Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

[Di-2-pyridyl ketone N^4,N^4-(butane-1,4-diyl)thiosemicarbazonato-κ^3N,N',S]dioxovanadium(V)

Varughese Philip,[a] E. Manoj,[a] M. R. Prathapachandra Kurup[a]* and Munirathinam Nethaji[b]

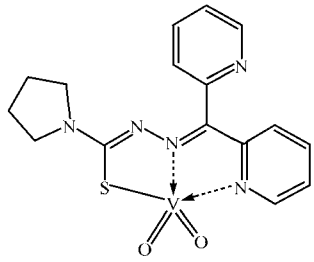
[a]Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India, and [b]Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India
Correspondence e-mail: mrp@cusat.ac.in

Received 11 July 2005
Accepted 22 September 2005
Online 22 October 2005

The V^V atom in the title complex, $[V(C_{16}H_{16}N_5S)O_2]$, is five-coordinate in a highly distorted square-pyramidal geometry, with the pyridyl N, the azomethine N and the thiolate S atoms of the di-2-pyridyl ketone N^4,N^4-(butane-1,4-diyl)thiosemicarbazone ligand and one oxo ligand occupying the basal coordination positions, while the second oxo ligand occupies the apical position. The molecules are interconnected by weak intermolecular interactions, mainly of the C—H···O type, involving the apical oxo atom.

Comment

Thiosemicarbazones possessing NNS, NNO and ONS donor sites have emerged as an important class of biologically active ligands in the past few decades. The biological activity of thiosemicarbazones is related to their chelating ability with transition metal ions, bonding through their S and N atoms (Klayman *et al.*, 1984), and also to the parent aldehyde or ketone (Padhye & Kauffman, 1985; Lukevics *et al.*, 1995). Among thousands of screened compounds (Klayman *et al.*, 1979), 2-acetylpyridine thiosemicarbazones having the N4 atom disubstituted or as a part of the ring system possess the highest activity as antimalarial agents. Compared with the extensive studies on 2-acetylpyridine thiosemicarbazones (Garg *et al.*, 1988), there are few reports on the metal complexes of thiosemicarbazones derived from di-2-pyridyl ketone (Duan *et al.*, 1996; Philip *et al.*, 2004). Vanadium coordination is seen in a variety of chemical and biological systems, thereby extending the inorganic pharmacology of thiosemicarbazones. Much of the biochemistry of vanadium is centered around the ability of vanadate ions, $[H_2V^VO_4]^-$, to adopt either a four-coordinate tetrahedral geometry or a five-coordinate trigonal–bipyramidal geometry (Crans, 1994). The establishment of the presence of a V^{IV}/V^V equilibrium in the reducing environment of living cells (Degani *et al.*, 1981; Li *et al.*, 1996), and the range of biological activities, including antitumor, fungicidal, bactericidal, anti-inflammatory and antiviral activities, of thiosemicarbazones (Sreekanth & Kurup, 2003), prompted us to undertake the crystal structure determination of the title compound, (I).



(I)

Recently, di-2-pyridyl ketone 4-methylthiosemicarbazone, acting as a pentadentate ligand towards rhenium carbonyls (Pereiras-Gabian *et al.*, 2005), has been reported. We have reported the crystal structures of the present ligand, di-2-pyridyl ketone N^4,N^4-(butane-1,4-diyl)thiosemicarbazone (Usman *et al.*, 2002; hereafter NBT), di-2-pyridyl ketone 4-methyl-4-phenylthiosemicarbazone (Philip *et al.*, 2004) and the transition metal complexes of these ligands (Philip *et al.*, 2004, 2005). We report here the first vanadium complex of the NBT ligand with the ligand in the tridentate form.

In the formation of (I), the NBT moiety loses one H atom from its tautomeric thiol form and coordinates to vanadium through atoms N1, N3 and S1, which together with the O2 oxo ligand form the basal plane of a highly distorted square pyramid (Fig. 1 and Table 1). The atoms defining the basal plane have an average deviation of 0.190 (4) Å from the plane; the second oxo ligand, O1, fills the apical position, and atoms V1 and O1 lie 0.539 (1) and 2.132 (2) Å from this plane. The O2—V1—N3 and O1—V1—N3 angles of 133.74 (8) and 116.82 (8)° are consistent with this description. The increase in C—S bond length from 1.671 (4) to 1.734 (2) Å together with a decrease in the N4—C12 bond length from 1.374 (4) to 1.329 (2) Å in the compound (I) compared with NBT confirms the coordination in the thiolate form. The *E* configuration

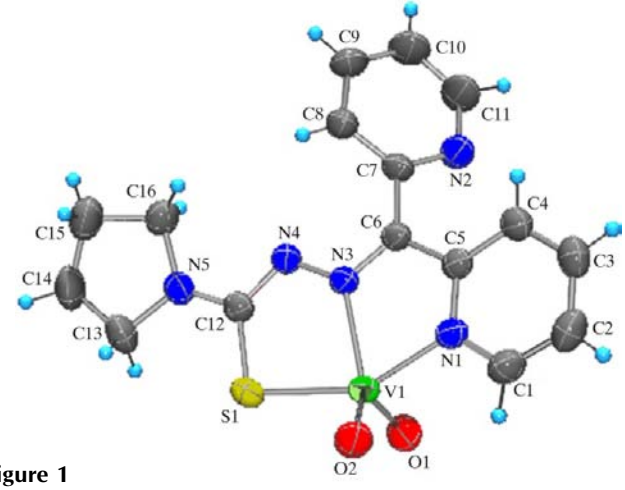


Figure 1
A view of compound (I), shown with 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

  DOI: 10.1107/S0108270105030337

about the C6—N3 and C12—N4 bonds relative to the N3—N4 bond of the thiosemicarbazone group is retained in (I).

Typically, vanadium(V) forms square-pyramidal five-coordinate complexes or octahedral six-coordinate complexes, except when significant steric constraints, such as those provided by a protein, are present (Mokry & Carrano, 1993). In (I), the τ value for the complex is 0.279, indicating a significant distortion towards the trigonal–bipyramidal form (Addison *et al.*, 1984; Cornman *et al.*, 1997). This configuration is in agreement with the values found in the dioxovanadium(V) complex of 2-[2-(*N*,*N*′-dimethylaminoethyliminomethyl]phenol (Xie *et al.*, 2004). The formation of (I) in a highly distorted square-pyramidal rather than trigonal–bipyramidal geometry may be attributed to the electronic and/or steric requirements.

The V1—O1 distance is 0.009 (2) Å shorter than the V1—O2 distance, in agreement with values in similar dioxovanadium complexes (Sreekanth *et al.*, 2003; Xie *et al.*, 2004), but in contrast to another dioxovanadium complex (Maurya *et al.*, 2002), where the two V—O distances are equal. The O—V—O angle is similar to those reported previously for the *cis*-VO_2 moiety in other complexes (Xie *et al.*, 2004; Sreekanth *et al.*, 2003; Melchior *et al.*, 1999; Asgedom *et al.*, 1996; Ligtenbarg *et al.*, 1999; Maurya *et al.*, 2002). The V1—N1 bond is 0.098 (2) Å shorter than the V1—N3 bond, thus confirming the strength of the pyridyl *N*-coordination; this situation is also found in the dioxovanadium complex of 2-acetylpyridine morpholyl-3-thiosemicarbazone (Sreekanth *et al.*, 2003) and the dioxovanadium complex of the ligand derived from 2-acetylpyridine and *S*-benzyldithiocarbazate (Maurya *et al.*, 2002). The thiosemicarbazone moiety, comprising atoms C6, N3, N4, C12, S1 and N5, shows a slight deviation from planarity after coordination, the maximum out of plane deviation at atom N4 changing from 0.0140 (1) Å for NBT to −0.0667 (3) Å for (I).

Ring-puckering analyses (Cremer & Pople, 1975) reveal that the pyrrolidine ring (*Cg*3), comprising atoms N5, C13, C14, C15 and C16, is closest to a twist form on atoms C14 and C15, with puckering parameters q_2 = 0.337 (3) Å and φ = 278.1 (4)°, in contrast to the approximate envelope conformation in NBT. On complex formation, the thiosemicarbazone group forms two new five-membered rings, *viz.* *Cg*1 [comprising atoms N3, N4, C12, S1 and V1, with a maximum out-of-plane deviation of 0.0608 (3) Å for atom N3] and *Cg*2 [comprising atoms N1, C5, C6, N3 and V1, with a maximum deviation of 0.057 (2) Å for atom N3]. The other two rings, *Cg*4 (N1/C1–C5) and *Cg*5 (N2/C7–C11), are planar pyridyl rings; the *Cg*4 ring is close to being coplanar with the thiosemicarbazone moiety, with a dihedral angle of 9.48 (1)° between their planes. The coordination of the azomethine N atom to the V^V atom results in a slight redistribution of electron density along the thiosemicarbazone chain. This leads to a barely significant increase in length of 0.014 (4) Å for the azomethine C6—N3 bond, a decrease in length of 0.045 (4) Å for the N4—C12 bond and an insignificant decrease of 0.002 (4) Å in the N3—N4 bond length in the complex compared with NBT.

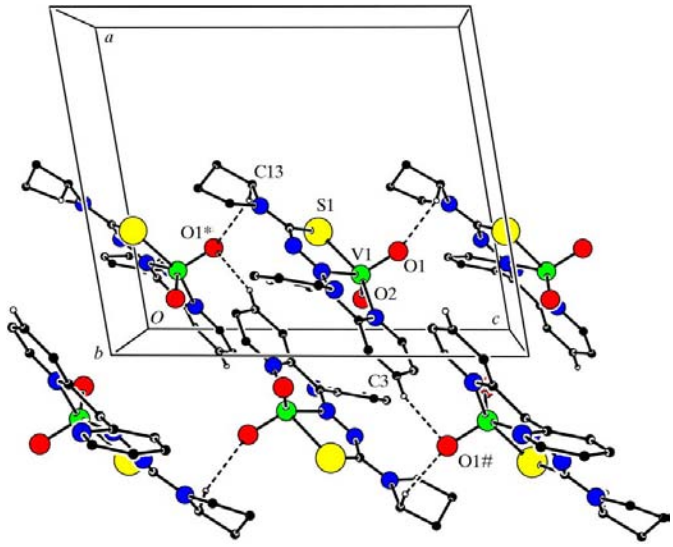


Figure 2
Part of the unit-cell of (I), viewed along the *b* axis, with the main intermolecular hydrogen bonds shown as dashed lines (Table 2). The asterisk (*) and hash (#) symbols indicate atoms at equivalent positions $(x, \frac{1}{2}-y, z-\frac{1}{2})$ and $(-x, \frac{1}{2}+y, \frac{3}{2}-z)$, respectively.

In the crystal packing, each molecule is linked principally through one normal and one weak intermolecular C—H···O hydrogen bond utilizing oxo atom O1 (Fig. 2 and Table 2). These V═O···H—C interactions are in agreement with previous reports (Mokry & Carrano, 1993). The crystal structure cohesion may also be reinforced by weak aromatic π–π stacking interactions and a weak V1— O2···π interaction with pyridyl ring *Cg*5 [symmetry code: $-x, 1-y, 1-z$; at a distance of 3.899 (3) Å and with an angle subtended at O2 of 143.46 (8)°]. The latter type of interaction has not been observed before for similar systems.

Experimental

The NBT ligand was prepared as described by Usman *et al.* (2002). A solution of the ligand (5 mmol) in dichloromethane (20 ml) was mixed with an equimolar amount of vanadyl(IV) acetylacetonate dissolved in the same solvent (10 ml). The mixture was stirred for 24 h and the resulting solution was allowed to stand at room temperature. After slow evaporation, orange–red crystals of the complex separated out; these were collected by filtration, washed with ether and dried over P_4O_{10} *in vacuo*. Single crystals suitable for X-ray diffraction were collected by slow evaporation of a solution in a 1:1 (*v*/*v*) mixture of methanol and dichloromethane. Elemental analysis found: C 48.9, H 4.16, N 17.77%; calculated: C 48.86, H 4.10, N 17.80%.

Crystal data

$[V(C_{16}H_{16}N_5S)O_2]$
M_r = 393.34
Monoclinic, $P2_1/c$
a = 11.718 (5) Å
b = 10.794 (5) Å
c = 13.868 (6) Å
β = 99.727 (8)°
V = 1728.9 (14) Å^3
Z = 4
D_x = 1.511 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 545 reflections
θ = 2.4–28.1°
μ = 0.72 mm^{-1}
T = 293 (2) K
Rectangular, orange–red
0.40 × 0.25 × 0.22 mm

Data collection

Bruker SMART APEX CCD diffractometer	4189 independent reflections
ω scans	3223 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.021$
$T_{min} = 0.763$, $T_{max} = 0.859$	$\theta_{max} = 28.1^\circ$
15040 measured reflections	$h = -15 \rightarrow 14$
	$k = -14 \rightarrow 14$
	$l = -17 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0682P)^2 + 0.1736P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.112$	$\Delta\rho_{max} = 0.35$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.20$ e Å^{-3}
4189 reflections	
226 parameters	
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

V1—O1	1.6080 (17)	S1—C12	1.734 (2)
V1—O2	1.6174 (16)	N3—C6	1.311 (2)
V1—N1	2.0781 (17)	N3—N4	1.359 (2)
V1—N3	2.1763 (16)	N4—C12	1.329 (2)
V1—S1	2.3613 (9)	N5—C12	1.326 (3)
O1—V1—O2	109.11 (9)	O2—V1—S1	96.97 (6)
O1—V1—N1	97.39 (8)	N1—V1—S1	150.45 (5)
O2—V1—N1	95.79 (8)	N3—V1—S1	78.20 (5)
O1—V1—N3	116.82 (8)	C12—S1—V1	99.23 (7)
O2—V1—N3	133.74 (8)	C6—N3—N4	118.24 (14)
N1—V1—N3	73.72 (6)	N3—C6—C5	113.91 (15)
O1—V1—S1	103.39 (7)	N3—C6—C7	124.95 (17)
N1—C5—C6—N3	6.8 (2)	N3—C6—C7—N2	−138.0 (2)
C4—C5—C6—N3	−169.71 (17)	N3—C6—C7—C8	41.7 (3)

Table 2
Hydrogen-bond and short-contact geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13*a*···O1^{i}	0.97	2.54	3.411 (3)	149
C3—H3···O1^{ii}	0.93	2.65	3.544 (3)	162

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$.

The H atoms were fixed geometrically and treated as riding on the parent C atoms, with C—H distances of 0.93–0.97 Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by the SARD program of Kerala State Council for Science Technology and Environment, Thiruvananthapuram. The authors also acknowledge the DST IRPHA for the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1108). Services for accessing these data are described at the back of the journal.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Asgedom, G., Sreedhara, A., Kivikoski, J., Valkonen, J., Kolehmainen, E. & Rao, C. P. (1996). *Inorg. Chem.* **35**, 5674–5683.

Bruker (1998). *SMART* (Version 5.0) and *SAINT* (Version 4.0). Bruker AXS Inc., Madison, Wisconsin, USA.

Cornman, C. R., Geiser-Bush, K. M., Rowley, S. P. & Boyle, P. D. (1997). *Inorg. Chem.* **36**, 6401–6408.

Crans, D. C. (1994). *Comments Inorg. Chem.* **16**, 35–76.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Degani, H., Gochin, M., Karlish, S. J. D. & Shechter, Y. (1981). *Biochemistry*, **20**, 5795–5799.

Duan, C.-Y., Wu, B.-M. & Mak, T. C. W. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3485–3490.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Garg, B. S., Kurup, M. R. P., Jain, S. K. & Bhoon, Y. K. (1988). *Transition Met. Chem.* **13**, 92–95.

Klayman, D. L., Bartoserich, J. F., Griffin, T. S., Mason, C. J. & Scovill, J. P. (1979). *J. Med. Chem.* **22**, 885–893.

Klayman, D. L., Scovill, J. P., Bruce, J. & Bartosevich, F. (1984). *J. Med. Chem.* **27**, 84–87.

Li, J., Elberg, G., Crans, D. C. & Shechter, Y. (1996). *Biochemistry*, **35**, 8314–8318.

Ligtenbarg, A. G. J., Spek, A. L., Hage, R. & Feringa, B. L. (1999). *J. Chem. Soc. Dalton Trans.* pp. 659–661.

Lukevics, E., Jansone, D., Rubina, K., Abele, E., Germane, S., Leite, L., Shymaska, M. & Popelis, J. (1995). *Eur. J. Med. Chem.* **30**, 983–986.

Maurya, M. R., Khurana, S., Zhang, W. & Rehder, D. (2002). *Eur. J. Inorg. Chem.* **7**, 1749–1760.

Melchior, M., Thompson, K. H., Jong, J. M., Rettig, S. J., Shuter, E., Yuen, V. G., Zhou, Y., McNeill, J. H. & Orvig, C. (1999). *Inorg. Chem.* **38**, 2288–2293.

Mokry, L. M. & Carrano, C. J. (1993). *Inorg. Chem.* **32**, 6119–6121.

Padhye, S. & Kauffman, G. B. (1985). *Coord. Chem. Rev.* **63**, 127–135.

Pereiras-Gabian, G., Vazquez-Lopez, E. M., Braband, H. & Abram, U. (2005). *Inorg. Chem.* **44**, 834–836.

Philip, V., Suni, V., Kurup, M. R. P. & Nethaji, M. (2004). *Polyhedron*, **23**, 1225–1233.

Philip, V., Suni, V., Kurup, M. R. P. & Nethaji, M. (2005). *Polyhedron*, **24**, 1133–1142.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. Bruker AXS Inc., Madison, Wisconsin, USA.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Sreekanth, A. & Kurup, M. R. P. (2003). *Polyhedron*, **22**, 3321–3332.

Sreekanth, A., Sivakumar, S. & Kurup, M. R. P. (2003). *J. Mol. Struct.* **655**, 47–58.

Usman, A., Razak, I. A., Chantrapromma, S., Fun, H.-K., Philip, V., Sreekanth, A. & Kurup, M. R. P. (2002). *Acta Cryst.* C**58**, o652–o654.

Xie, M.-J., Ping, Y.-S., Zheng, L.-D., Hui, J.-Z. & Peng, C. (2004). *Acta Cryst.* E**60**, m1382–m1383.