alternating difference Fourier maps and least-squares cycles employing the Enraf–Nonius (1979) Structure Determination Package. $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ was minimized, where $w = 1/\sigma^2(|F_o|)$. All atoms were refined anisotropically. An observed systematic dependence of $w(|F_o| - |F_c|)^2$ on $\sin\theta/\lambda$ implied the need for a secondary-extinction correction of the form $F_c = |F_c|/(1 + gI_c)$; the refined extinction coefficient, g, was 3.43×10^{-6}. Final $R = 0.017$, $wR = 0.032$ and $S = 0.76$ for 56 variables. At convergence, $(\Delta/\sigma)_{max} = 0.01$, $(\Delta\rho)_{max} = 0.26$ and $(\Delta\rho)_{min} = -0.31$ e Å^{-3} on final difference Fourier map. Atomic scattering factors, including anomalous-dispersion correction, were taken from International Tables for X-ray Crystallography (1974, Vol. IV). No disorder or other nonroutine problems arose. Positional and equivalent isotropic displacement parameters are given in Table 1. The structure is depicted in Fig. 1 where the atom-numbering scheme is also defined. A unit-cell diagram is shown in Fig. 2.*

Related literature. The crystal structure as a whole, like that of UCl$_5$ (Smith, Johnson & Elson, 1967), is based on a cubic closest packing of the halogen atoms, with the Nb atoms occupying one fifth of the octahedral holes in adjacent pairs. This arrangement has also been reported for PaBr$_5$ (Brown, Petcher & Smith, 1969). The existence of two polymorphs of NbCl$_5$ was first inferred in 1949 from a study of the temperature dependence of the vapor pressure of NbCl$_5$ (Alexander & Fairbrother, 1949). A few years later X-ray structural studies were carried out for

Table 1. Positional and equivalent isotropic displacement parameters and their e.s.d.'s for NbCl$_5$

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

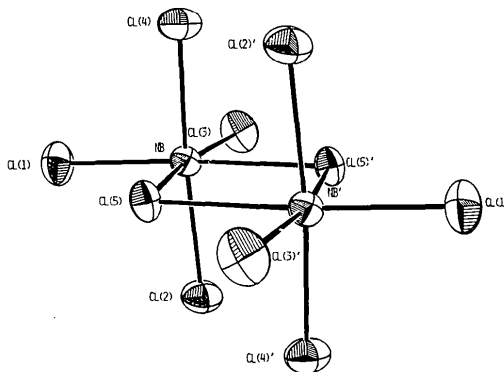|	x	y	z	B_{eq} (Å^2)
Nb	0.05276 (2)	0.35958 (2)	0.83641 (2)	2.008 (4)
Cl(1)	0.13345 (9)	0.37584 (6)	0.57090 (7)	3.38 (1)
Cl(2)	0.32739 (8)	0.38259 (6)	0.93677 (8)	3.21 (1)
Cl(3)	0.0450 (1)	0.14125 (6)	0.8710 (1)	3.54 (1)
Cl(4)	−0.23452 (8)	0.37618 (6)	0.77438 (8)	3.17 (1)
Cl(5)	0.03866 (7)	0.61022 (5)	0.86139 (6)	2.300 (9)

Fig. 1. ORTEP (Johnson, 1965) drawing of the Nb$_2$Cl$_{10}$ unit. Atoms are represented by displacement ellipsoids at the 50% level.
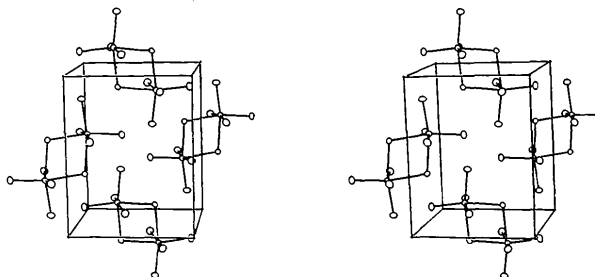

Fig. 2. Unit-cell diagram for NbCl$_5$. Atoms are represented by displacement ellipsoids at the 20% level. Axes orientation: c across, b down, a toward viewer.

one of the polymorphs (Douglass & Staritzky, 1957; Zalkin & Sands, 1958). In 1978 it was suggested (Müller, 1978) that the other polymorph had a structure similar to that of UCl$_5$ and PaBr$_5$ and cited unpublished results of Henke as evidence. A thorough literature search revealed no additional information on that polymorph. While this work was in press a third polymorph has been described (Hoenle & von Schnering, 1990). Structural work on MoCl$_5$ (Sands & Zalkin, 1959), WCl$_5$ (Boorman, Greenwood, Hildon & Whitfield, 1967; Cotton & Rice, 1978), ReCl$_5$ (Mucker, Smith & Johnson, 1968), OsCl$_5$ (Burns & O'Donnell, 1979), NbBr$_5$ (Rolsten, 1958), UBr$_5$ (Levy, Taylor & Wilson, 1978), TaI$_5$ (Müller, 1979) and UI$_5$ (Müller & Kolitsch, 1974) has been also reported. NQR (Pisarev, Semin, Drobot, Kuznetsov & Bryukhova,

References

ALEXANDER, K. M. & FAIRBROTHER, F. (1949). *J. Chem. Soc.* **1**, S223–S227.

BOORMAN, P. M., GREENWOOD, N. N., HILDON, M. A. & WHITFIELD, H. J. (1967). *J. Chem. Soc. A*, pp. 2017–2018.

BROWN, D., PETCHER, T. J. & SMITH, A. J. (1969). *Acta Cryst.* **B25**, 178–182.

BURNS, R. C. & O'DONNELL, T. A. (1979). *Inorg. Chem.* **18**, 3081–3076.

COTTON, F. A. & RICE, C. E. (1978). *Acta Cryst.* **B34**, 2833–2834.

DOUGLASS, R. M. & STARITZKY, E. (1957). *Anal. Chem.* **29**, 315–316.

DROBOT, D. V. & PISAREV, E. A. (1984). *Russ. J. Inorg. Chem.* **29**, 1461–1462.

ENRAF–NONIUS (1979). *Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.

HOENLE, W. & VON SCHNERING, H. G. (1990). *Z. Kristallogr.* **191**, 135.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

LEVY, J. H., TAYLOR, J. C. & WILSON, P. W. (1978). *J. Inorg. Nucl. Chem.* **40**, 1055–1057.

MUCKER, K., SMITH, G. S. & JOHNSON, Q. (1968). *Acta Cryst.* **B24**, 874–879.

MÜLLER, U. (1978). *Acta Cryst.* **A34**, 256–267.

MÜLLER, U. (1979). *Acta Cryst.* **B35**, 2502–2509.

MÜLLER, U. & KOLITSCH, W. (1974). *Z. Anorg. Allg. Chem.* **410**, 32–38.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

PISAREV, E. A., SEMIN, G. K., DROBOT, D. V., KUZNETSOV, S. I. & BRYUKHOVA, E. V. (1978). *Russ. J. Inorg. Chem.* **23**, 1171–1182.

ROLSTEN, R. F. (1958). *J. Phys. Chem.* **62**, 126–127.

SANDS, D. E. & ZALKIN, A. (1959). *Acta Cryst.* **12**, 723–726.

SHELDRICK, G. M. (1986). *SHELXS86.* Program for the solution of crystal structures. Univ. of Göttingen, Germany.

SMITH, G. S., JOHNSON, Q. & ELSON, R. E. (1967). *Acta Cryst.* **22**, 300–303.

ZALKIN, A. & SANDS, D. E. (1958). *Acta Cryst.* **11**, 615–619.

Structure of Barium Vanadium(III) Diphosphate

BY L. BENHAMADA, A. GRANDIN, M. M. BOREL, A. LECLAIRE* AND B. RAVEAU

Laboratoire de cristallographie et sciences des matériaux, CRISMAT, ISMRa, Boulevard du Maréchal Juin, 14050 Caen CEDEX, France

Abstract. $BaV_2(P_2O_7)_2$, $M_r = 587 \cdot 1$, monoclinic, $C2/c$, $a = 10 \cdot 6213$ (8), $b = 10 \cdot 4685$ (7), $c = 9 \cdot 7063$ (13) Å, $\beta = 103 \cdot 074$ (9)°, $V = 1051 \cdot 3$ Å^3, $Z = 4$, $D_x = 3 \cdot 71$ Mg m^{-3}; $\lambda(Cu\ K\alpha) = 1 \cdot 54056$ Å, $\mu = 51 \cdot 12$ mm^{-1}, $F(000) = 1096$, $T = 294$ K, $R = 0 \cdot 038$, $wR = 0 \cdot 044$ for 1023 independent reflections with $I > 3\sigma(I)$. Framework is built up from corner-sharing VO_6 octahedra and P_2O_7 diphosphate groups which delimit tunnels where the barium cations are located.

Experimental. The preparation of $BaV_2(P_2O_7)_2$ was performed in two steps. First a mixture of $H(NH_4)_2$-PO_4, V_2O_5 and $BaCO_3$ in appropriate ratios was heated in a platinum crucible for 2 h at 653 K to decompose the phosphate and carbonate; in a second step, the appropriate amount of vanadium was added and the product was ground up and placed in an evacuated silica ampoule for 60 h at 973 K. It was then cooled at a rate of 9 K h^{-1} to 773 K and quenched to room temperature. A green crystal, $0 \cdot 103 \times 0 \cdot 051 \times 0 \cdot 039$ mm, was used on an Enraf-

Table 1. *Positional parameters and their e.s.d.'s*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Ba	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	1·015 (9)
V(1)	0	0·5480 (1)	$\frac{1}{4}$	0·37 (2)
V(2)	0	0	0	0·33 (2)
P(1)	0·0606 (1)	0·3105 (2)	0·0571 (2)	0·38 (2)
P(2)	0·2810 (1)	0·4571 (2)	0·2015 (2)	0·40 (2)
O(1)	0·0673 (5)	0·3348 (5)	−0·0937 (5)	0·73 (8)
O(2)	−0·0323 (4)	0·4008 (4)	0·1073 (5)	0·58 (8)
O(3)	0·0226 (4)	0·1742 (4)	0·0823 (6)	0·78 (8)
O(4)	0·2005 (4)	0·3276 (5)	0·1567 (6)	0·72 (8)
O(5)	0·3505 (4)	0·4925 (5)	0·0874 (6)	0·94 (8)
O(6)	0·1825 (4)	0·5593 (5)	0·2114 (5)	0·71 (8)
O(7)	0·3705 (4)	0·4181 (5)	0·3393 (5)	0·78 (8)

Nonius CAD-4 diffractometer. Unit cell from least squares on 25 reflections $\pm 2\theta$, $36 < 2\theta < 44°$. Intensity measurement by $(\omega-2/3\theta)$ scan of $(1 + 0 \cdot 14 \tan\theta)°$ with a $(1 + \tan\theta)$ mm counter aperture slit, determined by a study of some reflections in the $\omega-\theta$ plane. Three standards (400, 311, 022) for count every 3000 s, no appreciable trends. 1204 reflections measured up to $\theta = 78°$ ($h - 13,13$ k 0,13 l 0,12). Scanning speed adjusted to obtain $\sigma(I)/I < 0 \cdot 018$ or