Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Tetrakis(dimethylamido)vanadium(IV)

Stuart R. Dubberley, Ben R. Tyrrell and Philip Mountford*

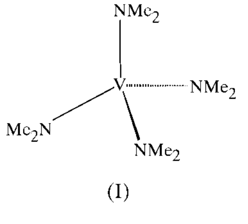
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, England
Correspondence e-mail: philip.mountford@chem.ox.ac.uk

Received 11 April 2001
Accepted 17 May 2001

The title compound, $[V(C_2H_6N)_4]$, (I), has non-crystallographic D_{2d} molecular symmetry and contains an approximately tetrahedrally coordinated V atom with dimethylamido ligands. Each N atom features a nearly trigonal planar geometry. There are two independent molecules of (I) in the asymmetric unit. The results are compared with those previously reported for gas-phase electron-diffraction studies [Haaland, Rypdal, Volden & Andersen (1992). *J. Chem. Soc. Dalton Trans*. pp. 891–895].

Comment

The study of transition metal amido complexes has been an important area of chemistry since the pioneering work in the 1960s and early 1970s (Lappert *et al.*, 1980, and references therein), and continues to attract considerable interest (Gade, 2000, and references therein). Within the large family of complexes with secondary amido ligands of the type NR_2 (where R is a hydrocarbyl or other non-H group), the simplest are the mononuclear homoleptic dimethylamido species $[M(NMe_2)_n]$ (n = 4, 5 or 6). The following members of this family have been crystallographically characterized: $[Nb(NMe_2)_5]$ (Heath & Hursthouse, 1971), $[Ta(NMe_2)_5]$ (Batsanov *et al.*, 1999), $[Mo(NMe_2)_4]$ (Chisholm *et al.*, 1978), $[Mo(NMe_2)_6]$ (Chisholm *et al.*, 1987) and $[W(NMe_2)_6]$ (Bradley *et al.*, 1969). Tetrakis(dimethylamido)zirconium, usually referred to as a four-coordinate species, '$[Zr(NMe_2)_4]$', actually adopts the NMe_2-bridged dimeric structure $[Zr_2(\mu\text{-}NMe_2)_2(NMe_2)_6]$ in the solid state (Chisholm *et al.*, 1988). While no first row transition metal dimethylamido complex has been crystallographically characterized, gas-phase diffraction studies of $[M(NMe_2)_4]$ [M = Ti or V, (I)] have been reported (Haaland *et al.*, 1992).



(I)

In the course of our studies on early transition metal amido chemistry (Skinner *et al.*, 2000), we obtained crystals of (I). The unit cell contains two crystallographically independent molecules, the geometric features of which are essentially identical. Molecules of (I) feature molecular D_{2d} symmetry, as illustrated in Fig. 1, where (I) is viewed along the molecular C_2 (coincident with S_4) axis; the molecular mirror planes contain V1(A)/N1(A)/N4(A) and V1(A)/N2(A)/N3(A). The angles between the normals to the planes comprising these atoms is 91.6 (2) and 91.7 (2)° for the systems containing V1 and V1A, respectively. The V—N distances and V—N—C angles span the typical ranges reported for vanadium amides (Fletcher *et al.*, 1996; Allen & Kennard, 1993). The angles subtended at V1 and V1A fall into two groups, with the division between the values being more pronounced for V1 on which further discussion will focus. The N1—V1—N4 and N2—V1—N3 angles of 115.28 (6) and 111.42 (6)° are significantly larger than the ideal tetrahedral angle of *ca* 109.5°, while the remaining four N—V1—N angles [range 106.26 (5)–100.00 (6)°] are less. The N atoms are approximately sp^2-hybridized (*i.e.* having a near-trigonal planar coordination). However, the sums of the angles subtended at each N atom span the ranges 355.2 (3)–358.1 (3)° (for V1, average = *ca* 357.2°) and 355.4 (3)–356.7 (3)° (for V1A, average = *ca* 356.1°), showing that there is a slight but persistent degree of pyramidalization of these atoms. As Fig. 2 emphasizes for atoms N2 and N3 of the molecule containing V1, the sense of distortion is to move the methyl C atoms (*i.e.* C3, C4, C5 and C6) into the more 'open' N2—V1—N3 aperture. This feature is repeated for all of the NMe_2 groups and may reflect intramolecular steric effects.

The molecular structure of $[V(NMe_2)_4]$, (I), is analogous to that of the d^2 molybdenum tetrakis(dimethylamido) complex $[Mo(NMe_2)_4]$ (Chisholm *et al.*, 1978), which also has molecular D_{2d} symmetry but shows no apparent trends in the N—Mo—N angles within reported errors. No congeneric group 5 d^1 dimethylamido complexes $[M(NMe_2)_4]$ (M = Nb or Mo) have been crystallographically characterized. However, homologous pseudo-tetrahedral heavier congeners of (I) with the

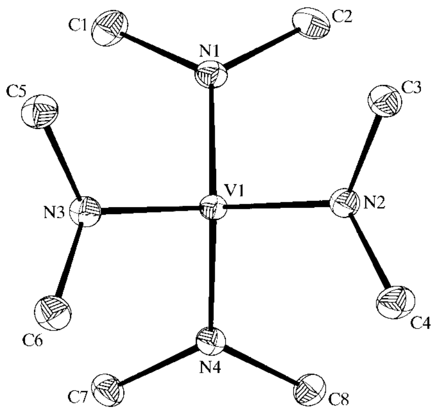


Figure 1
View of one of the two crystallographically independent molecules of (I) along the molecular C_2 (S_4) axis with the atom-numbering scheme. The numbering scheme for the second molecule is the same except that the suffix 'A' is added to the numerical labels. The displacement parameters are drawn at the 25% probability level and H atoms have been omitted for clarity.

© 2001 International Union of Crystallography • Printed in Great Britain – all rights reserved

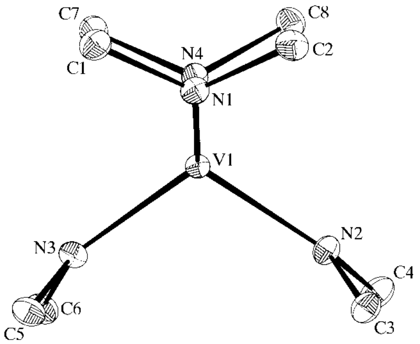


Figure 2
View of one of the two crystallographically independent molecules of (I) perpendicular to one of the molecular mirror planes and emphasizing the pyramidilization of the N2 and N3 atoms. The displacement parameters are drawn at the 25% probability level and H atoms have been omitted for clarity.

bulkier amido ligands NPh_2 and NEt_2 have been reported, namely $[Nb(NPh_2)_4]$ (Bott *et al.*, 1995) and $[Ta(NEt_2)_2(NPh_2)_2]$ (Suh & Hoffman, 1996), respectively. These Nb and Ta complexes have approximate D_{2d} symmetry within the core $M(NC_2)_4$ units.

As mentioned, Haaland *et al.* (1992) have reported the gas-phase electron-diffraction (GED) structure of $[V(NMe_2)_4]$, (I), which was found to be approximately D_{2d} symmetrical. It is interesting to compare the X-ray and GED results. The GED model was fitted assuming S_4 molecular symmetry and planar amido groups (*i.e.* local C_2 symmetry for the NMe_2 fragments). The agreement between the X-ray and GED structures is excellent (for non-H atom distances) to very good (for non-H atom angles) as shown by the following data (given as GED values, followed by X-ray derived values in brackets for both molecules): V—N = 1.879 (4) Å [range 1.8652 (12)–1.8721 (12), average *ca* 1.87 Å], N—C = 1.457 (3) Å [range 1.4512 (19)–1.457 (2)°, average *ca* 1.45 Å], V—N—C = 123.2 (3)° [range 120.0 (1)–124.7 (1)°, average *ca* 122.7°], and N—V—N = 100.6 (5) and 114.1 (1)° (two independent values) [between pairs of atoms lying on the same molecular mirror planes: range 110.73 (5)–115.28 (6)°, average *ca* 112.2°; between pairs of atoms related by molecular C_2' axes: range 106.26 (5)–110.03 (6)°, average *ca* 108.1°]. From the two structure determinations (GED and X-ray) it is evident that there is a clear and persistent deviation of the N—V—N angles from those expected for a regular tetrahedron, as expected on electronic grounds (Haaland *et al.*, 1992).

Comparisons can also be made between the neutral d^1 vanadium(4+) complex (I) and the d^2 anionic tetrakis(diphenylamido)vanadium(3+) species $[V(NPh_2)_4]^-$ (Song *et al.*, 1996), and with the cationic d^0 tetrakis(diethylamido)-vanadium(5+) species $[V(NEt_2)_4]^+$ (Choukroun *et al.*, 1998). For $[V(NEt_2)_4]^+$, the V—N distances span the range 1.817 (3)–1.847 (3) Å (average = *ca* 1.83 Å) and for $[V(NPh_2)_4]^-$, the V—N distances span the range 1.988 (7)–2.004 (7) Å (average = *ca* 1.99 Å). The average V—N distances for the vanadium(5+) and vanadium(3+) complexes lie either side of that (*ca* 1.87 Å) for (I), in line with the general expected changes in atomic radius with formal oxidation state (without taking into particular account the different N-substituents in the three complexes) and their electronic structures (Chisholm *et al.*, 1978; Chisholm & Clark, 1987). Neither of the complexes $[V(NEt_2)_4]^+$ or $[V(NPh_2)_4]^-$ possess D_{2d} symmetry in the solid state, also as predicted by theoretical treatments of the bonding in $[M(NR_2)_4]$ complexes, nor are there any apparent trends in the N—V—N angles.

Experimental

Tetrakis(dimethylamido)vanadium was prepared according to previously described procedures (Haaland *et al.*, 1992). Sublimation (298 K, 2 × 10^{-3} mbar) of the crude product afforded the title compound as very air-sensitive dark-green blocks.

Crystal data

$[V(C_2H_6N)_4]$
$M_r = 227.25$
Triclinic, $P\bar{1}$
$a = 8.2903$ (2) Å
$b = 12.0158$ (2) Å
$c = 13.8350$ (3) Å
$\alpha = 75.6616$ (10)°
$\beta = 79.4036$ (11)°
$\gamma = 84.9664$ (9)°
$V = 1311.18$ (5) Å^3

$Z = 4$
$D_x = 1.151$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5348 reflections
$\theta = 1.0$–27.5°
$\mu = 0.73$ mm^{-1}
$T = 150$ K
Block, dark green
0.30 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
CCD scans
Absorption correction: multi-scan (*DENZO*; Otwinowski & Minor, 1997)
$T_{min} = 0.864$, $T_{max} = 0.864$
10654 measured reflections

5886 independent reflections
4773 reflections with $I > 2\sigma(I)$
$R_{int} = 0.02$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$

Refinement

Refinement on F
$R = 0.033$
$wR = 0.043$
$S = 1.05$
5883 reflections
427 parameters
All H-atom parameters refined

Chebychev polynomial with 5 parameters (0.895, 0.532, 0.456, −0.0541, −0.147) (Carruthers & Watkin, 1979)
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.83$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

V1—N1	1.8721 (12)	V1*A*—N2*A*	1.8653 (12)
V1—N2	1.8692 (13)	V1*A*—N3*A*	1.8691 (13)
V1—N3	1.8664 (13)	V1*A*—N4*A*	1.8681 (13)
V1—N4	1.8721 (12)	N1*A*—C1*A*	1.457 (2)
V1*A*—N1*A*	1.8652 (12)		
N1—V1—N2	106.53 (6)	N1*A*—V1*A*—N2*A*	107.16 (5)
N1—V1—N3	108.41 (6)	N1*A*—V1*A*—N3*A*	109.74 (6)
N2—V1—N3	111.42 (6)	N2*A*—V1*A*—N3*A*	111.48 (6)
N1—V1—N4	115.28 (6)	N1*A*—V1*A*—N4*A*	110.73 (5)
N2—V1—N4	109.00 (6)	N2*A*—V1*A*—N4*A*	110.03 (6)
N3—V1—N4	106.26 (5)	N3*A*—V1*A*—N4*A*	107.73 (6)
V1—N1—C1	123.67 (11)	V1*A*—N1*A*—C1*A*	123.3 (1)
V1—N1—C2	123.62 (11)	V1*A*—N1*A*—C2*A*	120.92 (11)
V1—N2—C3	122.5 (1)	V1*A*—N2*A*—C3*A*	124.7 (1)
V1—N2—C4	123.70 (11)	V1*A*—N2*A*—C4*A*	120.0 (1)
V1—N3—C5	122.77 (11)	V1*A*—N3*A*—C5*A*	124.03 (13)
V1—N3—C6	121.60 (11)	V1*A*—N3*A*—C6*A*	120.92 (11)
V1—N4—C7	122.6 (1)	V1*A*—N4*A*—C7*A*	121.02 (11)
V1—N4—C8	123.8 (1)	V1*A*—N4*A*—C8*A*	123.65 (11)

Acta Cryst. (2001). C**57**, 902–904 Stuart R. Dubberley *et al.* • $[V(C_2H_6N)_4]$ **903**

Three low-angle reflections (100, 110, 020) with severely underestimated $|F_o|$ were omitted from the refinement cycles. Otherwise refinement was carried out against all unique data. The range of refined C—H bond lengths is 0.89 (3)–1.02 (3) Å.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin, Prout *et al.*, 1996); molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996); software used to prepare material for publication: *CRYSTALS*.

We thank the EPSRC for the provision of a diffractometer and a studentship (to BRT). We also wish to acknowledge the use of the EPSRC's Chemical Database at Daresbury.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1056). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.

Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 1045–1050.

Batsanov, A. S., Churakov, A. V., Howard, J. A. K., Hughes, A. K., Johnson, A. J., Kingsley, A. J., Neretin, I. S. & Wade, K. (1999). *J. Chem. Soc. Dalton Trans.* pp. 3867–3876.

Bott, S. G., Hoffman, D. M. & Rangarajan, S. P. (1995). *Inorg. Chem.* **34**, 4305–4310.

Bradley, D. C., Chisholm, M. C., Heath, C. E. & Hursthouse, M. B. (1969). *J. Chem. Soc. D*. pp. 1261–1262.

Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* A**35**, 698–699.

Chisholm, M. H. & Clark, D. L. (1987). *Comments Inorg. Chem.* **6**, 23–40.

Chisholm, M. H., Cotton, F. A. & Extine, M. W. (1978). *Inorg. Chem.* **17**, 1329–1332.

Chisholm, M. H., Hammond, C. E. & Huffman, J. C. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1423–1424.

Chisholm, M. H., Hammond, C. E. & Huffman, J. C. (1988). *Polyhedron*, **7**, 399–400.

Choukroun, R., Moumboko, P., Chevalier, S., Etienne, M. & Donnadieu, B. (1998). *Angew. Chem. Int. Ed.* **37**, 3169–3172.

Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.

Gade, L. H. (2000). *Chem. Commun.* pp. 173–181.

Haaland A., Rypdal, K., Volden, H. V. & Andersen, R. A. (1992). *J. Chem. Soc. Dalton Trans.* pp. 891–895.

Heath, C. & Hursthouse, M. B. (1971). *J. Chem. Soc. D*, pp. 143–144.

Lappert, M. F., Power, P. P., Sanger, A. R. & Srivastava, R. S. (1980). *Metal and Metalloid Amides*. Chichester: Ellis Horwood–Wiley.

Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.

Skinner, M. E. G., Cowhig, D. A. & Mountford, P. (2000). *Chem. Commun.* pp. 1167–1168.

Song, J.-I. & Gambarotta, S. (1996). *Chem. Eur. J.* **2**, 1258–1263.

Suh, S. & Hoffman, D. M. (1996). *Inorg. Chem.* **35**, 5015–5018.

Watkin, D. J., Prout, C. K., Carruthers, R. J. & Betteridge, P. (1996). *CRYSTALS*. University of Oxford, England.

Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. University of Oxford, England.