default settings of the refinement program. The water H atoms were found from difference Fourier maps and were treated as riding atoms. The H atoms bonded to C17 show rotational disorder about the twofold axis and their occupancies were fixed at 0.5. In the nitrate group, one O atom was found disordered about a twofold axis. The N50 atom lies on the axis, whereas the original peak for the O51 atom was found about 0.75 Å to the side of it. The disorder of NO_3 was modeled using the *SADI* and *DFIX* instructions in the *SHELXL*97 program (Sheldrick, 1997*a*), where N—O and O···O distances were restrained. The O51 atom was constrained to a special position, lying on the crystallographic twofold axis, and was refined isotropically with 0.5 site occupancy. The highest peak (1.45 e Å^{-3}) and deepest hole (-0.70 e Å^{-3}) are located 0.95 and 0.75 Å, respectively, from O51.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *SET*4 in *CAD*-4 *EXPRESS*. Data reduction: *HELENA* (Spek, 1996). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *ZORTEP* (Zsolnai *et al.*, 1996). Software used to prepare material for publication: *SHELXL*97. All calculations were performed on a PC/PentiumII computer running *LINUX*.

This work was supported by PADCT, CNPq and FINEP.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1031). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1636–1639

The twinned structure of the μ-isopropoxido-diisopropoxido(p-tolylimido)-vanadium(V) dimer,† twin refinement against CCD area-detector data

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(*Received 12 February 1999; accepted 5 March 1999*)

Abstract

The title compound, $[V_2(C_7H_7N)_2(C_3H_7O)_6]$, crystallizes as a non-merohedrical twin in the triclinic space group $P\bar{1}$. The twin operation is a twofold rotation around the reciprocal [110] direction, leading to split reflections. The intensities of both twin domains were evaluated separately and the structure refinement resulted in a population ratio of 72.6 (1):27.4 (1). The molecular geometry of this dimeric compound is in line with similar vanadium compounds found in the literature. The vanadium is in a distorted trigonal-bipyramidal environment. The dimer is formed by the asymmetric bridging of two isopropoxido groups with bond lengths of 1.8560 (13) and 2.2151 (13) Å.

Comment

Catalytic polymerization of α-olefins by the use of homogeneous systems is of commercial interest for the production of tailored polymers (Ewen, 1997). Although group IV metal-based systems generally show enhanced activity, vanadium catalysts have several favourable properties, for example, in the production of polymers with a narrow molecular-weight distribution, in the preparation of copolymers or in the generation of syndiotactic polypropylene (Murphy & Turner, 1997). In the context of our investigations in this field, we succeeded in the crystallization of the title compound, (I). While the association in solution was established to be monomeric by cryoscopic molecular-weight determination in benzene, we were interested in the aggregation in the crystalline state. It is known from similar com-

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† Systematic name: di-μ-isopropoxido-bis[diisopropoxido(4-methylphenylimido)vanadium(V)].

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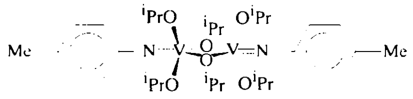
ISSN 0108-2701 © 1999

pounds that dimerization is possible (Priebsch & Rehder, 1985).



(I)

The complex turned out to be dimeric in the solid state, with two isopropoxido groups bridging two V atoms (Fig. 1). The coordination environment of each vanadium is completed with two isopropoxido and one *p*-tolylimido molecule. The dimer expresses a crystallographic C_i symmetry and an approximate non-crystallographic C_{2h} symmetry. The exact C_{2h} symmetry is broken mainly by the orientation of the phenyl ring; the dihedral angle of the phenyl ring with respect to the central V—O2—V^{i}—O2^{i} plane is 77.46 (6)° instead of 90° [symmetry code: (i) $-x$, $1-y$, $1-z$]. The bonds of the bridging O atoms to the V atoms are not symmetrical, with O2—V distances of 1.8560 (13) and 2.2151 (13) Å. Notwithstanding this large difference, both distances indicate bonding interactions on the basis of atomic radii. The V—O2—V^{i} angle of 107.33 (6)° is an additional indication of bonding. Nevertheless, the non-bridging isopropoxido groups show shorter distances to vanadium [1.8014 (14) and 1.8037 (14) Å] than the μ-isopropoxido group.

The geometry at the imido N atom is nearly linear [C1—N1—V 176.18 (16)°], as in all known vanadium–imido compounds. The V—N1 distance of 1.6709 (16) Å is longer than in comparable *tert*-butylimido compounds, which is to be expected because of the electron-withdrawing effect of the phenyl group. Other vanadium–phenylimido complexes show V—N distances in the same range (Murphy & Turner, 1997).

The vanadium centre is five-coordinate with a geometry best described as a distorted trigonal bipyramid. The O1, O2 and O3 atoms form the basal plane, with N1 and O2^{i} situated in axial positions. This means that the axial positions are occupied by the shortest [1.6709 (16) Å] and the longest bond [2.2151 (13) Å]. This is in conflict with valence-shell electron-pair repulsion (VSEPR) theory, which was extended recently to include vanadium(V) complexes (Gillespie *et al.*, 1996). VSEPR theory would predict the shortest bonds to be equatorial and the longest to be axial in the trigonal bipyramid. In the present case, the violation of the VSEPR model may be caused by the dimer formation. But more reasonably, the steric requirements of the whole ligands should be taken into account here, and not only the nearest bonds to the metal.

In the crystal, the molecules are packed as planes with [001] and [$1\bar{1}0$] as base vectors (Fig. 2). There are no intermolecular bonds either in the plane or between the planes. This gives rise to the possibility of stacking faults and this is exactly what was found, a twin with 110 as the twin axis. A 180° rotation around the twin axis leaves the orientation of the plane nearly unchanged, because the *a* and *b* axes have similar lengths. Of course, the twin operation changes the positions and orientations of the dimers in the plane. The treatment of this twin problem is described in the *Experimental* section.

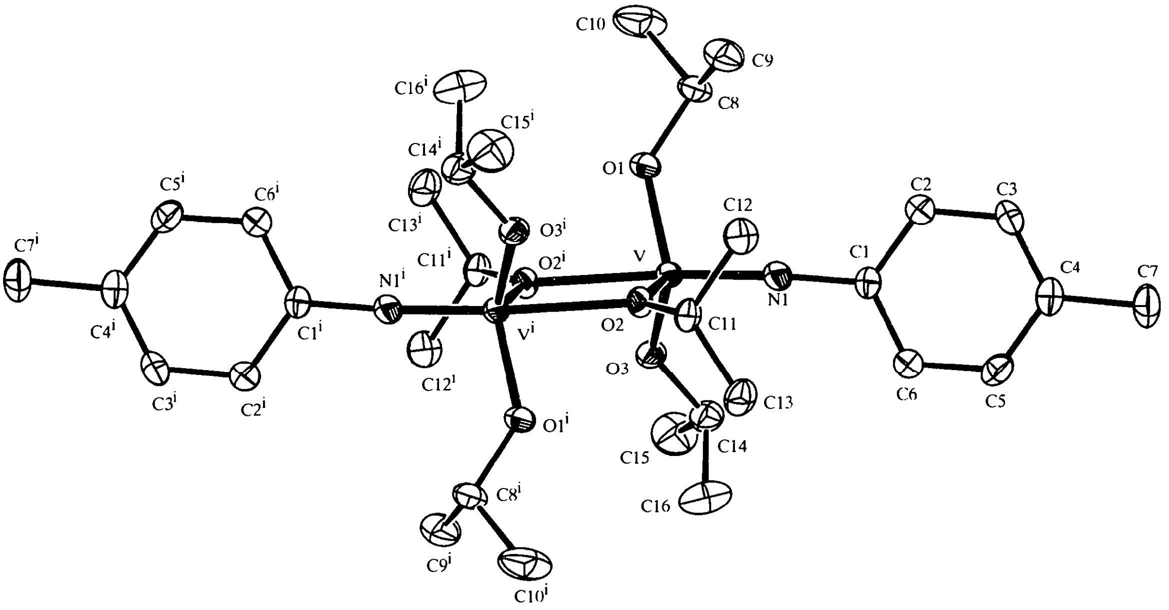


Fig. 1. Displacement-ellipsoid plot of the dimer (50% probability level), including the atom-numbering scheme. H atoms have been omitted for clarity. [Symmetry code: (i) $-x$, $1-y$, $1-z$.]

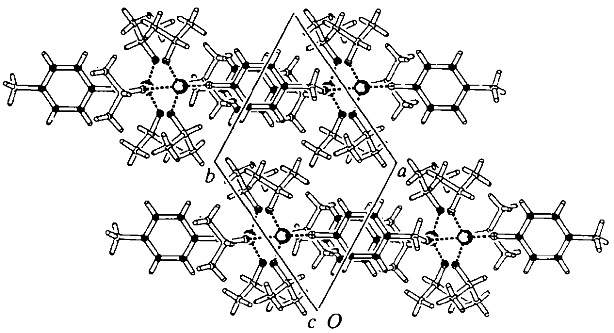


Fig. 2. Projection on the crystallographic *ab* plane, showing the molecular packing in two-dimensional sheets running parallel to *c*. The twin axis is up and perpendicular to the sheets.

Experimental

$VO(O^iPr)_3$ was prepared according to literature procedures (Prandtl & Hess, 1913). A solution of *p*-tolyl isocyanate (4.13 ml, 32.7 mmol) and $VO(O^iPr)_3$ (7.29 g, 32.4 mmol) in octane (30 ml) was refluxed for 3 h, after which the solvent was removed *in vacuo*. Recrystallization from hexane at 243 K gave dark-orange crystals (7.20 g, 67%; m.p. 316 K). Analysis for $C_{16}H_{28}NO_3V$: calculated C 57.65, H 8.47, N 4.20%; found C 57.72, H 8.53, N 4.18%; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.37 (*d*, 18H, $^3J_{H,H}$ = 6.1 Hz, $OCHMe_2$), 2.35 (*s*, 3H, NAr—Me), 5.13 (septet, 3H, $^3J_{H,H}$ = 6.1 Hz, $OCHMe_2$), 7.03 and 7.08 (*AB*, 4H, $^3J_{H,H}$ = 8.5 Hz, NAr); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.2 (NAr—Me), 26.9 ($OCHMe_2$), 79.6 (broad, $OCHMe_2$), 125.2 (NAr—C^2 and NAr—C^6), 128.9 (NAr—C^3 and NAr—C^5), 135.5 (NAr—C^4), NAr—C^1 not observed; ^{51}V NMR ($CDCl_3$, 78.9 MHz): δ −611 ($t_{1:1:1}$, $^1J_{V,N}$ = 114 Hz).

Crystal data

$[V_2(C_7H_7N)_2(C_3H_7O)_6]$
$M_r = 666.67$
Triclinic
$P\overline{1}$
$a = 9.7491 (6)$ Å
$b = 10.0291 (6)$ Å
$c = 11.1681 (5)$ Å
$\alpha = 85.297 (4)°$
$\beta = 71.869 (4)°$
$\gamma = 61.3013 (18)°$
$V = 907.28 (9)$ Å^3
$Z = 1$
$D_x = 1.220$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters: see *Experimental* text
$\mu = 0.555$ mm^{-1}
$T = 150 (2)$ K
Plate
$0.50 \times 0.38 \times 0.06$ mm
Dark orange

Data collection

Nonius KappaCCD diffractometer
φ scans ($\kappa = 0$) + additional ω scans
Absorption correction: none
18 748 measured reflections
18 748 independent reflections

16 570 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.174$
$S = 1.186$
18 748 reflections
191 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 3.2555P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.672$ e Å^{-3}
$\Delta\rho_{min} = -0.455$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

V—N1	1.6709 (16)	V—O2	1.8560 (13)
V—O3	1.8014 (14)	V—O2'	2.2151 (13)
V—O1	1.8037 (14)	N1—C1	1.389 (2)
N1—V—O3	100.17 (7)	N1—V—O2'	173.38 (7)
N1—V—O1	103.29 (7)	O3—V—O2'	80.79 (6)
O3—V—O1	113.52 (7)	O1—V—O2'	82.14 (6)
N1—V—O2	101.31 (7)	O2—V—O2'	72.67 (6)
O3—V—O2	118.48 (6)	V—O2—V'	107.33 (6)
O1—V—O2	116.22 (6)		

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

Intensities were measured with a Nonius KappaCCD diffractometer. An initial orientation matrix and initial cell parameters were obtained by indexing, integrating and post-refinement with the *DENZO* software (Otwinowski & Minor, 1997). A number of reflections not indexed by this orientation matrix was then extracted from the measured CCD images. These reflections were indexed with the program *DIRAX* (Duisenberg, 1992). Both orientation matrices are related by a twofold rotation around 110. All frames were then evaluated twice using the *EVAL*14 software (Duisenberg, 1998), once with the first orientation matrix, equivalent to the *DENZO* matrix, and subsequently with the second, obtained by rotation of the *DENZO* matrix. Both data sets were given different batch numbers for *SHELXL*97 (Sheldrick, 1997) refinement with *HKLF*5. Overlapping reflections, as signalled by *EVAL*14, occur twice in the reflection list with the indices of both domains.

The twin refinement was performed with *SHELXL*97 using the data in *HKLF*5 format and refinement of batch scale factors (Herbst-Irmer & Sheldrick, 1998). Symmetry equivalent reflections were not merged (*SHELXL*97 procedure); all measured intensities were treated as independent data in the refinement. R_{int} is not defined in this case. The refinement resulted in a ratio of 72.6 (1):27.4 (1) for the two twin domains.

Data collection: *COLLECT* (Nonius, 1998). Cell refinement: see above. Data reduction: see above. Program(s) used to solve structure: *DIRDIF*97 (Beurskens *et al.*, 1997). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *PLATON* (Spek, 1998). Software used to prepare material for publication: *SHELXL*97.

The investigations were supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (CW–NWO). The synthetic work was carried out in connection with NIOK, The Netherlands Institute for Catalysis Research, and supported by the Department of Economic Affairs of The Netherlands.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1541). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1639–1641

Diiodobis(4-methoxybenzaldehyde thiosemicarbazone-*S*)cadmium(II)

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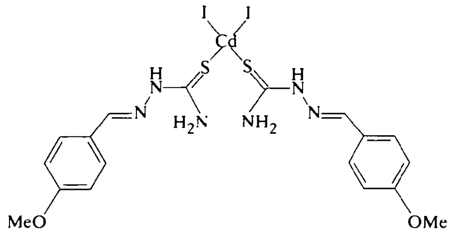
(Received 25 May 1999; accepted 23 June 1999)

Abstract

The title complex, $[CdI_2(C_9H_{11}N_3OS)_2]$, contains distorted tetrahedral $[CdI_2L_2]$ units (where L is 4-methyoxybenzaldehyde thiosemicarbazone), in which L molecules are *S*-bonded in a monodentate mode to the cadmium ion. Principal dimensions include Cd—S 2.5875 (10) and 2.5795 (10) Å, and Cd—I 2.7020 (4) and 2.7470 (4) Å.

Comment

Transition metal complexes of thiosemicarbazones have been studied extensively and have been the subject of several recent reviews (Campbell, 1975; Padhye & Kauffman, 1985; Lukevics *et al.*, 1995). Thiosemicarbazones have been shown to exhibit a range of biological activities, which is considered to be related to their ability to chelate metals. Recently, there has been considerable interest in the chemistry of Schiff base compounds containing thiosemicarbazones and their IIB group metal complexes, due to their non-linear optical properties (Xu *et al.*, 1987; Hu *et al.*, 1995; Tian *et al.*, 1997). It might be expected that the design and synthesis of IIB metal complexes derived from thiosemicarbazone may be a possible way of obtaining potential non-linear optical materials. In this paper, the synthesis and crystal structure of the title complex, (I), are reported.



(I)

The molecular structure of (I), together with the atom-labelling scheme, is shown in Fig. 1. The crystals contain individual neutral $[CdI_2L_2]$ molecules. In (I), the Cd—S [2.5875 (10) and 2.5795 (10) Å] and Cd—I [2.7470 (4) and 2.7020 (4) Å] distances are almost equal, and are comparable with compounds with terminal *M*—S and *M*—I bonds. Thus, the strong distortion in the tetrahedral environment of the four donor atoms in (I) is explained on the basis of strong stereo interactions between the two molecules of the ligand in the complex. Comparing (I) with the free ligand (Tian *et al.*, 1997), some bond distances are different. The obvious lengthening of the C—S bond distances in (I) is as expected for a C═S double bond, and reflects the coordination of the ligand to the S atom. The angles around the Cd atom in (I) vary from 100.02 (3) to 115.73 (1)°. The bond lengths in the two thiosemicarbazone groups show slight differences and the C═N, N—N, N—Csp^2 and C═S bond distances are similar to the values reported in the literature (Fun *et al.*, 1995; Tian *et al.*, 1996), which shows that the molecule is in the keto tautomeric form. The C═N bond is in the *E* configuration.

In similar thiosemicarbazone derivatives, there is crystallographic evidence of both *N*,*S*-chelates and monodentate *S*- or *N*-ligands. $[CdI_2L_2]$ complexes present crystallographic evidence for *S*-bonding. The preference for S atoms (a softer donor than N) is not

Acta Crystallographica Section C
ISSN 0108-2701 © 1999