A Vanadyl(V) Complex with a Pincer-type Thiobis(phenolate) and an Acetylacetonate Co-ligand, VO(tbp)(acac)

Rahman Bikas[a], Hassan Hosseini Monfared[a], Somayeh Alami[b], Ingo Pantenburg[c], and Gerd Meyer[c]

[a] Department of Chemistry, Zanjan University, 45195-313, Zanjan, I. R. Iran
[b] Young Research Club, Islamic Azad University of Tabriz, P. O. Box 1655, Tabriz, I. R. Iran
[c] Department für Chemie, Institut für Anorganische Chemie, Universität zu Köln, Greinstraße 6, 50939 Köln, Germany

Reprint requests to Dr. H. H. Monfared. Fax: +98 241 5283203. E-mail: monfared@znu.ac.ir

Z. Naturforsch. **2010**, *65b,* 1457 – 1461; received June 29, 2010

A new vanadyl(V) complex with the tridentate, pincer-type *O*,*S*,*O*-ligand thiobis(phenolate), tbp, was synthesized from the reaction of vanadium(IV) oxide bis(acetylacetonate), VO(acac)$_2$, and 2,2′-thio-bis(4-methylphenol), H$_2$tbp, in refluxing methanol in high yield. Single-crystal X-ray diffraction structure analysis revealed for VO(tbp)(acac) that the vanadium atom is octahedrally coordinated with an O_5,*S*-donor environment where the thiobis(phenolate) ligand is *O*,*S*,*O*-bonded to the vanadyl(V) center facially in a tridentate dinegative fashion. Cyclic voltammetric experiments carried out with its solution in dimethyl sulfoxide revealed an irreversible peak at −0.768 V (*vs*. Ag/AgCl) relating to the V^{5+}/V^{4+} reduction process.

Key words: Oxovanadium(V), Thiobis(phenolate), Complex, Molecular Structure, Cyclic Voltammetry

Introduction

The element vanadium plays an important role in many biological processes. Numerous high-valent vanadium compounds have been studied for their promising insulin-mimetic effects, anticancer activity and antiviral properties [1, 2]. Two classes of vanadium enzymes, *viz.* vanadium nitrogenases and vanadate-dependent haloperoxidases, have been found in nature so far, and their structures and properties have stimulated the search for structural and functional model compounds [3 – 8].

Furthermore, oxovanadium complexes are used in oxidation and oxotransfer catalysis [9, 10]. Alpha-olefin polymerization catalyzed by some vanadium(V) complexes has been reported [11, 12]. Moreover, the role of vanadium complexes in catalytically conducted redox reactions [13, 14], and potential medicinal applications such as the treatment of diabetes type I and type II [15], have stimulated interest in the stereochemistry and reactivity of such compounds. In most cases the active site contains one of the two motifs VO^{3+} or VO^{2+} coordinated by oxygen and nitrogen atoms. The strong affinity of these two motifs towards *O*,*N*-donor ligands is probably due to their hard acidic nature, and selective stabilization of these two motifs depends upon the basicity of donor atoms.

On the other hand, the chemistry of sulfur- or selenium-containing bisphenol ligands and their transition metal complexes is of interest because of their versatile structural, magnetic, catalytic and electron transfer activity [16, 17]. Such complexes serve as functional models for various biomolecules having potential ability to form one-electron oxidized phenoxyl radicals rendering catalytic oxidations of organic molecules [18 – 20]. Multinuclear complexes, and especially binuclear species, were found to catalyze the oxidative deamination of primary amines [21], providing rare examples of copper amine oxidase enzymes. Phenol-containing ligands [22 – 24] have also been used in aerial oxidation of primary alcohols and amines catalyzed by Cu(II) complexes [25] attracting considerable attention in the bioinorganic chemical community because of the widespread occurrence in oxygen-dependent enzymatic oxidations.

As part of our continuing efforts to develop vanadyl (VO^{3+}) complexes with various multidentate ligands [26], this work deals with the synthesis and structure of a new oxovanadium(V) complex of a chelating dianionic *O*,*S*,*O*-type thiobis(phenolate), tbp, ligand.

0932–0776 / 10 / 1200–1457 $ 06.00

Experimental Section

Materials and instrumentations

Vanadium(IV) oxide bis(acetylacetonate), VO(acac)$_2$, and *p*-cresol were purchased from Merck and used as received. Solvents of the highest grade commercially available (Merck) were used without further purification. IR spectra were recorded in KBr discs with a Bruker FT-IR spectrophotometer. UV/Vis solution spectra were recorded on a thermospectronic Helios Alpha spectrometer. Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyzer. ^{1}H and ^{13}C NMR spectra of the ligand and of the complex in CDCl$_3$ solution were recorded on Bruker 250 and 400 MHz spectrometers, and chemical shifts are given in ppm relative to tetramethylsilane. Cyclovoltammetric experiments were performed using a Metrohm computrace voltammetric analyzer model 757 VA. Data collection for X-ray structure determination was performed on a Stoe IPDS II diffractometer.

Synthesis of 2,2′-thio-bis(4-methylphenol) (H$_2$tbp)

2,2′-Thio-bis(4-methylphenol) (H$_2$tbp) was synthesized according to reported procedures [33]. Yield 65 % (16 mg), m. p. 114 – 115 °C. – Anal. for $C_{14}H_{14}O_2S$ (246.32): calcd. C 68.26, H 5.73; found C 68.19, H 5.75. – FT-IR (KBr): ν = 3067 (s, vbr), 2921 (s), 2859 (m), 1608 (m), 1587 (m), 1503 (vs), 1453 (s), 1412 (s), 1359 (s), 1287 (vs), 1227 (m), 1137 (m), 1057 (w), 945 (vs), 880 (m), 824 (m), 711 (m), 567 (w), 526 (w), 489 cm^{-1} (w). – ^{1}H NMR (250.13 MHz, CDCl$_3$, 25 °C, TMS): δ = 2.27 (s, 6 H), 6.82 (d, J = 8.30 Hz, 2 H), 7.05 (m, 2 H), 7.16 (d, J = 8.33 Hz, 2 H) and 8.64 (s, 2 H). – UV/Vis (CH$_3$OH): $\lambda_{\max}(\lg\varepsilon_{\max})$ = 208 (4.72), 248 (3.95$^{\text{sh}}$) and 299 nm (3.95).

*Synthesis of the complex [VO(tbp)(acac)] (**1**)*

A methanolic solution (20 mL) of the ligand precursor H$_2$tbp (2.00 mmol) was added dropwise to a methanolic solution (20 mL) of VO(acac)$_2$ (2.00 mmol), and the mixture was refluxed for 2 h. The resulting solution was allowed to undergo slow evaporation at r. t. After 2 d dark-violet single crystals suitable for X-ray diffraction were obtained. Yield 81 % (665 mg). – Anal. for $C_{19}H_{19}O_5SV$ (410.36): calcd. C 55.61, H 4.67; found C 55.58, H 4.66. – FT-IR (KBr): ν = 3268 (m, br), 3019 (m, br), 1717 (m), 1565 (s), 1531 (s), 1466 (s), 1345 (m), 1273 (s), 1243 (s), 1052 (m), 987 (vs), 894 (w), 815 (m), 758 (vs), 603 (w), 462 cm^{-1} (w). – ^{1}H NMR (400.13 MHz, CDCl$_3$, 25 °C, TMS): δ = 2.12 (s, 6 H, two CH$_3$ of acac), 2.26 (s, 6 H, two aryl-CH$_3$), 5.93 (s, 1 H, =C*H*- of acac), 6.58 – 7.26 (m, 6 H). – ^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 19.73 (2 C, aryl-CH$_3$), 25.16 (2 C, CH$_3$ of acac), 103.76 (1 C), 125.16 (4 C), 130.75 (2 C), 132.49 (2 C), 134.04 (2 C), 167.12 (2 C), 191.14 (2 C, C=O). – UV/Vis (CH$_3$OH): $\lambda_{\max}(\lg\varepsilon_{\max})$ = 205 (4.70), 286 nm (4.09).

Table 1. Crystal data and structure refinement parameters for **1**.

Empirical formula	[VO(tbp)(acac)], $C_{19}H_{19}O_5SV$
Formula weight, g mol^{-1}	410.34
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
a, Å	7.891(1)
b, Å	15.716(2)
c, Å	15.515(2)
β, deg	93.18(1)
Volume, Å^3	1921.2(5)
Z	4
Density (calc.), g cm^{-3}	1.42
Absorption coefficient, mm^{-1}	0.7
F(000), e	848
θ range for data collection, deg	1.85 – 27.28
Index ranges *hkl*	±10, ±20, ±19
Refl. collected / unique / R_{int}	28517 / 4271 / 0.1493
Refl. with $I \geq 2\sigma(I_0)$	1998
Data completeness, %	98.9
Data / restraints / parameters	4271 / 0 / 235
Final $R1/wR2$ [$I \geq 2\sigma(I_0)$]	0.0495 / 0.0800
$R1/wR2$ indices (all data)	0.1352 / 0.0985
Goodness of fit on F^2	0.815
Largest diff. peak / hole, e Å^{-3}	0.26 / −0.25

Electrochemical measurements

For cyclic voltammetry studies, a conventional three-electrode system was used with a polished glassy carbon electrode (area 3.14 mm^2) as working electrode and a platinum wire counter electrode. The reference electrode was an aqueous Ag/AgCl saturated electrode, separated from the bulk of the solution by a bridge with solvent and supporting electrolyte. The electrolytic medium consisted of 0.1 mol L^{-1} lithium perchlorate (LiClO$_4$) as supporting electrolyte in dimethyl sulfoxide; experiments were carried out at r. t. The solution was freshly prepared before use and purged with N$_2$ saturated with solvent for *ca.* 15 min prior to taking measurements in order to remove dissolved O$_2$. The voltammogram was recorded under various scan rates in the range from −2.0 to −1.0 V *vs.* Ag/AgCl.

X-Ray diffraction data collection and refinement

Data collection for X-ray structure determination was performed on a Stoe IPDS II diffractometer using graphite-monochromatized MoK_α radiation (0.71073 Å) at 293(2) K ($0° \leq \omega \leq 180°$, $\varphi = 0°$, $0° \leq \omega \leq 166°$, $\varphi = 90°$, $\Delta\omega = 2°$, 173 frames). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data [27]. The programs used are X-AREA [27], including X-RED [28] and X-SHAPE [29] for data reduction and absorption correction, and the WinGX suite of programs [30], including Sir-92 [31] and Shelxl-97 [32] for structure solution and refinement. The hydrogen atoms were placed in idealized positions and constrained to ride on their parent atom. The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Table 1 contains the crystal data and numbers pertinent to data collection and structure refinement.

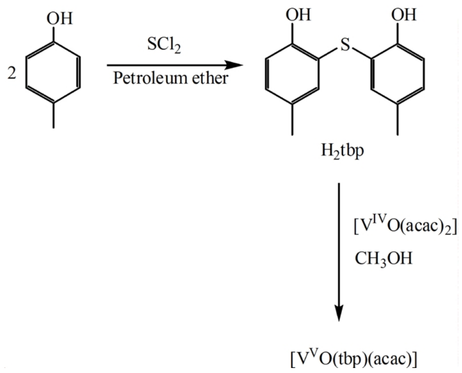
CCDC-781486 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The thiobis(phenol) H_2tbp was synthesized by the reaction of sulfur dichloride with *p*-cresol in dry petroleum ether; recrystallization of the crude product gave the desired symmetric pincer-type tridentate *O*,*S*,*O*-donor ligand in excellent purity [33, 34]. The oxovanadium(V) complex of this thiobis(phenolate) was prepared in high yield from the reaction of H_2tbp with an equimolar amount of VO(acac)$_2$ in refluxing methanol during two hours (Scheme 1).

Table 2. Selected bond lengths (Å) and angles (deg) in the crystal structure of **1**.

V1–O1	1.588(3)	O1–V1–O11	98.89(13)
V1–O21	1.856(3)	O1–V1–O21	100.79(13)
V1–O11	1.849(3)	O11–V1–O21	94.94(11)
V1–O33	1.977(3)	O1–V1–O31	100.53(13)
V1–O31	1.955(3)	O11–V1–O31	88.63(11)
V1–S1	2.795(1)	O21–V1–O31	157.54(11)
O21–C21	1.342(4)	O1–V1–O33	101.64(14)
O11–C11	1.349(4)	O11–V1–O33	159.21(11)
O33–C33	1.279(5)	O21–V1–O33	84.47(12)
O31–C31	1.283(5)	O31–V1–O33	84.44(12)
C31–C32	1.372(7)	O21–V1–S1	76.86(8)
C32–C33	1.392(7)	O1–V1–S1	175.76(11)
S1–C26	1.783(4)	O11–V1–S1	77.91(8)
S1–C16	1.784(4)	O31–V1–S1	82.27(8)



Scheme 1. Synthesis of the oxovanadium(V) thiobis-(phenolate) complex [VO(tbp)(acac)] (**1**).

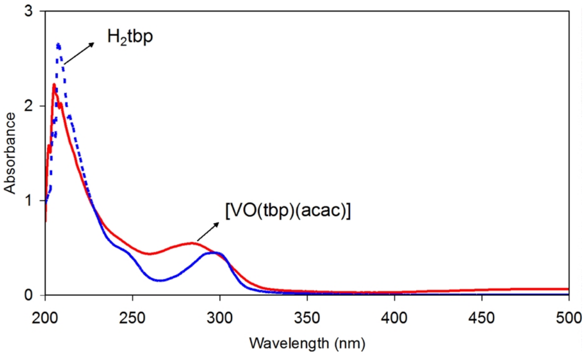


Fig. 1 (color online). Electronic spectra of H_2tbp (blue) and [VO(tbp)(acac)] (red) in CH_3OH.

The electronic spectra of the ligand and the complex (**1**) show very similar absorption peaks (Fig. 1). The electronic spectrum of the complex in methanol exhibits two bands at 205 and 286 nm which may be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the ligand, respectively. There is a noticeable blue shift of the $n \rightarrow \pi^*$ transition of the ligand upon coordination.

Description of the structures

In order to define the coordination sphere conclusively, a single-crystal X-ray diffraction study of **1** was undertaken. Crystallographic data are listed in Table 1. A plot of the molecular structure with the atom numbering scheme adopted is shown in Fig. 2, and selected interatomic distances and angles are summarized in Table 2. The packing of the molecules in crystals of **1** as

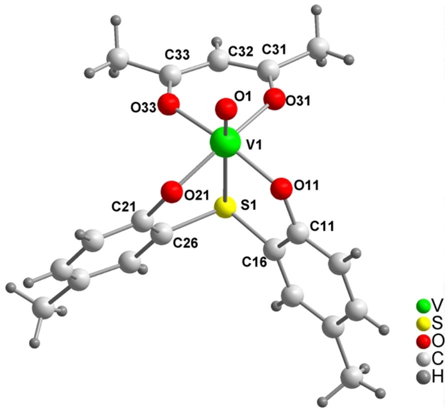


Fig. 2. The molecular structure of [VO(tbp)(acac)] (**1**) in the crystal with the atom numbering scheme used.

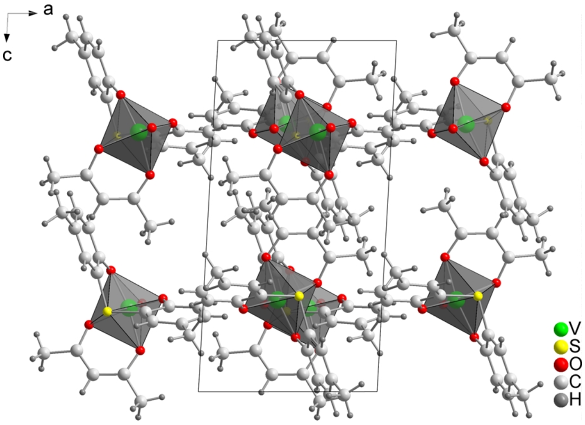


Fig. 3. Packing of the molecules in crystals of **1** as projected onto the *ac* plane.

projected onto the *ac* plane is shown in Fig. 3. The unit cell contains four molecules of **1**, the space group is $P2_1/c$.

In complex **1** the vanadium atom is octahedrally coordinated in an O_5S donor environment. A terminal V=O-type oxygen atom occupies an axial position at a distance of 1.588(3) Å. The OSO donor thiobis(phenolate) pincer-type ligand coordinates facially with the sulfur atom *trans* to the terminal V=O fragment. The two oxygen atoms of the bidentate acetylacetonate ligand occupy the remaining two sites. The equatorial VO_4 unit is far from planar. The displacement by 0.344 Å of the vanadium atom from the mean plane comprising the two independent phenolate oxygen atoms O11, O21 and the two acetylacetone oxygen atoms, O31 and O33 is towards the oxo oxygen atom. The *O*,*S*,*O*-donor ligand forms two five-membered chelate rings with bite angles of about 77° (O_{phenolat}–V–S). The vanadium to oxygen bond lengths follow the order V–oxo oxygen < V–phenolate oxygen < V–acetylacetonate oxygen. The two diagonal angles O11–V–O33 and O21–V–O31, 159.21(11) and 157.54(11)°, respectively, are significantly smaller than 180°. This deviation from the ideal octahedral geometry may be caused by the small bite angles made by the two phenolate oxygen atoms and the tripodal sulfur atom at the vanadium atom (O11–V1–S1 = 77.91(8) and O21–V1–S1 = 76.86(8)°). This is again due to a remarkably longer V–S distance (2.795(1) Å). This phenomenon may be explained in terms of a *trans* influence of the oxo group, which occupies the other axial position at a normal distance of 1.588(3) Å [26]. The distance of the vanadium atom to the terminal oxygen atom (O1) is at the lower end of the range typically observed for oxovanadium(V) complexes [35, 36]. The short V–O1 distance thereby indicates the presence of a vanadium–oxygen double bond which is commonly found in VO^{3+} complexes. The two phenyl rings in this system are planar and retain their aromaticity. The two mean planes formed by the aromatic rings intersect at an angle of about 69°.

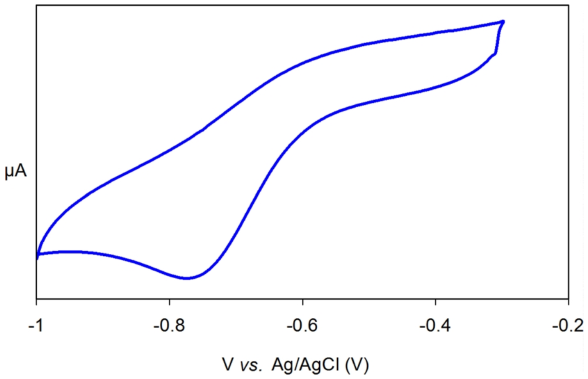


Fig. 4. Cyclic voltammogram of 10^{-3} mol L^{-1} [VO(acac)-(tbp)] (**1**) in DMSO and $LiClO_4$ (0.1 mol L^{-1}); scan rate 100 mV s^{-1} in the potential range −1.0 to −0.2 V.

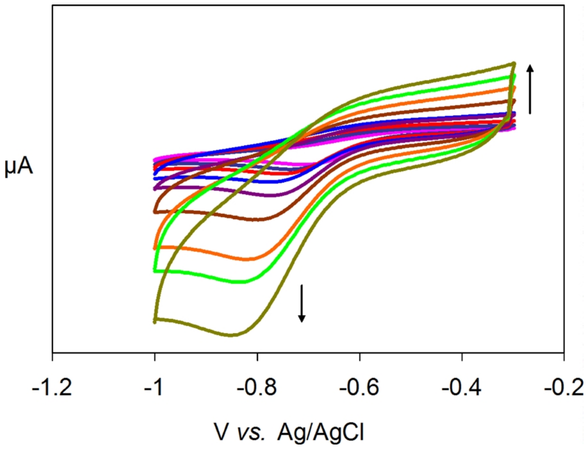


Fig. 5. Cyclic voltammogram of 10^{-3} mol L^{-1} [VO(tbp)-(acac)] (**1**) in DMSO and $LiClO_4$ (0.1 mol L^{-1}); scan rates 10, 25, 50, 75, 100, 150, 200, 300 and 400 mV s^{-1}.

Electrochemical studies

Electrochemical measurements (cyclic voltammetry) were carried out to probe the redox stability of complex **1** in solution. The cyclic voltammogram in dimethylsulfoxide displays an irreversible reduction peak at −0.768 V (*vs.* Ag/AgCl) due to the VO^{3+}-

VO^{2+} couple (Fig. 4). Fig. 5 illustrates the cyclic voltammograms of complex **1** at different scan rates from 10 to 400 mV s^{-1}. This behavior is also diagnostic of an irreversible electron transfer process.

Acknowledgement

This research was supported by the Zanjan University and the Universität zu Köln.

---

[1] K. H. Thompson, C. Orvig, *Coord. Chem. Rev*. **2001**, *219*, 1033.
[2] P. Noblio, M. Vieites, B. S. Prarajòn-Costa, E. J. Baran, H. Cerecetto, P. Draper, M. Gonzáles, O. Piro, E. E. Castellano, A. Azqueta, L. de Ceráin, A. Monge-Vega, D. Gambino, *J. Inorg. Biochem*. **2005**, *99*, 443.
[3] R. R. Eady, *Coord. Chem. Rev.* **2003**, *237*, 23.
[4] M. Weyand, H.-J. Hecht, M. Kiess, M.-F. Liaud, H. Vitler, D. Schomburg, *J. Mol. Biol.* **1999**, *293*, 595.
[5] R. Wever, W. Hemrika in *Handbook of Metalloproteins*, Vol. 2 (Eds.: A. Messerschmidt, R. Huber, T. Poulos, K. Wieghardt), Wiley, Chichester, **2001**, p. 1417.
[6] W. Plass, *Angew. Chem.* **1999**, *111*, 960; *Angew. Chem. Int. Ed.* **1999**, *38*, 909.
[7] D. Rehder, G. Antoni, G. M. Licini, C. Schulzke, B. Meier, *Coord. Chem. Rev.* **2003**, *237*, 53.
[8] D. Rehder, *Bioinorganic Vanadium Chemistry*, John Wiley & Sons, Chichester **2008**.
[9] T. Hirao, M. Mori, Y. Oshiro, *J. Org. Chem.* **1990**, *55*, 358.
[10] T. Hirao, T. Fujii, T. Tanaka, Y. Oshiro, *J. Chem. Soc., Perkin Trans.* **1994**, *1*, 3.
[11] G. W. Coates, P. D. Hustad, S. Reinartz, *Angew. Chem.* **2002**, *114*, 2340; *Angew. Chem. Int. Ed.* **2002**, *41*, 2236.
[12] F. Wolff, C. Lorber, R. Choukroun, B. Donnadieu, *Inorg. Chem.* **2003**, *42*, 7839.
[13] A. Butler, M.J. Clague, G.E. Meister, *Chem. Rev.* **1994**, *94*, 625.
[14] D.C. Crans, J.J. Smee, E. Gaidamauskas, L. Yang, *Chem. Rev.* **2004**, *104*, 849.
[15] D.C. Crans, *J. Inorg. Biochem.* **2000**, *80*, 123.
[16] M. Mijanuddin, A. Ray, P.C. Mondal, J. Marek, M. Ali, *J. Mol. Struct.* **2007**, *826*, 17.
[17] T. Thompson, S. D. Pastor, G. Rihs, *Inorg. Chem.* **1999**, *38*, 4163.
[18] P. Chaudhuri, M. Hess, U. Flörke, K. Wieghardt, *Angew. Chem.* **1998**, *110*, 2340; *Angew. Chem. Int. Ed.* **1998**, *37*, 2217.
[19] F. Thomas, G. Gelbon, I. G. Luneau, E. S. Aman, J.-L. Pierre, *Angew. Chem.* **2002**, *114*, 3173; *Angew. Chem. Int. Ed.* **2002**, *41*, 3047.
[20] Y. Wang, J. L. DuBois, K. O. Hodgson, T. D. P. Stack, *Science* **1998**, *279*, 537.
[21] T. K. Paine, T. Weyhermüller, K. Wieghardt, P. Chaudhuri, *Dalton Trans.* **2004**, 2092.
[22] T. K. Paine, T. Weyhermüller, K. Wieghardt, P. Chaudhuri, *Inorg. Chem.* **2002**, *41*, 6538.
[23] S. Mukherjee, T. Weyhermüller, E. Bothe, K. Wieghardt, P. Chaudhuri, *Eur. J. Inorg. Chem.* **2003**, 863.
[24] T. K. Paine, E. Rentschler, T. Weyhermüller, P. Chaudhuri, *Eur. J. Inorg. Chem.* **2003**, 3167.
[25] T. K. Paine, T. Weyhermüller, K. Wieghardt, P. Chaudhuri, *Dalton Trans.* **2004**, 2092.
[26] H. H. Monfared, R. Bikas, P. Mayer, *Inorg. Chim. Acta* **2010**, *363*, 2574.
[27] X-AREA (version 1.16), Stoe & Cie GmbH, Darmstadt (Germany) **2003**.
[28] X-RED (version 1.22), Data Reduction Program, Stoe & Cie GmbH, Darmstadt (Germany) **2001**.
[29] X-SHAPE (version 1.06), Crystal Optimisation for Numerical Absorption Correction, Stoe & Cie GmbH, Darmstadt (Germany) **1999**.
[30] L.J. Farrugia, WINGX, A MS-Windows System of Programs for Solving, Refining and Analysing Single Crystal X-ray Diffraction Data for Small Molecules, University of Glasgow, Glasgow, Scotland (U. K.) **2005**. See also: L.J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.
[31] A. Altomare, G. Cascarano, C. Giacovazzo, SIR-92, A Program for the Automatic Solution of Crystal Structures by Direct Methods; see *J. Appl. Crystallogr.* **1993**, *26*, 343.
[32] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.
[33] W. S. Gump, J. C. Vitucci, *J. Am. Chem. Soc.* **1945**, *67*, 238.
[34] A. Shockravi, R. Alizadeh, A. Moghimi, E. Rostami, S.B. Tabrizi, *Phosphorus Sulfur Silicon Relat. Elem.* **2003**, *178*, 2519.
[35] W. Plass, *Eur. J. Inorg. Chem.* **1998**, 799.
[36] S. Nica, M. Rudolph, H. Görls, W. Plass, *Inorg. Chim. Acta* **2007**, *360*, 1743.