# 1-D Supramolecular Arrangement of $[{C_6H_5NNN(O)C_6H_5}V(O)_2(C_5H_5N)]$ and $[{O_2NC_6H_4NNN(O)C_6H_5}V(O)_2(C_5H_5N)]$ through Hydrogen Bonding – Stabilization of *cis*-Dioxovanadium(V)(Pyridyne) Fragments with 1,3-Disubstituted Triazenido 1-Oxide Anions as Ligands

### Manfredo Hörner\*, Bernardo Almeida Iglesias, Paulo Roberto Martins, Paulo Cesar Mendes Villis, and Lorenzo do Canto Visentin

Santa Maria, RS, Brazil, Departamento de Química - Universidade Federal de Santa Maria

Received December 19th, 2007.

Abstract. The reaction of 1,3-*bis*(phenyl)triazene 1-oxide with VOSO<sub>4</sub>·5H<sub>2</sub>O in the presence of potassium ethanolate in ethanol yields yellow vitreous crystals of  $[\{C_6H_5NNN(O)C_6H_5\}V(O)_2(C_5H_5N)]$  (1) and  $[\{O_2NC_6H_4NNN(O)C_6H_5\}V(O)_2(C_5H_5N)]$  (2) after recrystallization from acetone/pyridine. 1 and 2 complex molecules are associated to  $[\{C_6H_5NNN(O)C_6H_5\}V(O)_2(C_5H_5N)]_2$  and  $[\{O_2NC_6H_4NNN(O)C_6H_5\}V(O)_2(C_5H_5N)]_2$  and  $[\{O_2NC_6H_4NNN(O)C_6H_5\}V(O)_2(C_5H_5N)]_2$  dimeric units through centrosymmetric C–H···O interactions, respectively. The centrosymmetric dimers – related to each other by translation – are connected to on-dimensional chains along to the crystallographic

direction [010] in the case of **1**, and along to the crystallographic direction [100] in the case of **2**, generating a supramolecular 1-D arrangement, respectively. The single-crystal X-ray structural analysis of **1** and **2** are the first reported in the literature bearing a triazenido 1-oxide anion stabilizing a *cis*-dioxovanadium(V) fragment.

Keywords: Vanadium; Triazenido 1-oxide; Cis-dioxovanadium(V); Hydrogen bonds

ject of investigation including coordination polymers, alternative strategies have been employed to promote self-

#### Introduction

Vanadium in very small amounts occurs as an essential element for biological relevant systems. In particular, oxovanadium cations, such as  $[VO]^{2+}$  and  $[VO_2]^+$  plays an important role for the synthesis of small molecules and its investigation as mimetic species to understand the reactivity of biologically relevant macromolecules including vanadium on its active centre. On the other side, hydrogen bonding is an important non-covalent interaction in structural investigations and relative to the reactivity of molecules with biological importance. From this point of view, diverse biological reaction mechanisms can be related to hydrogen bonding due to its energy range situated between van der Waals interactions and covalent bonds [1]. Related to the oxovanadium(V) chemistry including hydrogen bonding and its importance in biologically relevant systems, recently was published a structural study discussing vanadium(V) complexes with N-salicylidenehydrazides as ligands [2].

In recent years, considerable attention has been given to the investigation of metal complexes able to support extended molecular associations through intermolecular secondary non-covalent interactions. In the optic of this sub-

1058

assembling of molecular entities. Intrinsic electronic and structural modifications on multidentate ligand systems in order to promote intermolecular associations, as for example through metal-metal, metal-ligand, dipole-dipole, Coulombic, metal-arene  $\pi$ , and  $\pi - \pi$  interactions [3, 4], are fundamental with respect of the dimensionality of resulting supramolecular arrays. From this point of view, molecular self-assembly via classical and non-classical hydrogen bonding are also noteworthy [3, 5, 6]. In particular concerning peroxovanadium(V) complexes involving a central  $VO(\eta^2 - O_2)^+$  moiety, recently the single-crystal structure analysis viewing the supramolecular arrangement via nonclassical C-H-O intermolecular interactions has been published, in which paper the authors called attention about the lack of structural studies of such compounds with attention to the supramolecular arrangements through noncovalent intermolecular interactions such hydrogen bonding, as well as  $\pi - \pi$  interactions [7]. Beside the structural relations and the strategic func-

Beside the structural relations and the strategic functionalization of the main ligand unit, the presence of secondary ligands on the coordination sphere of the metal atom increases the tendency of the complex entities *via* secondary intermolecular interactions. From this point-ofview, deprotonated triazene 1-oxides are of interest due to its chelating coordination mode as four-electron donors and the stabilization of metal-oxo cations. Despite that complexes of vanadium(IV) and vanadium(V) (including the  $[VO_2]^+$  moiety) with 3-hydroxy-1,3-diphenyltriazene has

<sup>\*</sup> Prof. Dr. Manfredo Hörner Universidade Federal de Santa Maria Departamento de Química Caixa Postal 5031
97.110-970 Santa Maria, RS / Brazil E-mail: hoerner@smail.ufsm.br

been described in 1963 [8], such complexes have not so far been characterized by single-crystal X-ray structural analysis. As part of our investigations of the crystal structure of metal complexes with triazenido 1-oxide ligands able to support supramolecular arrangements in the solid state, herein we report the synthesis and the structure analysis on single crystal of triazenido 1-oxide complexes including *cis*-dioxovanadium(V) cations bearing an one-dimensional arrangement *via* secondary hydrogen bonding.

#### **Results and Discussion**

Crystal data and experimental parameters are given in Table 1. Selected bond distances and angles of the title complexes are listed in Table 2; Figure 1 and Figure 2 shows the molecular structure of the entities of  $[\{C_6H_5NNN(O)C_6H_5\}V(O)_2(C_5H_5N)]$  (1) and  $[\{O_2NC_6H_4NNN(O)C_6H_5\}V(O)_2(C_5H_5N)]$  (2) in a thermal ellipsoid representation [9]. Figure 3 and Figure 4 show the unit cells of 1 and 2 slightly inclined toward the [001] direction including a section of the one-dimensional arrangement *via* secondary C-H···O interactions.

The single asymmetric mononuclear entities  $[\{C_6H_5NNN(O)C_6H_5\}V(O)_2(C_5H_5N)]$  and  $[\{O_2NC_6H_4NNN(O)C_6H_5\}V(O)_2(C_5H_5N)]$  show one deprotonated 1,3-*bis*(phenyl)triazenido 1-oxide and 1-phenyl-3-(4-nitrophenyl)triazenido 1-oxide ion, acting as bidentate ligands (four-electron donors), respectively. Both the molecular structures of **1** and **2** shows the commonly observed

Table 1 Crystal data and structure refinement for complexes 1 and  $\mathbf{2}$ 

	1	2		
Empirical formula	$C_{17}H_{15}N_4O_3V$	$C_{17}H_{14}N_5O_5V$		
Formula weight	374.27	419.27		
T / K	295(2)	295(2)		
Radiation, $\lambda / (A)$	0.71073	0.71073		
Crystal system, space group	monoclinic, $P2_1c$	monoclinic, $P2_1c$		
Unit cell dimensions, a, b, c /A	a = 16.1661(4)	a = 11.0089(14)		
	b = 6.75510(10)	b = 23.182(3)		
	c = 16.6738(4)	c = 7.3528(10)		
	$\beta = 113.781(2)$	$\beta = 109.050(7)$		
Volume /Å <sup>3</sup>	1666.24(6)	1773.7(4)		
Z, Calculated Density $/g.cm^{-3}$	4, 1.492	4, 1.570		
Absorption coefficient /mm <sup>-1</sup>	0.620	0.601		
F(000)	768	856		
Crystal size /mm	0.31 x 0.12 x 0.12	0.36 x 0.05 x 0.03		
Theta range /°	2.96 to 25.50	3.42 to 25.50		
Index ranges	$-19 \le h \le 19$	$-13 \le h \le 13$		
	$-8 \le k \le 8$	$-27 \le k \le 28$		
	$-20 \le l \le 20$	$-8 \le l \le 8$		
Reflections collected	14684	15551		
Independent reflections	$3100 [R_{int} = 0.0360]$	$3292 [R_{int} = 0.1009]$		
Completeness to theta max.	99.9 %	99.6 %		
Max. and min. transmission	0.9294 and 0.8311	0.9822 and 0.8127		
Refinement method	Full-matrix least-squares on $F^2$			
Data / restraints / parameters	3100 / 0 / 226	3292 / 0 / 253		
Goodness-of-fit on $F^2$	1.076	0.840		
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0347$	$R_1 = 0.0461$		
	$wR_2 = 0.0886$	$wR_2 = 0.0995$		
R indices (all data)	$R_1 = 0.0474$	$R_1 = 0.1158$		
o .	$wR_2 = 0.0949$	$wR_2 = 0.1121$		
Largest diff. peak and hole /e. $A^{-3}$	0.212 and -0.276	0.239 and -0.391		

Table 2 Selected bond lengths / Å and angles / ° for complexes 1 and 2

	1	2		
V-O1	1.974(2)	1.991(2)		
V-O2	1.612(2)	1.601(2)		
V-O3	1.613(2)	1.614(2)		
V-N11	2.074(2)	2.066(3)		
V-N31	2.120(2)	2.115(3)	2.115(3)	
N13-O1	1.339(2)	1.338(3)		
N12-N11	1.305(2)	1.315(3)	1.315(3)	
N12-N13	1.285(2)	1.276(3)		
N11-C21	1.428(3)	1.411(4)		
N13-C11	1.423(3)	1.439(4)		
N1-C24	-	1.453(4)		
N1-011	-	1.220(3)		
N1-012	-	1.221(4)		
N11-V-O1	73.76(6)	73.85(9)		
O2-V-O3	109.88(9)	124.05(12)		
O2-V-O1	126.26(9)	126.64(11)		
O3-V-O1	123.76(8)	124.05(12)		
O2-V-N11	97.65(8)	95.89(11)		
O3-V-N11	97.64(8)	100.50(11)		
O1-V-N11	73.76(6)	73.85(9)		
O2-V-N31	94.71(7)	95.76(11)		
O3-V-N31	98.36(8)	96.25(11)		
O1-V-N31	81.48(6)	81.58(9)		
N11-V-N31	155.09(7)	155.14(10)		
C11-N13-O1	118.5(2)	119.2(3)		
C11-N13-N12	121.6(2)	120.2(3)		
N12-N13-O1	119.9(2)	120.5(2)		
N13-N12-N11	111.5(2)	111.5(3)		
N12-N11-C21	113.8(2)	111.9(3)		
O11-N1-O12	-	123.1(3)		



Fig. 1 View of the molecular structure with atom-labeling scheme of  $[\{C_6H_5NNN(O)C_6H_5\}V(O)_2(C_5H_5N)]$  [9]. Displacement ellipsoids at the 50 % level and H atoms with arbitrary radii.

*trans* stereochemistry about the N11–N12 fragment with double-bond character of the triazenido 1-oxide ligand. Compared with non-coordinated triazene 1-oxides, a typical feature of the coordinated deprotonated triazenido 1-oxide ligand is the lengthening of the N–O bond. These bond distances [N13–O1 = 1.339(2) (1) and 1.338(3) Å (2)] are comparatively longer than the N–O bond length observed in 3-(*o*-carboxyphenyl)-1-ethyltriazene 1-oxide [N–O = 1.288(3) Å] [10]. The V=O bond lengths of the [VO<sub>2</sub>]<sup>+</sup> moiety [V–O2 = 1.612(2), V–O3 = 1.613(2) Å (1) and V–O2 = 1.601(2), V–O3 = 1.614(2) Å (2)] are in good



Fig. 2 View of the molecular structure with atom-labeling scheme of  $[{O_2NC_6H_4NNN(O)C_6H_5}V(O)_2(C_5H_5N)]$  [9]. Displacement ellipsoids at the 50 % level and H atoms with arbitrary radii.



**Fig. 3** View of the supramolecular, 1-D assembling of  $[\{C_6H_5NNN(O)C_6H_5\}V(O)_2(C_5H_5N)]$  toward the slightly inclined [001] direction. The one-dimensional arrangement occurs along to the crystallographic direction [010] *via* non-classical Hydrogen bonds (indicated as dashed lines) C32–H32···O2' and C35–H35···O3''; symmetry codes ('): *x*, 1+*y*, *z*, (''): –*x*, –*y*, –*z*. Atoms with arbitrary radii. Hydrogen atoms different to the non-classical hydrogen bonding omitted for clarity.

agreement with those found in the similar compound (pyridine-2-carbaldehyde N'-(4-(dimethylamino)benzoyl)hydrazonato-N,N",O)-dioxo-vanadium(V), hereafter **3** [V-O = 1.612(5) Å and 1.615(11) Å] [11]. The V-O bond lengths including the N-oxide moiety [V-O1 = 1.974(2) (1) and 1.991(2) Å (2)] are similar with the V-O<sub>Ligand</sub> bond distance observed in (3) [V-O = 1.952(12) Å] [11]. The distorted trigonal-bipyramidal coordination geometry of each



**Fig. 4** View of the supramolecular, 1-D assembling of  $[{O_2NC_6H_4NNN(O)C_6H_5}V(O)_2(C_5H_5N)]$  toward the slightly inclined [001] direction. The one-dimensional arrangement occurs along to the crystallographic direction [100] *via* non-classical Hydrogen bonds (indicated as dashed lines) C14–H14···O2' and C36–H36···O11'' ; symmetry codes ('): 1+x, y, z, (''): -x, -y, -z. Atoms with arbitrary radii. Hydrogen atoms different to the non-classical hydrogen bonding omitted for clarity.

vanadium(V) ion is established by two terminal oxo ligands in positions *cis* to each other, and one neutral pyridine, in which the axial angles N31–V–N11 of 155.09(7)° (1) and 155.14(10)° (2), deviates significantly from the ideal angle. The V–N<sub>Py</sub> bond lengths [V–N31 = 2.120(2) (1) and 2.115(3) Å (2)] are similar with the V–N bond distance including the pyridine fragment in 3 [V–N = 2.116(10) Å] [11], but shorter than those V–N<sub>Py</sub> bond lengths found in the similar compound chloro-dioxo-dipyridine-vanadium [V–N<sub>Py</sub> = 2.130 and 2.133 Å] [12].

The interplanar angles between the terminal phenyl rings and between the phenyl rings and the NNNO moiety, indicates the lack of planarity of the triazenido 1-oxide ligand in both the complexes 1 and 2. For 1 [the angles between the C11-C16 phenyl ring and N11/N12/N13/O1 plane, C21-C26 phenyl ring and N11/N12/N13/O1 plane, and between the phenyl rings C11-C16 and C21-C26 are 9.2(2)°,  $11.0(1)^{\circ}$ , and  $17.0(1)^{\circ}$ , respectively], and for 2 [the angles between the C11-C16 phenyl ring and N11/N12/N13/O1 plane, C21-C26 phenyl ring and N11/N12/N13/O1 plane, and between the phenyl rings C11-C16 and C21-C26 are  $5.0(1)^\circ$ ,  $9.9(1)^\circ$ , and  $5.4(1)^\circ$ , respectively]. Due to the intermolecular non-classic hydrogen bonds C-H...O, the pyridine ring and the NNNO moiety are not co-planar in complex 1 [angle between the N31-C36 ring and N11/N12/ N13/O1 plane is 29.7(1)°], and in complex 2 [angle between the N31-C36 ring and N11/N12/N13/O1 plane is 35.2(1)°]. The intermolecular non-classic hydrogen bonds C-H-O in complex 2 also hinder the co-planarity between the O11/N1/NO12 nitro group and the C21-C26 ring [11.4(4)°].

Table 3 Hydrogen-bonding geometric parameters /Å,  $^{\circ}$  for complexes 1 and 2

D-H···A	D-H	$H \cdots A$	$D \cdots A$	$D-\mathrm{H}^{}A$	
Complex 1 C32–H32···O2' C35–H35···O3"	0.93 0.93	2.54 2.60	3.293(3) 3.290(3)	138 132	
Complex <b>2</b> C36-H36···O11″ C14-H14···O2′	0.93 0.93	2.56 2.44	3.294(5) 3.350(4)	136 166	

(D = donor atom, A = acceptor atom)

Symmetry codes: (') x, 1+y, z, (") -x, -y, -z for complex (1)

Symmetry codes: (') 1+x, y, z, (") -x, -y, -z for complex (2)

In complex 1 the  $[{C_6H_5NNN(O)C_6H_5}V(O)_2(C_5H_5N)]$ molecules are associated to  $[{C_6H_5NNN(O)C_6H_5}V(O)_2-$ (C<sub>5</sub>H<sub>5</sub>N)]<sub>2</sub> dimeric units through centrosymmetric nonclassical C-H···O hydrogen bonds [C35···O3" 3.290(3) Å; symmetry code: (") -x, -y, -z] (Table 3). The dimers compose a twelve-membered ring with a chair conformation in which the V and V" atoms are distanced at 6.2523(7) Å. The dimeric units – related to each other by translation - associate to one-dimensional chains along to the crystallographic direction[010] via additional centrosymmetric non-classical C-H-O hydrogen bonds  $[C32\cdots O2' = 3.293(3) \text{ Å}; \text{ symmetry code: (') } x, 1+y, z]$ (Table 3). In the 1-D supramolecular arrangement of complex 1, two pyridine molecules related to each other by an inversion centre, acts as bridges between two [VO<sub>2</sub>]<sup>+</sup> fragments – equivalent by an inversion centre – via non-classical C-H...O hydrogen bonds involving terminal oxo-ligands attached to the vanadium centres.

Complex 2 attains a supramolecular arrangement similar to 1.  $[{O_2NC_6H_4NNN(O)C_6H_5}V(O)_2(C_5H_5N)]_2$  dimeric units results from  $[{O_2NC_6H_4NNN(O)C_6H_5}V(O)_2-$ (C<sub>5</sub>H<sub>5</sub>N)] complex molecules associated through centrosymmetric non-classical C-H-O hydrogen bonds [C36...O11'' = 3.294(5) Å; Symmetry code: ('') -x, -y, -z](Table 3). Compared with 1, the distance between the vanadium atoms at 7.797(1) Å is significantly longer. The dimeric units associate by translation to one-dimensional chains along to the crystallographic direction [100] via additional centrosymmetric non-classical C-H-O hydrogen bonds [C14...O2' = 3.350(4) Å; symmetry code: (')1+x, y, z] (Table 3). In the case of complex 2, the 1-D supramolecular arrangement includes NC<sub>6</sub>H<sub>4</sub>NO moieties belonging to a centrosymmetric pair of [O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NNN(O)C<sub>6</sub>H<sub>5</sub>]<sup>-</sup> ligands, acting as bridges between two  $[VO_2]^+$  fragments equivalent by inversion. The resulting dimeric units are then connected via non-classical C-H-O hydrogen bonds involving terminal oxo-ligands attached to the vanadium centres.

The single-crystal X-ray structural analysis of the title compounds are the first reported in the literature related to triazenido 1-oxide anions stabilizing *cis*-dioxovanadium(V) fragments.

#### **Experimental Section**

A single crystal fixed on a glass fiber was used for the X-ray data collection. Data were collected with a Bruker APEX II CCD areadetector diffractometer and graphite-monochromatized Mo-K<sub> $\alpha$ </sub> radiation using *COSMO* program [13]. Cell refinement, data reduction and the absorption correction were performed using *SAINT* and *SADABS* programs, respectively [13]. The structure of complexes **1** and **2** were solved by direct methods [14] and refined on  $F^2$  with anisotropic temperature parameters for all non H atoms [15]. H atoms of the aromatic groups were positioned geometrically (C-H = 0.93 Å for  $Csp^2$  atoms) and treated as riding on their respective C atoms, with  $U_{iso}$ (H) values set at  $1.2U_{eq}Csp^2$ . The crystallographic parameters and details of data collection and refinement are given in Table 1.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC no. 638028 and 638029. Further details of the crystal structures investigations are available free of charge via www.ccdc.cam.ac.uk/ conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

#### Preparation of [{ $C_6H_5NNN(O)C_6H_5$ }V(O)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)], [1,3-Bis(phenyl)triazenide 1-oxide- $\kappa^2N^3$ ,O]pyridinecis-dioxovanadium(V) (1)

Pale-yellow 1,3-*bis*(phenyl)triazene 1-oxide (50 mg, 0.23 mmol) was dissolved in 15 mL of ethanol at 35 °C, and treated with one KOH pellet. Stirring was maintained for 10 min, while the reaction mixture turns dark-yellow. A solution of VOSO<sub>4</sub> · 5H<sub>2</sub>O (60 mg 0.24 mmol) in water (5 mL) was added under continuous stirring. After 10 min an olive-green solid was formed. The precipitation was completed after keeping the reaction system at 5 °C. This solid was filtered-off, washed with small portions of cool water, and vacuum dried over P<sub>2</sub>O<sub>5</sub>. Yellow crystals of complex 1, suitable for X-ray analysis, were obtained within 60 days at room temperature by recrystallization from a acetone (15 mL)/pyridine (2 mL) mixture.

**Properties:** yellow block-shaped with vitreous brilliancy crystals.  $C_{17}H_{15}N_4O_3V$  (374.27). Yield: 70 mg (0.19 mmol), 80 % based on VOSO<sub>4</sub>·5H<sub>2</sub>O. Melting point: 139 °C.

Solid free ligand C<sub>6</sub>H<sub>5</sub>N(H)-N=N( $\rightarrow$ O)C<sub>6</sub>H<sub>5</sub> (213.23). IR (KBr), bands as a whole: 3146 [s, v(N-H)], 1605 [vs, v(C=C)], 1517 [vs,  $\delta$ (N-H)], 1444 [s,  $v_s$ (N=N)], 1293 [w, v(N $\rightarrow$ O)], 1215 [vs,  $v_s$ (N-N)], 1180 cm<sup>-1</sup> [s,  $v_{as}$ (N $\rightarrow$ O)].

 $C_{17}H_{14}N_5O_5V$  (419.27). IR (KBr), bands as a whole: the  $\nu$ N–H band is absent. 1244 [s,  $\nu$ (N–O)], 1181 [w,  $\nu_s$ (N–N)], 1069 [m,  $\nu_{as}$ (N–O)], 937 cm<sup>-1</sup> [vs,  $\nu$ (V=O)].

#### **Preparation** of

## $[{O_2NC_6H_4NNN(O)C_6H_5}V(O)_2(C_5H_5N)], [1-phenyl-3-(4-nitrophenyl)triazenide 1-oxide-<math>\kappa^2N^3,O]$ pyridine-cis-dioxovanadium(V)

Yellow 1-phenyl-3-(4-nitrophenyl)triazene 1-oxide (0.05 g, 0.19 mmol) was dissolved in 10 mL of ethanol at 35 °C, and treated with one KOH pellet. Stirring was continued for 10 min, while the

reaction mixture changed to dark-purple. A solution of  $VOSO_4 \cdot 5H_2O$  (50 mg 0.20 mmol) in water (5 mL) was added under continuous stirring. After 10 min an olive-green solid was formed. The precipitation was completed after keeping the reaction system at 5 °C. This solid was filtered-off, washed with small portions of cool water, and vacuum dried over  $P_2O_5$ . Yellow crystals of complex 1, suitable for X-ray analysis, were obtained within 40 days at room temperature by recrystallization from a acetone (15 mL)/ pyridine (2 mL) mixture.

**Properties:** yellow block-shaped with vitreous brilliancy crystals.  $C_{17}H_{14}N_5O_5V$  (419.27). Yield: 60 mg (0.15 mmol), 75 % based on VOSO<sub>4</sub> · 5H<sub>2</sub>O. Melting point: 211 °C.

Solid free ligand  $O_2NC_6H_4N(H)-N=N(\rightarrow O)C_6H_5$  (258.23). IR (KBr), bands as a whole: 3200 [s, v(N-H)], 1605 [vs, v(C=C)], 1525 [vs,  $\delta(N-H)$ ], 1517 [vs,  $v_{as}(NO_2)$ ], 1470 [s,  $v_s(N=N)$ ], 1336 [vs,  $v_s(NO_2)$ ], 1298 [w,  $v(N\rightarrow O)$ ], 1225 [s,  $v_s(N-N)$ ], 1181 cm<sup>-1</sup> [s,  $v_{as}(N\rightarrow O)$ ].

 $C_{17}H_{14}N_5O_5V$  (419.27). IR (KBr), bands as a whole: the  $\nu$ N–H band is absent. 1515 [s,  $\nu_{as}(NO_2)$ ], 1333 [vs,  $\nu_s(NO_2)$ ], 1239 [vs,  $\nu(N-O)$ ], 1185 [m,  $\nu_s(N-N)$ ], 1112 [m,  $\nu_{as}(N-O)$ ], 934 cm<sup>-1</sup> [s,  $\nu(V=O)$ ].

Acknowledgements. This work received partial support from CNPq (proc. 477569/2006-4), and FAPERGS/PRONEX (Proc. 98/0451.6). M.H. thanks CNPq (proc. 309008/2006-9), P.R.M. thanks CNPq/ PIBIC, and B.A.I., P.C.M.V. and L.C.V. thanks CAPES for grants. Diffractometer was supported by the Financiadora de Estudos e Projetos (FINEP, CT-Infra 03/2001).

#### References

- G. R. Desiraju, T. Steiner, The Weak Hydrogen Bond In Structural Chemistry and Biology, IUCr Monographs on Crystallography 9, Oxford University Press Inc., New York, 1999.
- [2] W. Plass, Coord. Chem Rev. 2003, 237, 205.
- [3] H. W. Roesky, M. Andruh, Coord. Chem Rev. 2003, 236, 91.
- [4] H. Chowdhury, S. H. Rahaman, R. Ghosh, S. K. Sarkar, H.-K. Fun, B. K. Ghosh, J. Mol.Struct. 2007, 826, 170.
- [5] S. J. Langford, C. P. Woodward, Polyhedron 2007, 26, 338.
- [6] K.-T. Youm, J. Ko, M. J. Jun, Polyhedron 2006, 25, 2717.
- [7] S. Pacigová, R. Gyepes, J. Tatiersky, M. Sivák, *Dalton Trans.* 2008, 121.
- [8] R. L. Dutta, S. Lahiry, J. Indian Chem. Soc. 1963, 40, 67.
- [9] K. Brandenburg. *DIAMOND* 3.1a. 1997–2005, Version 1.1a. Crystal Impact GbR, Bonn, Germany.
- [10] C. Samanta, A. K. Mukherjee, M. Mukherjee, Acta Crystallogr. 1998, C54, 1544.
- [11] S. Pal, K. R. Radhika, S. Pal, Z. Anorg. Allg. Chem. 2001, 627, 1631.
- [12] M. Motevalli, D. Shah, S. A. A. Shah, A. C. Sullivan, *Polyhedron* 1996, 15, 2387.
- [13] Bruker AXS Inc., Madison, Wisconsin, USA, © 2005, COSMO (Version 1.48), SAINT (Version 7.06°), SADABS (Version 2.10).
- [14] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, and R. Spagna, SIR2004, J. Appl. Cryst., 2005, 38, 381.
- [15] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.