

Affinement basé sur les  $F$ , programme à matrice complète. Facteurs de diffusion des *International Tables for X-ray Crystallography* (1974, Tome IV, pp. 99, 149). Paramètres affinés:  $x$ ,  $y$ ,  $z$  et  $\beta_{ij}$  de Pt, O, N et C. Corrections d'absorption: programme *DIFABS* (Walker & Stuart, 1983). Valeurs maximale et minimale du coefficient de correction: 1,364 et 0,845.  $R = 0,021$ ,  $wR = 0,029$ ,  $w = 1/\sigma^2(F)$ ,  $S = 1,175$ ,  $(\Delta/\sigma)_{\max} = 0,01$ ,  $|\Delta\rho|_{\max} = 0,9$  (2) e  $\text{\AA}^{-3}$ . Programmes de calcul du système *SDP* (B. A. Frenz & Associates, Inc., 1982). Fig. 1 et 2: *ORTEPII* (Johnson, 1976). Angles entre les plans moyens: *BP7C* (Ito & Sugawara, 1983). Ordinateur DEC PDP11/44.

Il a été vérifié qu'en remplaçant les coordonnées  $x$ ,  $y$  et  $z$  de chacun des atomes respectivement par  $1-x$ ,  $1-y$  et  $1-z$ , on obtient, pour le facteur  $R$ , une valeur significativement plus élevée que celle indiquée ci-dessus. Les atomes de carbone asymétriques C(5) et C(25) ont la configuration  $S$ .

Les coordonnées atomiques relatives et les facteurs de température isotropes équivalents sont rapportés dans le Tableau 1, les longueurs et les angles des liaisons dans le Tableau 2.\* La Fig. 1 représente la molécule édifiée autour de Pt(1) et indique les numéros attribués à ses atomes. La Fig. 2 est une vue stéréoscopique de la structure.

Les numéros utilisés pour désigner les atomes de la deuxième molécule s'obtiennent en ajoutant le

\* Les listes des facteurs de structure observés et calculés, des coefficients d'agitation thermique anisotrope, des paramètres des atomes d'hydrogène, des distances des atomes aux plans moyens et des distances interatomiques intermoléculaires ont été déposées aux archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 53930: 15 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

nombre 20 aux numéros des atomes homologues de la première.

**Littérature associée.** Structures associées: structure de l'acide L-pyroglutamique (van Zoeren, Oonk & Kroon, 1978); structure cristalline et moléculaire de l'acide pyroglutamique (Pattabhi & Venkatesan, 1974) (ce mémoire décrit le racémique); bis(oxo-5 proline)platinate(II) de sodium dihydrate (Viossat, Khodadad & Rodier, 1990); structure du bis[ $\mu$ -(oxo-5 proline- $N^1, O^5$ )]-bis[chloro(diméthylsulfoxyde)platine(II)] trihydrate (Viossat, Khodadad, Rodier & Guillard, 1990); tétra[bis(oxo-5 proline)platinate(II) de potassium] pentahydrate (Viossat, Rodier, Nguyen Huy Dung & Guillard, 1986).

#### References

- B. A. FRENZ & ASSOCIATES, INC. (1982). *Structure Determination Package*. College Station, Texas, EU, et Enraf-Nonius, Delft, Pays-Bas.
- ITO, T. & SUGAWARA, Y. (1983). *BP7C*. Institut de Recherches en Physique et en Chimie, Wako-Shi, Saitama 351, Japon.
- JOHNSON, C. K. (1976). *ORTEPII*. Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee, EU.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. de York, Angleterre, et de Louvain, Belgique.
- PATTABHI, V. & VENKATESAN, K. (1974). *J. Chem. Soc. Perkin Trans. 2*, pp. 1085-1089.
- VISSAT, B., KHODADAD, P. & RODIER, N. (1990). *Acta Cryst. C46*, 2062-2065.
- VISSAT, B., KHODADAD, P., RODIER, N. & GUILLARD, O. (1990). *Acta Cryst. C46*, 894-896.
- VISSAT, B., RODIER, N., NGUYEN HUY DUNG & GUILLARD, O. (1986). *Acta Cryst. C42*, 659-662.
- WALKER, N. & STUART, D. (1983). *Acta Cryst. A39*, 159-166.
- ZOEREN, E. VAN, OONK, H. A. & KROON, J. (1978). *Acta Cryst. B34*, 1898-1900.

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## Structure of $\text{Nb}_4(\mu_3\text{-Cl})_2(\mu_2\text{-Cl})_4\text{Cl}_4(\text{PMe}_3)_6$

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**Abstract.** Bis( $\mu_3$ -chloro)-tetrakis( $\mu_2$ -chloro)-tetrachlorohexakis(trimethylphosphine)tetrakisniobium,  $\text{Nb}_4(\mu_3\text{-Cl})_2(\mu_2\text{-Cl})_4\text{Cl}_4(\text{PMe}_3)_6$ ,  $M_r = 1182.63$ ,

orthorhombic,  $Pbca$ ,  $a = 15.911$  (8),  $b = 22.21$  (1),  $c = 12.054$  (4)  $\text{\AA}$ ,  $V = 4260$  (3)  $\text{\AA}^3$ ,  $Z = 4$ ,  $D_x = 1.844$   $\text{g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$   $\text{\AA}$ ,  $\mu = 18.8$   $\text{cm}^{-1}$ ,  $F(000) = 2344$ ,  $T = 295$  K,  $R = 0.069$ , 3030 unique observed reflections. Synthesis by reduc-

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tion of  $\text{NbCl}_5$  with  $\text{Na}/\text{Hg}$  in the presence of  $\text{PMe}_3$ . Molecule is located on the center of inversion. Five single bonds between the four Nb atoms and the metal-metal distances range from 2.913 (3) to 2.986 (3) Å. Disregarding the metal-metal bonds, each Nb atom has distorted octahedral coordination.

**Experimental.** The title compound was synthesized in the following manner.  $\text{NbCl}_5$  (2.00 g, 7.39 mmol) and 20 ml toluene were placed in a 100 ml round bottom flask, equipped with a gas inlet, and cooled to 263 K.  $\text{PMe}_3$  (0.75 ml, 7.38 mmol) and 30 ml toluene were placed in another 100 ml flask and cooled to 263 K. The  $\text{PMe}_3$  mixture was transferred, *via* cannula, into the former flask.  $\text{Na}/\text{Hg}$  (7.4 ml, 2 M solution) was slowly added and the mixture stirred for 6 h at room temperature. The red solution formed was filtered, the Hg precipitate washed with 20 ml toluene and filtered into the flask containing the initial filtrate. 25 ml of this solution was transferred into a Schlenk tube and layered with 20 ml hexane. Slow diffusion of the hexane layer into the toluene layer afforded red-brown crystals of the title compound. One crystal of an irregular geometry of dimensions 0.20 × 0.05 × 0.10 mm was mounted inside a capillary. Cell constants were derived from least-squares refinement based on 25 reflections having  $16 < 2\theta < 25^\circ$ , using a Rigaku AFC5R diffractometer. Intensity data were collected with  $2\theta$ - $\omega$  scan technique with  $4 < 2\theta < 55^\circ$ , scan speed  $6^\circ \text{ min}^{-1}$ , max. four scan repetitions ( $h = 0 \rightarrow 19$ ,  $k = 0 \rightarrow 29$ ,  $l = 0 \rightarrow 16$ ). Three standard reflections ( $\bar{2}83$ ,  $48\bar{1}$ ,  $\bar{3}72$ ), measured every 150 reflections, revealed no decay of the crystal. Data were corrected for Lorentz and polarization effects, and for absorption effects based on  $\psi$  scans of six reflections near  $\chi = 90^\circ$  using the empirical method of North, Phillips & Matthews (1968); relative  $T_{\text{min}} = 0.818$ ,  $T_{\text{max}} = 0.999$ . 3030 data collected and aver-

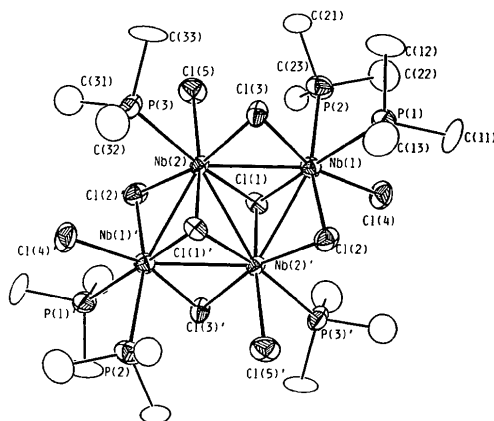


Fig. 1. An ORTEP drawing of  $\text{Nb}_4(\mu_3\text{-Cl})_2(\mu_2\text{-Cl})_4\text{Cl}_4(\text{PMe}_3)_6$ , showing the atomic numbering scheme. Thermal ellipsoids have been drawn at 50% probability.

Table 1. Positional and equivalent isotropic thermal parameters with *e.s.d.*'s for  $\text{Nb}_4\text{Cl}_{10}(\text{PMe}_3)_6$

	x	y	z	$B_{\text{eq}}$ (Å <sup>2</sup> )
Nb(1)	-0.0056 (1)	0.09920 (9)	0.0996 (2)	2.09 (3)
Nb(2)	0.0366 (1)	0.03078 (9)	-0.0989 (2)	1.81 (3)
Cl(1)	0.1046 (3)	0.0204 (2)	0.0857 (5)	2.3 (1)
Cl(2)	-0.0484 (3)	0.1239 (2)	-0.0901 (5)	2.8 (1)
Cl(3)	-0.1384 (4)	0.0512 (3)	0.1480 (4)	2.7 (1)
Cl(4)	0.1104 (4)	0.1728 (3)	0.0944 (7)	3.9 (1)
Cl(5)	0.0106 (4)	0.0486 (3)	-0.2993 (5)	3.7 (1)
P(1)	-0.1067 (4)	0.1932 (3)	0.1350 (5)	2.9 (1)
P(2)	0.0361 (4)	0.1037 (3)	0.3188 (5)	3.2 (1)
P(3)	0.1726 (4)	0.0919 (3)	-0.1592 (6)	2.9 (1)
C(11)	-0.058 (2)	0.268 (1)	0.123 (2)	3.9 (6)*
C(12)	-0.162 (2)	0.199 (1)	0.268 (2)	4.3 (6)*
C(13)	-0.197 (2)	0.196 (1)	0.037 (2)	4.0 (6)*
C(21)	-0.045 (2)	0.084 (1)	0.422 (2)	3.6 (5)*
C(22)	0.068 (2)	0.180 (1)	0.359 (2)	4.7 (7)*
C(23)	0.131 (2)	0.063 (1)	0.359 (2)	3.8 (6)*
C(31)	0.156 (2)	0.171 (1)	-0.195 (2)	4.2 (6)*
C(32)	0.264 (2)	0.094 (1)	-0.066 (2)	4.2 (6)*
C(33)	0.223 (2)	0.065 (1)	-0.290 (2)	4.5 (6)*

\* Refined isotropically.

The equivalent isotropic displacement parameter,  $B_{\text{eq}}$ , is calculated as:  $1/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$ .

Table 2. Selected bond lengths (Å) and valence angles (°) with *e.s.d.*'s for  $\text{Nb}_4\text{Cl}_{10}(\text{PMe}_3)_6$

Nb(1)	Nb(2)	2.913 (3)	Nb(2)	Nb(2)'	2.986 (3)		
Nb(1)	Nb(2)'	2.929 (3)	Nb(2)	Nb(2)'	2.486 (6)		
Nb(1)	Cl(1)	2.483 (5)	Nb(2)	Cl(1)'	2.524 (5)		
Nb(1)	Cl(2)	2.448 (7)	Nb(2)	Cl(2)'	2.475 (6)		
Nb(1)	Cl(3)	2.438 (6)	Nb(2)	Cl(3)	2.507 (6)		
Nb(1)	Cl(4)	2.466 (6)	Nb(2)	Cl(5)	2.482 (6)		
Nb(1)	P(1)	2.671 (7)	Nb(2)	P(3)	2.655 (7)		
Nb(1)	P(2)	2.726 (7)					
Nb(2)	Nb(1)	Nb(2)'	61.48 (7)	Cl(1)	Nb(2)	Cl(2)'	106.1 (2)
Cl(1)	Nb(1)	Cl(2)	107.0 (2)	Cl(1)	Nb(2)'	Cl(3)	82.1 (2)
Cl(1)	Nb(1)	Cl(3)	108.7 (2)	Cl(1)	Nb(2)'	Cl(5)'	163.5 (2)
Cl(1)	Nb(1)	Cl(4)	86.4 (2)	Cl(1)	Nb(2)'	P(3)'	86.4 (2)
Cl(1)	Nb(1)	P(1)	170.9 (2)	Cl(1)	Nb(2)'	Cl(2)	83.5 (2)
Cl(1)	Nb(1)	P(2)	85.4 (2)	Cl(1)	Nb(2)'	Cl(3)'	105.2 (2)
Cl(2)	Nb(1)	Cl(3)	94.6 (2)	Cl(1)	Nb(2)'	Cl(5)	89.1 (2)
Cl(2)	Nb(1)	Cl(4)	92.1 (2)	Cl(1)	Nb(2)'	P(3)	166.7 (2)
Cl(2)	Nb(1)	P(1)	78.8 (2)	Cl(2)	Nb(2)'	Cl(3)'	166.1 (2)
Cl(2)	Nb(1)	P(2)	164.8 (2)	Cl(2)	Nb(2)'	Cl(5)'	79.5 (2)
Cl(3)	Nb(1)	Cl(4)	160.8 (2)	Cl(2)	Nb(2)'	P(3)	91.7 (2)
Cl(3)	Nb(1)	P(1)	77.4 (2)	Cl(3)	Nb(2)'	Cl(5)	89.7 (2)
Cl(3)	Nb(1)	P(2)	89.7 (2)	Cl(3)	Nb(2)'	P(3)	77.3 (2)
Cl(4)	Nb(1)	P(1)	86.3 (2)	Cl(5)	Nb(2)'	P(3)	77.8 (2)
Cl(4)	Nb(1)	P(2)	79.5 (3)	Nb(1)	Cl(1)	Nb(2)'	71.8 (2)
P(1)	Nb(1)	P(2)	87.9 (2)	Nb(1)	Cl(1)	Nb(2)	71.6 (1)
Nb(1)	Nb(2)	Nb(1)'	118.52 (9)	Nb(2)	Cl(1)	Nb(2)'	73.2 (2)
Nb(1)	Nb(2)'	Nb(2)	59.52 (7)	Nb(1)	Cl(2)	Nb(2)'	72.6 (2)
Cl(10)	Nb(2)	Cl(1)'	106.8 (2)	Nb(1)	Cl(3)	Nb(2)	72.6 (2)

aged to 1427 unique observed reflections,  $F_o^2 > 3\sigma(F_o^2)$ . Scattering factors were those of *Structure Determination Package* (Frenz, 1985). The Nb, Cl and P atoms were located by direct methods, *SHELXS86* (Sheldrick, 1986), and the remainder of the molecule was located and refined by alternating difference Fourier maps with least-squares cycles using *SDP*. The H atoms were not included in the model and all but C atoms were refined anisotropically. Final  $R = 0.0694$  and  $wR = 0.0841$ , where  $w = \sigma^2(F_o)^{-1}$  and  $S = 1.490$  and 127 variables. The largest shift/*e.s.d.* in the final least squares was 0.03; the maximum residual electron density in the final

difference Fourier map was 1.002 e Å<sup>-3</sup>. An *ORTEP* (Johnson, 1965) drawing of the molecule is shown in Fig. 1. Final positional and equivalent isotropic thermal parameters are listed in Table 1;\* some selected distances and angles are listed in Table 2.

**Related literature.** A previous report (Cotton & Shang, 1988) described the same tetranuclear cluster in the compound Nb<sub>4</sub>Cl<sub>10</sub>(PMe<sub>3</sub>)<sub>6</sub>·2C<sub>4</sub>H<sub>8</sub>O, the incorporated thf having been present in the reaction solution. In this work no thf was present at any time

\* Lists of structure factors, anisotropic thermal parameters and complete bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53973 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and a different crystalline form containing no solvent of crystallization was obtained.

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#### References

- COTTON, F. A. & SHANG, M. (1988). *J. Am. Chem. Soc.* **110**, 7719–7722.  
 FRENZ, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*, Version 3.0. Enraf-Nonius, Delft, The Netherlands.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.  
 NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.  
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

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## Structure of Pentakis(3,3',4,4'-tetramethyl-2,2',5,5'-tetrathiafulvalenium) Dodeca-μ-chloro-octahedro-hexakis(chlorotantalate) Dichloromethane Solvate (2/1): (TMTTF)<sub>5</sub>[Ta<sub>6</sub>Cl<sub>18</sub>].0.5CH<sub>2</sub>Cl<sub>2</sub>

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**Abstract.** [C<sub>10</sub>H<sub>12</sub>S<sub>4</sub>]<sub>5</sub>[Ta<sub>6</sub>Cl<sub>18</sub>].0.5CH<sub>2</sub>Cl<sub>2</sub>, *M*<sub>r</sub> = 3068.62, triclinic, *P*1̄, *a* = 12.931 (5), *b* = 13.712 (5), *c* = 14.302 (6) Å, α = 114.31 (3), β = 97.01 (4), γ = 99.10 (5)°, *V* = 2232 Å<sup>3</sup>, *Z* = 1, *D*<sub>x</sub> = 2.283 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 82.99 cm<sup>-1</sup>, *F*(000) = 1495, *T* = 293 K, *R* = 0.058 based on 3221 observed reflections with *I* ≥ 3σ(*I*). Four partially oxidized TMTTF molecules form stacks parallel to the [001] direction and one additional neutral TMTTF molecule, lying on the (010) plane, is perpendicular to this stack. The stacking mode of the TMTTF molecules is not regular. The separation between adjacent molecules ranges from 3.49 to 3.60 Å. The bond distances within the anion [average Ta—Ta: 2.959 (1); Ta—Cl<sup>l</sup>: 2.437 (6); Ta—Cl<sup>e</sup>: 2.502 (6) Å, where Cl<sup>l</sup> and Cl<sup>e</sup> are bridging and non-bridging Cl atoms, respectively] are in the range expected for a [Ta<sub>6</sub>Cl<sub>18</sub>]<sup>3-</sup> unit. The disordered dichloromethane

solvent molecule is located near the (0,0,<sup>1</sup>/<sub>2</sub>) position with a statistical occupancy.

**Experimental.** The compound was grown on a platinum wire electrode by anodic oxidation of the organic donor (2 × 10<sup>-3</sup> M) in a mixture of DMF (85%) (DMF = *N,N*-dimethylformamide) and dichloromethane (15%) under low constant current (*I* = 0.95 μA) in the presence of tetraethylammonium [(Et<sub>4</sub>N)<sub>3</sub>Ta<sub>6</sub>Cl<sub>18</sub>] salts of the anion (10<sup>-2</sup> M) as supporting electrolyte.

Black crystal 0.09 × 0.07 × 0.07 mm. Enraf-Nonius CAD-4 diffractometer, graphite-crystal-monochromatized Mo *K*α radiation. Cell dimensions: least-squares refinement from setting angles of 25 centered reflections (θ ≤ 15°). Intensities collected by θ–2θ scans. The crystals of the title compound are unstable. In fact, after several days the intensities of the three standard reflections decreased slightly and the data collection procedure was stopped. Three standard reflections measured every hour: no fluctuation in intensities in the set of reflections used in

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