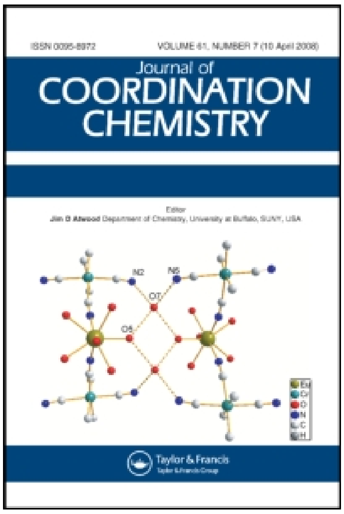


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

VANADYL(IV) COMPLEXES OF SULFUR-CONTAINING LIGANDS WITH BIOLOGICAL AND PHARMACOLOGICAL RELEVANCE

Evangelina Hernández[a]; Paula G. Murga[a]; Evelina G. Ferrer[a]; Patricia A. M. Williams[a]
[a] Centro de Quimica Inorgánica (CEQUINOR), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina

To cite this Article Hernández, Evangelina , Murga, Paula G. , Ferrer, Evelina G. and Williams, Patricia A. M.(2000) 'VANADYL(IV) COMPLEXES OF SULFUR-CONTAINING LIGANDS WITH BIOLOGICAL AND PHARMACOLOGICAL RELEVANCE', Journal of Coordination Chemistry, 49: 4, 335 — 345

To link to this Article: DOI: 10.1080/00958970008022243

URL: http://dx.doi.org/10.1080/00958970008022243

J. Coord. Chem., 2000, Vol. 49, pp. 335–345
Reprints available directly from the publisher
Photocopying permitted by license only

VANADYL(IV) COMPLEXES OF SULFUR-CONTAINING LIGANDS WITH BIOLOGICAL AND PHARMACOLOGICAL RELEVANCE

EVANGELINA HERNÁNDEZ, PAULA G. MURGA,
EVELINA G. FERRER and PATRICIA A.M. WILLIAMS*

*Centro de Química Inorgánica (CEQUINOR), Facultad de Ciencias Exactas,
Universidad Nacional de La Plata, C. Correo 962, 1900-La Plata, Argentina*

(Received 3 December 1998; Revised 9 April 1999; In final form 5 August 1999)

The behavior of thiosalicylic acid (H_2TSA) and 6-mercaptopurine (MP) with vanadyl(IV) cation has been studied in solution at different ligand-to-metal ratios and pH values. The preparation and characterization of VO/TSA(I) and VO/MP(II) complexes in the solid state is reported. The chemical environment of V in (I) is consistent with S and O atoms of TSA and two hydroxy bridges between two metal centers. The nearest neighbor atoms to V in (II) are S and N provided by the ligand and O atoms from hydroxyl groups. These results have been supported by physicochemical studies.

Keywords: Vanadyl(IV); thiosalicylic acid; 6-mercaptopurine; spectroscopy;
thermal behavior; magnetic properties

INTRODUCTION

To obtain more information on the behavior of ligands that have biological and pharmacological activity, thiosalicylic acid (H_2TSA) and 6-mercaptopurine (MP) were chosen. Complexes generated from Ag(I) and Au(III) with H_2TSA showed antimicrobial activity for some bacteria.[1–3] The thioanalogue of the natural purine hypoxanthine, 6-MP is used as an established clinical agent for the therapy of human leukemias. In some cases, metal complexes of this base (Pt, Pd) showed higher anticancer activity than the

---

* Corresponding author. E-mail: williams@nahuel.biol.unlp.edu.ar.

free ligand. Some authors have speculated that the anticarcinogenic activity of 6-MP may be related to its metal-binding properties. This ligand also has a pronounced effect on the metabolism of Zn, Cu, Fe, Ca and Mg.[4]

There is much evidence showing that vanadium is an essential trace element for both plants and animals. In biological systems there are examples of enzymes which contain vanadium in the active site. The metal is bonded to, among others, S, O (homocitrate) and N (histidine residue) atoms in vanadium nitrogenase and carboxylate in vanadate-dependent haloperoxidases.[5,6] This is controversial because Messerschmidt *et al.*[7] recently demonstrated that this interaction does not occur. The insulin-like effect of vanadium compounds was also demonstrated. In the vanadyl cysteine methyl ester complex with S and NH_2 groups interacting through the metal, the lowering blood glucose power was established.[8]

There exist several structural model compounds in which sulfur atoms are involved in the coordination sphere. In these complexes the oxidation numbers of vanadium, coordination geometry and nuclearity are different. Such complexes are involved in biological processes where N_2 is reduced to N_2H_4 or NH_3.[5] Several studies concerning α-mercaptoacids were performed in aqueous solution using ESR and UV–VIS spectroscopy[9–13] but the information about solid complexes is very scarce.

In previous work we reported formation of a new Cu/H_2TSA/py complex.[14] In the present study we examine vanadium species. The systems VO(IV)/H_2TSA and VO(IV)/MP were investigated both in solution and solid state. We demonstrate solid green complexes of vanadyl(IV) cation with: (a) H_2TSA presents metal sulfide and carboxylate interactions together with the formation of two hydroxy bridges between two metal centers; (b) MP shows coordination through S and NH_2 groups.

EXPERIMENTAL

Chemicals

H_2TSA and MP were purchased from Sigma; $VOCl_2$ (50% aqueous solution) was purchased from Carlo Erba. They were used without further purification. The solvents used were reagent grade.

Instrumentation

The electronic absorption spectra were obtained with a Hewlett-Packard-8452 diode-array spectrophotometer using 1 cm-quartz cells.

Infrared spectra were obtained with a Perkin Elmer 580B spectrophotometer using the KBr pellet technique.

Room temperature magnetic susceptibilities were determined with a Cahn-2000 instrument, calibrated with $Hg[Co(SCN)_4]$ in the usual way, and magnetic field strength, 6 kG. Thermogravimetric (TG) and differential thermal analysis (DTA) were performed on a Shimadzu thermoanalytical system (models TG50 and DTA50, respectively), working with Pt crucibles in an oxygen flow (60 mL/min) and heating rate of 10°C/min. Alumina was used as a DTA standard.

Diffuse reflectance spectra were recorded on a Shimadzu UV-300 spectrophotometer using MgO as an internal standard.

Spectrophotometric Titrations

Spectrophotometric titrations were performed at pH 7, $\lambda = 596$ nm (system I) in aqueous solution and pH 4, $\lambda = 796$ nm (system II) in absolute ethanol solution, under nitrogen, monitoring the absorbance changes as a function of the metal-to-ligand ratio.

Preparation of Na_2TSA

Na_2TSA was obtained by mixing H_2TSA ($pK_{a1} = 5.44$; $pK_{a2} = 9.52$)[15] in 1/2 ratio in aqueous solution adding 1 M NaOH until a final pH value of 12. The disodium salt was precipitated and washed with methanol, filtered and dried at 60°C.

Preparation of $(NH_4)_4[(VO)_2(TSA)_2(OH)_4]$

An aqueous solution of 2 mmol of $VOCl_2$ and 12 mL of 6 N HCl was prepared. The above mixture was added dropwise to a solution of 4 mmol of H_2TSA in 12 mL of a 0.025 M NH_4Cl in NH_3. After 30 min of constant stirring under an N_2 atmosphere, a green precipitate was observed. The solid was filtered, washed with ethyl ether and dried in an oven at 60°C.

Anal. Calcd. for $C_{14}H_{28}N_4O_{10}S_2V_2$(%): C 29.1, H 4.8, N 9.7, S 11.1, V 17.6; found: C 29.6, H 4.9, N 9.2, S 11.2, V 17.3.

The magnetic moment at room temperature is $\mu_{eff} = 0.75$ BM.

Preparation of $Na_2[VO(MP)(OH)_3]$

To a solution of 2 mmol of MP in hot absolute ethanol (30 mL), 1 mmol of $VOCl_2$ was added. The pH was adjusted to a final value of 4 by adding concentrated NaOH solution. After 1 h of refluxing in inert atmosphere, a green powder formed. It was filtered and washed several times with water and absolute ethanol and dried at 60°C.

Anal. Calcd. for $C_5H_6N_4Na_2O_4SV$(%): C 14.8, H 3.9, N 13.8, S 7.9, V 12.6; found: C 14.9, H 3.5, N 13.3, S 7.6, V 12.1.

The magnetic moment at room temperature is $\mu_{eff} = 1.35$ BM.

RESULTS AND DISCUSSION

Solution Studies

Table I shows the UV–VIS spectra of an aqueous solution of H_2TSA/VO complex (I) and an absolute ethanolic solution of the MP/VO complex (II). In both cases the ligand-to-metal ratio was 2/1 and pH values 7 and 4, respectively.

The spectral pattern of the electronic spectrum of (I) is similar to those of vanadyl(IV) complexes with other α-mercaptoacid ligands (thioglycolic and thiolactic,[9–11] 2-mercaptosuccinic,[11 13] and *meso*-2,3-dimercaptosuccinic[11] acids). Based on these data we postulate formation of a bis chelate complex where the coordination occurs through both COO^- and S^- groups.

The same comparison has been done with the spectrum of complex II. Taking into account the position of the bands of vanadyl(IV) and amidate,[16] glutathione and some related ligands[17,18] we conclude that the coordination sphere is formed by the N and S donors of 6-MP and the oxygen provided by the hydroxyl group.

Spectrophotometric titrations for system (II) leads to a 2/1 L/M ratio (see Figure 1). For system (I) and pH 7 it was impossible to complete the titration due to the hydrolysis of vanadyl cation in the L/M < 2/1 ratio. Nevertheless the absorbance *vs.* L/M ratio plot gives a straight line up to 2/1, confirming the presence of a single species.

TABLE I Electronic absorption bands of H_2TSA/VO, 2/1 aqueous solution and MP/VO, 2/1 ethanolic solution and diffuse reflectance bands of both solid complexes

Assignments	*H_2TSA/VO* (nm)		*MP/VO* (nm)	
	Aqueous solution	*Diffuse reflectance*	*Ethanolic solution*	*Diffuse reflectance*
$^2B_2 \rightarrow E(1)$	686 (96)	740 (sh), > 840	796 (89)	> 840
$^2B_2 \rightarrow {}^2B_1$	596 (72)	570	598 (84)	560
$^2B_2 \rightarrow {}^2A_1$			484 (sh, 98)	380

Parenthesis: ε ($M^{-1} \cdot cm^{-1}$); sh: shoulder.

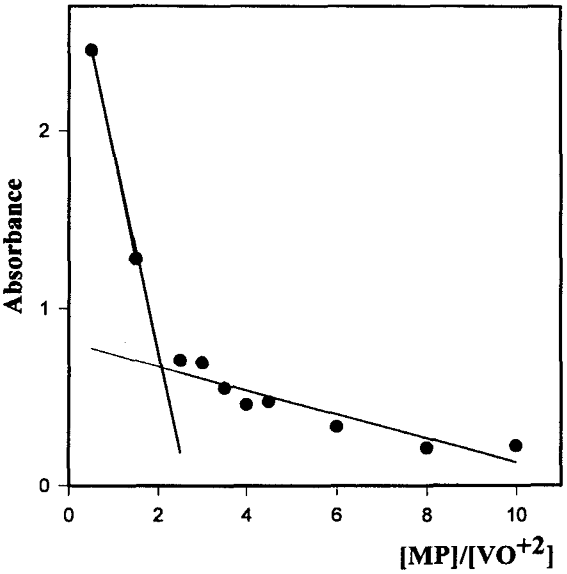


FIGURE 1 Spectrophotometric titration of VO^{2+} with 6-MP (2.5×10^{-2} M) at pH 4, under N_2 atmosphere, and at $\lambda = 796$ nm. Absolute ethanol was used as the solvent.

Solid State Studies

Diffuse Reflectance Spectra

The $^2B_2 \rightarrow E(1)$ transition of the vanadyl(IV) cation is displaced to red in both solid complexes (see Table I). The difference of solution and solid state electronic spectra for complex (II) is in agreement with a different coordination sphere and M/L ratio observed in solid (1/1, see below) and in solution phase (1/2). The different behavior of complex (I) cannot be explained in these terms because in solution it was not possible to determine the stoichiometry of the complex formed. A probable explanation of this behavior is that vanadyl(IV) forms monomer complexes with α-mercapto-acids in solution,[9–13] we could demonstrate the formation of a dimeric complex in the solid state (see below).

IR Spectra

Table II shows the IR spectra of H_2TSA, Na_2TSA and the VO/TSA system. The IR spectrum of the ligand shows an absorption at 2520 cm^{-1}, assigned to ν(SH), which is absent in the spectra of the sodium salt and the solid complex. This clearly indicates deprotonation of the SH group. Interaction of the S^- group with VO^{2+} could not be established.

TABLE II IR vibrational data of thiosalicyclic acid (H_2TSA), its sodium salt (Na_2TSA) and the vanadyl(IV) complex (VO/TSA) (Wavenumbers in cm^{-1})

Assignments	*H_2TSA*	*Na_2TSA*	*VO/TSA*
ν(S–H)	2520 (w)		
ν(COOH)	1678 (s)		
$\nu_a(COO^-)$		1575 (w)	1577 (s)
$\nu_s(COO^-)$		1449 (m)	Masked by $\nu_4(NH_4^+)$
δ(HNH)			1403 (vs)
Ring vibrations*	1038 (m)	1038 (m)	1038 (m)
ν(V=O)			962 (s)
δ(V–OH)			948 (sh)
ν(V–O–V)			730 (s)
ν(V–OH)			691 (m)

*Vibrational modes for *o*-substituted benzenes. vs = very strong, s = strong, m = medium, w = weak.

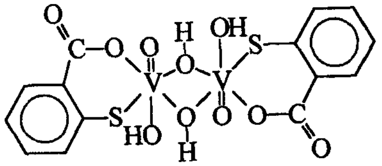
The absence of the band at 1678 cm^{-1} (ν(COOH)), in Na_2TSA and in the VO/TSA system as well denotes deprotonation of this group. Two new bands assigned to $\nu_a(COO^-)$ and $\nu_s(COO^-)$ replace this band. The difference between these two bands is a criterion of the mode of binding of the carboxylate group.[19] The presence of an ionic carboxylate group in the salt is suggested by the $\Delta(\nu_a(COO^-) - \nu_s(COO^-))$ value. The difference between the anti and symmetric stretching frequencies of carboxylate complexes has a similar value for monodentate COO^-, with hydrogen bonding between the uncoordinated carboxylate O atom and possible H atoms and in bridging COO^- groups.[19]

The decrease of the magnetic moment value of the VO/TSA system compared with a d^1 vanadium(IV) atom (1.73 BM) is indicative of formation of a dimer between the two metal centers which are held together by double bridges. In previous work[20] on the interaction of Captopril with VO^{2+} we showed the formation of two carboxylate bridges with $\mu_{eff} = 1.76$ BM. This demonstrates that the distance between the cations does not allow interaction. In this case the distance between the two vanadium atoms must be smaller. The complex might be hydroxy bridged where a direct exchange becomes possible between the metal centers in the *xy* plane.[21–23]

A new band that appears at 730 cm^{-1} related to ν(V–O–V)[24] supports the presence of the OH^- bridge. The characteristic bands of the terminal hydroxy groups are shown in Table II.[25]

The $\nu_4(NH_4^+)$ vibration observed in the IR spectrum of the solid complex masks the stretching $\nu_s(COO^-)$. The ν_3 band of the NH_4^+ cation is located at 3145 cm^{-1}. The position of the antisymmetric (ν_3) and bending (ν_4) vibrations of the ammonium cation is indicative of its T_d symmetry. The band at 1038 cm^{-1} is related to *o*-substituted benzenic ring vibrations.[26] The ν(V=O) band appears at 962 cm^{-1}.

It was concluded on the basis of infrared evidence that the complex has the following structure:



In Table III the characteristic frequencies for MP and the MP/VO system are presented. For MP the bands associated with ν(NH) are observed in the range 3500–3000 cm^{-1}.[27] The band located at 1274 cm^{-1} indicates the presence of the thione tautomeric form (C=S) in the ligand. The characteristic vibrations of the purine ring appear in the 1620–1500 cm^{-1} range.[28] Between 1500–1300 cm^{-1} the bands correspond to the (C–N) stretching because they are not affected by deuteration.[29] The OH vibration of the water molecule masks the stretching of the N–H group for the MP/VO system. The observed shift of the bands related to the vibrations of the ring (see Table III) is due to coordination of the metallic center with a nitrogen atom of the ring.

The striking disappearance of the thione vibration indicates the presence of the N=C–S form in the complex. Other marked changes can also be observed in the spectrum of VO/MP with a new band at 615 cm^{-1}. This band is assigned to the C–S bond, which has predominantly single bond

TABLE III IR vibrational data of 6-mercaptopurine (MP) and its vanadyl(IV) complex (VO/MP) (Wavenumbers in cm^{-1})

Assignments	*MP*	*VO/MP*
ν(N–H)	3431 (s)	
ν(N–H) + ν(OH)		3439 (br, s)
δ(N–H) + ν(C=C) + ν(C=N)	1612 (vs)	1613 (s)
ν(C=C) + ν(C=N)	1575 (s)	1577 (sh)
ν(C–N) + δ(C–H)	1528 (m)	1547 (m)
Purine ring vibrations	1407 (vs)	1387 (s)
ν(C–C) + ν(C–N)	1376 (sh)	
ν(C–N) + δ(N–H)	1343 (s)	1330 (w)
δ(N–H) + δ(C=S)	1274 (m)	
Imidazol ring vibrations	1225 (s) 1210 (sh)	1230 (w)
ν(V=O)		967 (s)
δ(V–OH)		938 (sh)
ν(V–OH)		659 (w)
ν(C–S)		615 (sh)

vs = very strong, s = strong, m = medium, sh = shoulder, w = weak, br = broad.

character with coordination of the metal through the S atom.[27] The band located at 967 cm^{-1} is associated with V=O stretching.

The deformation and stretching (V–OH) bands which appear at 938 and 659 cm^{-1}, respectively, support the presence of hydroxo ligands in the coordination sphere of the vanadium atom.[25]

The spectroscopic characteristics suggest that coordination to the metal take place through the S and N-7 atoms by formation of a five-member chelate ring.

The magnetic moment ($\mu_{eff} = 1.35$ BM) is somewhat smaller than the expected value for free vanadyl(IV) but in agreement with the presence of a d^1 atom.[21–23]

Thermogravimetric Studies

The thermal behavior of the two complexes was investigated by means of TG and DTA measurements under an oxygen flow.

H_2TSA/VO System

The degradation starts at *ca.* 221°C with a theoretical loss of 24.5% associated to the loss of ammonium and hydroxide groups, in good agreement with the $\Delta\omega_{exp} = 25.0\%$. A weak endothermic peak located at 250°C (DTA signal) accompanies this process (see Figure 2).

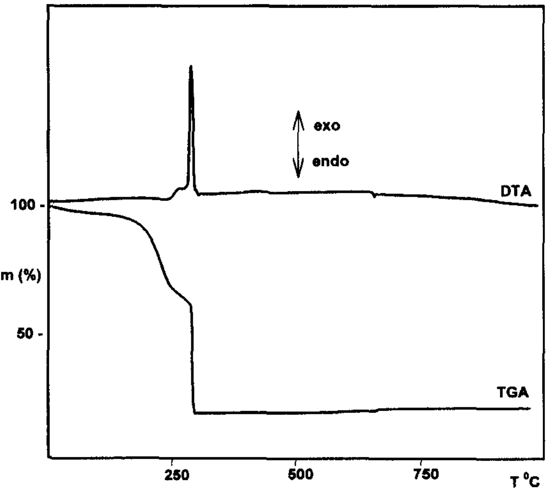


FIGURE 2 Thermogram of the solid $(NH_4)_4[(VO)_2(TSA)_2(OH)_4]$ complex. O_2 flow: 60 mL/min; heating rate: 10°C/min.

The last pyrolysis step occurs between 270–350°C, involving two exothermic DTA signals located at 284°C (lower intensity) and 324°C (higher intensity).

The final residue was characterized by X-ray spectroscopy as V_2O_5 and V_3S (PC-PDF 41-1426 and PC-PDF 29-1384, respectively).

The total weight loss of 76.5% agrees with the theoretical value of 76.2%. The total stoichiometry of this process is proposed as follows:

$$4(NH_4)_4[(VO)_2(TSA)_2(OH)_4] \xrightarrow{\phi,O_2} V_2O_5 + 2V_3S + \text{volatile products}$$

MP/VO System

Thermal degradation occurs in several overlapping steps (see Figure 3). The dehydration begins earlier and covers the range 25–320°C with the elimination of three water molecules in three successive stages (endothermic DTA signals: 97°C, 177°C and 304°C; $\Delta\omega\%_{calc}$ 13.3 and $\Delta\omega\%_{exp}$ 13.6).

$$Na_2[VO(MP)(OH)_3]\cdot 5H_2O \xrightarrow{\phi,O_2} Na_2[VO(MP)(OH)_3]\cdot 2H_2O + 3H_2O$$

Immediately after, the remaining water molecules are lost together with decomposition of the complex. The degradation product at this step is found to be $VOSO_4$ (detected by the IR spectrum). This behavior was also observed in $Cd(MP)_2\cdot 2H_2O$.[30] Two exothermic DTA signals were

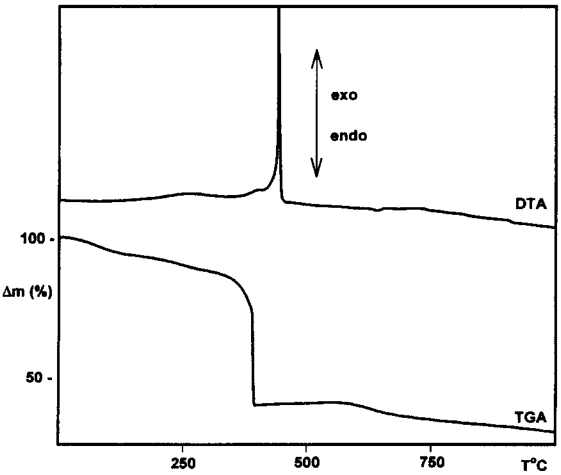


FIGURE 3 Thermogram of the solid $Na_2[VO(MP)(OH)_3]$ complex. O_2 flow: 60 mL/min; heating rate: 10°C/min.

observed at 359°C and 406°C (the latter was very strong; $\Delta\omega\%_{calc}$ 59.8 and $\Delta\omega\%_{exp}$ 59.4).

$$Na_2[VO(MP)(OH)_3]\cdot 2H_2O \xrightarrow{\phi,O_2} VOSO_4 + 2H_2O + \text{other volatile products}$$

Finally, subsequent degradation of the complex reveals a relatively stable intermediate that is a mixture of $VOSO_4$ and V_2O_5 of unknown stoichiometry. This solid residue is confirmed, unambiguously, by IR spectroscopy.

The very weak endothermic DTA signal observed in the two cases around 660–670°C, corresponding to the melting point of V_2O_5 (658°C),[31] confirms the presence of this oxide.

CONCLUSIONS

The two solid complexes obtained in this study between VO^{2+} and H_2TSA and 6-MP: $(NH_4)_4[(VO)_2(TSA)_2(OH)_4]$ (I) and $Na_2[VO(MP)(OH)_3]\cdot 5H_2O$ (II) could be characterized both in the solid state and in solution. The UV-VIS, diffuse reflectance and IR spectroscopies, together with magnetic, thermogravimetric and elemental analyses allow us to propose laboratory potential models having the same functional groups as in vanadium-containing nitrogenases. In system I the interaction of the metal occurs with the sulfur and oxygen atoms and system II also interacts with a nitrogen donor atom.

Acknowledgments

This work was supported by CONICET, CICPBA and Agencia Nacional de Promoción Científica y Tecnológica (PICT = 119).

References

[1] K. Nomiya, Y. Kondoh, K. Onoue, N.C. Kasuga, H. Nagano, M. Oda, T. Sudoh and S. Sakuma, *J. Inorg. Biochem.*, **58**, 255 (1995).

[2] K. Nomiya, H. Yokoyama, H. Nagano, M. Oda and S. Sakuma, *J. Inorg. Biochem.*, **60**, 289 (1995).

[3] T. Subrahmanyan, *J. Indian Chem. Soc.*, **LXV**, 589 (1988).

[4] E. Dubler, Metal complexes of sulfur-containing purine derivatives, in *Metal Ions in Biological Systems* (Eds: A. Sigel and H. Sigel, New York: Marcel Dekker, 1995), Vol. 32 and references therein, pp. 301–338.

[5] D. Rehder, *Angew. Chem. Int. Ed. Engl.*, **30**, 148 (1991).

[6] R.R. Eady, Vanadium nitrogenases of Azotobacter, in *Metal Ions in Biological Systems* (Eds: A. Sigel and H. Sigel, New York: Marcel Dekker, 1995), Vol. 31, pp. 363–405.
[7] A. Messerschmidt, L. Prade and R. Wever, *Biol. Chem.*, **378**, 309 (1997).
[8] C. Orvig, K.H. Thompson, M. Battell and J.H. Mc Neill, Vanadium compounds as insulin mimics, in *Metal Ions in Biological Systems* (Eds: A. Sigel and H. Sigel, New York: Marcel Dekker, 1995), Vol. 31, pp. 575–594.
[9] R.R. Reeder and P.H. Rieger, *Inorg. Chem.*, **10**, 1258 (1971).
[10] P.A.M. Williams, D.A. Barrio and S.B. Etcheverry, *J. Inorg. Biochem.*, **75**, 99 (1999).
[11] T. Kiss, P. Buglyó, G. Micera, A. Dessí and D. Sanna, *J. Chem. Soc. Dalton Trans.*, 1849 (1993).
[12] G. Micera and A. Dessí, *J. Inorg. Biochem.*, **33**, 99 (1988).
[13] R.P. Ferrari, E. Laurenti, S. Poli and L. Casella, *J. Inorg. Biochem.*, **45**, 21 (1992).
[14] E.G. Ferrer and P.A.M. Williams, *Polyhedron*, **16**, 3323 (1997).
[15] R.S. Ramakrishna and M.E. Fernandopulle, *J. Inorg. Nucl. Chem.*, **33**, 1940 (1971).
[16] A.D. Keramidas, A.B. Papaioannou, A. Vlahos, T.A. Kabanos, G. Bonas, A. Makriyannis, C.R. Rapropoulou and A. Terzis, *Inorg. Chem.*, **35**, 357 (1996).
[17] A. Dessí, G. Micera and D. Sanna, *J. Inorg. Biochem.*, **52**, 275 (1993).
[18] E.G. Ferrer, P.A.M. Williams and E.J. Baran, *J. Inorg. Biochem.*, **50**, 253 (1993).
[19] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn. (New York: John Wiley and Sons, 1986), pp. 231–233.
[20] P.A.M. Williams, E.G. Ferrer and E.J. Baran, *J. Coord. Chem.*, **42**, 261 (1997).
[21] V.T. Kalinnikov, V.V. Zelentsov, O.N. Kuz'Micheva and T.G. Aminov, *Russ. J. Inorg. Chem.*, **15**, 341 (1970).
[22] A. Syamal, *Coord. Chem. Rev.*, **16**, 309 (1975).
[23] S.L. Castro, M.E. Cass, F.J. Hollander and S.L. Bartley, *Inorg. Chem.*, **34**, 466 (1995).
[24] M.I. Khan, Y. Chang, Q. Chen, J. Salta, Y. Lee, C.J. O'Connor and J. Zubieta, *Inorg. Chem.*, **33**, 6340 (1994).
[25] E.G. Ferrer, S.B. Etcheverry and E.J. Baran, *Monatsh. Chem.*, **124**, 355 (1993).
[26] D. Lin-Vien, N.B. Colthup, W.F. Fateley and J.G. Grasselli, *Infrared and Raman Characteristic Frequencies of Organic Molecules* (Boston: Academic Press, Inc., 1991), pp. 277–284.
[27] J. Brigando and D. Colaitis, *Bull. Soc. Chim. Fr.*, **10**, 3440 (1969).
[28] R. Cini, A. Cinquantini, M. Sabat and L.G. Marzilli, *Inorg. Chem.*, **24**, 3903 (1985).
[29] C.L. Angell, *J. Chem. Soc.*, 504 (1961).
[30] E. Dubler and G. Hänggi, *Thermochim. Acta*, **234**, 201 (1994).
[31] R.J.H. Clark, Vanadium, in *Comprehensive Inorganic Chemistry* (Oxford: Pergamon Press, 1973), Vol. 3, p. 511.