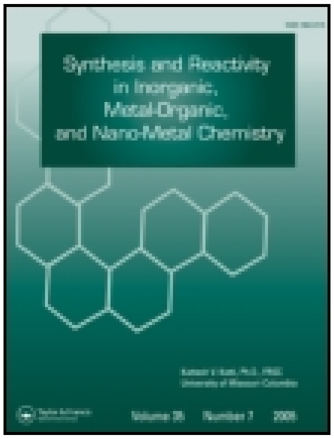
This article was downloaded by: [University of Western Ontario]
On: 13 November 2014, At: 00:43
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

An Oxo-Bridged Dinuclear Vanadium(V) Complex of N,N′-bis(salicylidene)-1,5-diimino-3-azapentane: Synthesis and Structure

Fu-Ming Wang [a]

[a] Department of Chemistry, Dezhou University , Dezhou Shandong , P. R. China

Accepted author version posted online: 01 Aug 2012.Published online: 05 Oct 2012.

To cite this article: Fu-Ming Wang (2012) An Oxo-Bridged Dinuclear Vanadium(V) Complex of N,N′-bis(salicylidene)-1,5-diimino-3-azapentane: Synthesis and Structure, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:10, 1386-1389, DOI: 10.1080/15533174.2012.680168

To link to this article: http://dx.doi.org/10.1080/15533174.2012.680168

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:1386–1389, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2012.680168

An Oxo-Bridged Dinuclear Vanadium(V) Complex of *N,N′*-bis(salicylidene)-1,5-diimino-3-azapentane: Synthesis and Structure

Fu-Ming Wang
Department of Chemistry, Dezhou University, Dezhou Shandong, P. R. China

The reaction of vanadyl acetylacetonate with *N,N′*-bis (salicylidene)-1,5-diimino-3-azapentane (H_2SDA) affords an oxo-bridged dinuclear Schiff base vanadium(V) complex, $[VO_2(HSDA)]_2$. The structure of the complex was characterized by elemental analysis, infrared spectroscopy, and single-crystal X-ray diffraction. The complex crystallizes as monoclinic space group $P2_1/n$, with $a = 6.619(2)$, $b = 32.592(3)$, $c = 8.715(2)$ Å, $\beta = 104.001(3)^\circ$, $V = 1824.2(7)$ Å^3, $Z = 4$, $R_1 = 0.0637$, $wR_2 = 0.1228$ for 1989 observed data. The complex exhibits a distorted octahedral geometry, involving in the equatorial plane the phenolate, imine, and amine donors of the Schiff base ligand and the bridging oxo O group and in the axial positions two other oxo O groups. The intramolecular V···V distance is 3.226(1) Å.

Keywords crystal structure, dinuclear complex, Schiff base, vanadium complex

INTRODUCTION

There is considerable interest in the biological chemistry of vanadium due to the recent discovery of two types of vanadium-dependent enzymes. One has a nitrogenase activity, catalyzing the reduction of dinitrogen to ammonia,[1] and the other has bromoperoxidase activity, catalyzing the peroxidedependent halogenation of organic compounds in the presence of halide ion.[2,3] The latter is thought to contain a vanadium(V) active site.[4] Vanadium has also attained increasing interest in the past few years because of its application in medicine especially for its insulin-mimetic behaviour.[5–7] The importance of vanadium in biological and medicinal chemistry has stimulated our interest in the coordination and reaction chemistry of this element. In the last years, a variety of vanadium complexes have been introduced as structural and/or functional models for biologically active vanadium compounds.[8–10] A few examples of oxovanadium complexes of Schiff bases derived from the reaction of salicylaldehyde and primary amines have also been prepared previously.[11–13] In this article we report the synthesis and structure of a new oxo-bridged dinuclear vanadium complex of the Schiff base ligand *N,N′*-bis(salicylidene)-1,5-diimino-3-azapentane (H_2SDA).

EXPERIMENTAL

Materials and Physical Measurement

Salicylaldehyde and diethylenetriamine were purchased from Aldrich Chemical Co. (USA) and used as received. All other chemicals and solvents were of analytical grade and used as received. Infrared spectrum was recorded on a Perkin-Elmer 783 spectrometer (Dezhou University, China) as KBr pellet. Microanalytical (C, H, N) data were obtained from a Perkin-Elmer 240C elemental analyzer (Dezhou University, China). Solution electrical conductivity was measured with the DDS-11a conductivity meter (INESA Scientific Instrument Co., Dezhou University, China). UV-vis spectrum was recorded on a Perkin-Elmer Lambda 9 instrument.

Preparation of the Complex $[VO_2(HSDA)]_2$

Salicylaldehyde (0.30 g, 2 mmol) and diethylenetriamine (0.10 g, 1 mmol) were added to 30 mL methanol and allowed to react for 1 h. Vanadyl acetylacetonate (0.26 g, 1 mmol), dissolved in 20 mL of methanol, was added to the solution. The final mixture was further stirred for 2 h at room temperature to obtain a clear yellow solution. X-ray quality single crystals were obtained by slow evaporation of the solution in air for a week. The crystals were filtered, washed with methanol and finally dried in vacuum over phosphorus pentoxide. Yield: 73%. Found (%): C, 54.8; H, 5.2; N, 10.7. Anal. Calcd. for $C_{18}H_{20}N_3O_4V$ (%): C, 55.0; H, 5.1; N, 10.7. IR frequencies in cm^{-1}: 3448, 3227, 1642, 1628, 1597, 1550, 1497, 1471, 1452, 1417, 1406, 1344, 1303, 1280, 1208, 1150, 1123, 1190, 1040, 1011, 975, 931, 894, 857, 803, 763, 623, 576, 551, 462, 443.

X-Ray Crystallography

A suitable single crystal of the complex was mounted on a thin glass fiber without protection. Cell dimensions were determined at 298 K from the setting angles of a Bruker

---

Received 20 December 2011; accepted 1 January 2012.

The Department of Chemistry of Dezhou University is acknowledged for financial support.

Address correspondence to Fu-Ming Wang, Department of Chemistry, Dezhou University, Dezhou Shandong 253023, P. R. China. E-mail: wfm99999@126.com

SMART 1000 CCD diffractometer (Dezhou University, China) using a graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation source. Data collection was completed using the $\omega/2\theta$ scan techniques. Pertinent cell parameters, data collection conditions, and refinement details are provided in Table 1. The structure was solved by direct methods, developed by successive difference Fourier synthesis and refined on F^2 by a full-matrix least-squares procedure using the SHELXL-97 program (Bruker AXS, Lanzhou University, China).[14] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. The amino hydrogen atom was located from a difference map, and with N–H distance restrained to 0.90(1) Å. The remaining hydrogen atoms were geometrically calculated and isotropically fixed at positions recalculated after each cycle of refinement [d(C-H) = 0.93–0.97 Å, d(O-H) = 0.82 Å, with the isotropic thermal parameter of $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\ U_{\mathrm{iso}}(\mathrm{C})$ and $1.5\ U_{\mathrm{iso}}(\mathrm{O})$]. In all the cases, absorption corrections based on multiscan using SADABS software (Bruker AXS, Lanzhou University, China)[15] were applied. Data reduction was accomplished using the SAINT plus software (Bruker AXS, Lanzhou University, China).[16] The crystal data and refinement details are listed in Table 1.

RESULTS AND DISCUSSION

The Schiff base H_2SDA was used to prepare complexes with Cu,[17,18] Gd, Tb, Nd, Sm, Pr,[19–21] Cd,[22] and Sn.[23] In the reported complexes, the Schiff base ligands coordinate to the metal atoms through all the five donor atoms. The vanadium complexes with H_2SDA have never been reported. In the present work, it is interesting that we have prepared an oxo-bridged dinuclear vanadium(V) complex, with three of the five donor atoms of the Schiff base ligand coordinate to each V atom, and with the other two forms an intramolecular O—H···N hydrogen bond. The molar conductance of a *ca* 0.10 mmol dm^{-3} solution of the complex in acetonitrile at 25°C is 8.3 Ω^{-1} cm^2 mol^{-1}. The data indicate nonelectrolytic behavior in the solution.[24] In the absorption spectrum of the complex, two absorption bands at 232 and 527 nm were observed. Absorption bands at 232 nm can be assigned to $\pi \rightarrow \pi^*$ transition based on the ligand. Absorption bands at 527 nm can be assigned to a $d_{xy} \rightarrow (d_{xz}, d_{yz})$ transition.

TABLE 1
Crystal data and structure refinement for the complex

Formula weight	$C_{18}H_{20}N_3O_4V$
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	6.619(2)
b (Å)	32.592(3)
c (Å)	8.715(2)
β (°)	104.001(3)
Volume (Å^3)	1824.2(7)
Z	4
D_{calc} (g cm^{-3})	1.432
Absorption coefficient (mm^{-1})	0.572
F(000)	816
Crystal size (mm)	0.30 × 0.28 × 0.27
Limiting indices	$-8 < h < 8, -41 < k < 41, -11 < h < 11$
Reflections collected/unique	14878/3972
Observed reflections [$I > 2\sigma(I)$]	1989
Completeness to θ = (%)	99.5
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3972/1/239
Goodness-of-fit on F^2	1.031
Final R indices [$I > 2\sigma(I)$]	0.0637
R indices (all data)	0.1228
Largest difference in peak and hole (e Å^{-3})	0.386, –0.279

Description of the Structure of the Complex

An ORTEP diagram of the complex is illustrated in Figure 1, and important bond lengths and angles are provided in Table 2. X-ray single-crystal structure analysis reveals that the complex possesses crystallographic inversion center symmetry,

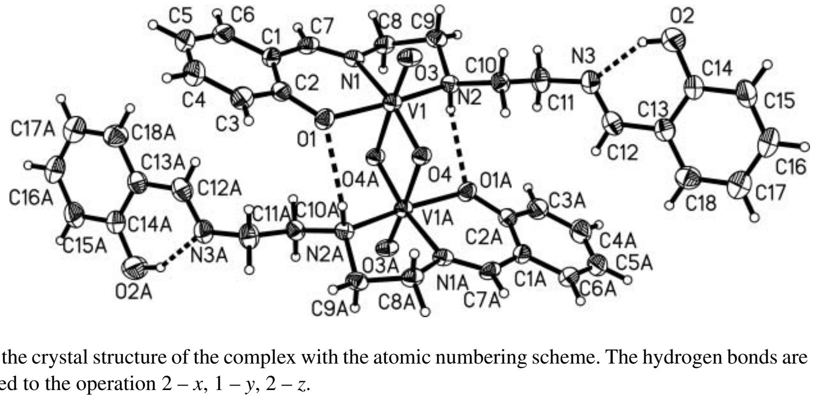


FIG. 1. An ORTEP drawing of the crystal structure of the complex with the atomic numbering scheme. The hydrogen bonds are shown as dashed lines. Symmetry atoms with the suffix A are related to the operation $2 - x, 1 - y, 2 - z$.

TABLE 2
Selected bond lengths (Å) and bond angles (°)

Bond lengths			
V1-O1	1.914(3)	V1-O3	1.614(3)
V1-O4	1.652(3)	V1-O4A	2.440(3)
V1-N1	2.152(3)	V1-N2	2.155(3)
Bond angles			
O3-V1-O4	107.33(14)	O3-V1-O1	101.67(14)
O4-V1-O1	98.20(12)	O3-V1-N1	99.88(13)
O4-V1-N1	151.27(13)	O1-V1-N1	84.91(13)
O3-V1-N2	92.52(13)	O4-V1-N2	92.17(13)
O1-V1-N2	158.99(13)	N1-V1-N2	77.37(13)
O3-V1-O4A	169.11(12)	O4-V1-O4A	77.67(12)
O1-V1-O4A	86.91(11)	N1-V1-O4A	73.97(11)
N2-V1-O4A	77.47(10)		

with the inversion center located at the midpoint of the two V atoms. There form two intermolecular N–H···O hydrogen bonds between the two [VO_2(HSDA)] units. The intramolecular V···V distance is 3.226(1) Å. Each V atom is six-coordinated with two distinct oxo groups being apparent. The distance between V1 and the oxo O3 proves it a typical double bond. The other oxo O4 group is involved in the bridge between V1 and V1A. The O4 atom is strongly coordinated to V1 (1.652(3) Å) and is weakly associated with V1A (2.440(3) Å). The remaining three coordination sites are occupied by the phenolate O (1.914(3) Å), imine N (2.152(3) Å), and amine N (2.155(3) Å) atoms of the Schiff base ligand. Thus, the coordination spheres of the vanadium atoms are best described as distorted octahedral geometry. The distortion of the octahedral coordination can also be observed form the coordinate bond angles. The *cis* angles surrounded at the V1 atom are range from 74.0(1) to 107.3(1)°, and the *trans* angles are range from 151.3(1) to 169.1(1)°. The coordinate bond lengths are within normal values.[25,26]

In the crystal of the complex, the [VO_2(HSDA)]$_2$ complex molecules are stack along the *a*-axis by weak $\pi\cdots\pi$ interactions, as shown in Figure 2.

IR Spectra

In the IR spectrum of the complex, the dioxo nature of the complex is confirmed by the presence of two V = O bands at 931 and 894 cm^{-1}. The $\nu_{C=N}$ in the complex are found at 1642 and 1628 cm^{-1}. The former can be assigned to the free C12 = N3 bond, and the later can be assigned to the coordinated C7 = N1 bond. The IR spectrum of the complex shows a single sharp band at 3227 cm^{-1} designated to the N-H stretching mode of the coordinated secondary amino group. The weak and broad absorption centered at 3448 cm^{-1} is attributed to the O-H bond, which participates in the formation of intramolecular O–H···N hydrogen bond.

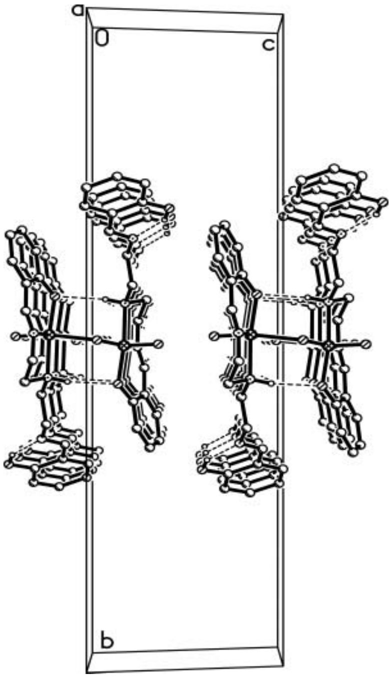


FIG. 2. The molecular packing of the complex, viewed along the *a*-axis. H atoms, except those related to hydrogen bonding, are omitted for clarity.

CONCLUSION

A novel centrosymmetric vanadium(V) complex with the Schiff base *N,N′*-bis(salicylidene)-1,5-diimino-3-azapentane has been prepared and characterized. The V atom is six-coordinated in an octahedral geometry. The Schiff base ligand coordinates to the V atom through three of the five donor atoms, with the other two generate an intramolecular O–H···N hydrogen bond.

SUPPLEMENTARY MATERIALS

Supplementary crystallographic data are available from the CCDC, Union Road, Cambridge CB2 1EZ, UK on request quoting the deposition number CCDC 859119 (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

REFERENCES

1. Robson, R. L.; Eady, R. R.; Richardson, T. H.; Miller, R. W.; Hawkins, M.; Postgate, J. R. The alternative nitrogenase of azotobacter-chroococcum is a vanadium enzyme. *Nature* **1986**, *322*, 388–390.
2. Vilter, H. Peroxidases from phaeophyceae: a vanadium(V)-dependent peroxidase from ascophyllum-nodosum. *Phytochem.* **1984**, *23*, 1387–1390.
3. de Boer, E.; van Kooyk, Y.; Tromp, M. G. M.; Plat, H.; Wever, R. Bromoperoxidase from ascophyllum-nodosum: a novel class of enzymes containing vanadium as a prosthetic group. *Biochim. Biophys. Acta* **1986**, *869*, 48–53.
4. de Boer, E.; Tromp, M. G. M.; Plat, H.; Krenn, G. E.; Wever, R. Vanadium(V) as an essential element for haloperoxidase activity in marine brown-algae: purification and characterization of a vanadium(V)-containing bromoperoxidase from laminaria-saccharina. *Biochim. Biophys. Acta* **1986**, *872*, 104–115.
5. Crans, D. C.; Trujillo, A. M.; Pharazyn, P. S.; Cohen, M. D. How environment affects drug activity: localization, compartmentalization and reactions

of a vanadium insulin-enhancing compound, dipicolinatooxovanadium(V). *Coord. Chem. Rev.* **2011**, *255*, 2178–2192.

6. Islam, M. N.; Kumbhar, A. A.; Kumbhar, A. S.; Zeller, M.; Butcher, R. J.; Dusane, M. B.; Joshi, B. N. Bis(maltolato)vanadium(III)-polypyridyl complexes: synthesis, characterization, DNA cleavage, and insulin mimetic activity. *Inorg. Chem.* **2010**, *49*, 8237–8246.
7. Mendes, I. C.; Botion, L. M.; Ferreira, A. V. M.; Castellano, E. E.; Beraldo, H. Vanadium complexes with 2-pyridineformamide thiosemicarbazones: in vitro studies of insulin-like activity. *Inorg. Chim. Acta* **2009**, *362*, 414–420.
8. Guilherme, L. R.; Massabni, A. C.; Cuin, A.; Oliveira, L. A. A.; Castellano, E. E.; Heinrich, T. A.; Costa-Neto, C. M. Synthesis, characterization, crystal structure, and biological studies of vanadium complexes with glycolic acid. *J. Coord. Chem.* **2009**, *62*, 1561–1571.
9. Crans, D. C.; Smee, J. J.; Gaidamauskas, E.; Yang, L. Q. The chemistry and biochemistry of vanadium and the biological activities exerted by vanadium compounds. *Chem. Rev.* **2004**, *104*, 849–902.
10. Ashiq, U.; Ara, R.; Mahroof-Tahir, M.; Maqsood, Z. T.; Khan, K. M.; Khan, S. N.; Siddiqui, H.; Choudhary, M. I. Synthesis, spectroscopy, and biological properties of vanadium(IV)–hydrazide complexes. *Chem. Biodivers.* **2008**, *5*, 82–92.
11. Khatri, P. K.; Singh, B.; Jain, S. L.; Sain, B.; Sinha, A. K. Cyclotriphosphazene grafted silica: a novel support for immobilizing the oxo-vanadium Schiff base moieties for hydroxylation of benzene. *Chem. Commun.* **2011**, *47*, 1610–1612.
12. Romanowski, G.; Wera, M. Mononuclear and dinuclear chiral vanadium(V) complexes with tridentate Schiff bases derived from *R*(-)-1,2-diaminopropane: synthesis, structure, characterization and catalytic properties. *Polyhedron* **2010**, *29*, 2747–2754.
13. Wazalwar, S. S.; Bhave, N. S.; Dikundwar, A. G.; Ali, P. Microwave assisted synthesis and antimicrobial study of Schiff base vanadium(IV) complexes of phenyl esters of amino acids. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2011**, *41*, 459–464.
14. Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr.* **2008**, *A64*, 112–122.
15. Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen, Göttingen, Germany, **1996**.
16. Bruker. *SAINT-Plus, Software Users Guide*, Version 6.0; Madison, WI: Bruker Analytical X-ray Systems, **1999**.
17. McKenzie, E. D.; Selvey, S. J. Copper(II) compounds with the potentially quinquedentate ligand *N,N'*-bissalicylidene-1,5-diimino-3-azapentane, including an X-ray structure-analysis of $[Cu_2(C_{18}H_{19}N_3O_2)_2]\cdot 2C_3H_6O$. *Inorg. Chim. Acta* **1985**, *101*, 127–133.
18. Quintero-Tellez, G.; Alvarez, C. M. G.; Bernes, S.; Alcantara-Flores, J. L.; Reyes-Ortega, Y. Bis{μ-2,2′-[(3-azapentane-1,5-diyl)bis(nitrilo methylidyne)]diphenolato} dicopper(II) dimethyl sulfoxide disolvate. *Acta Crystallogr.* **2008**, *E64*, m631.
19. Howell, R. C.; Spence, K. V. N.; Kahwa, I. A.; White, A. J. P.; Williams, D. J. The preparation and crystal and molecular structures of new luminescent Schiff-base complexes featuring coupled lanthanide(III) cations. *J. Chem. Soc., Dalton Trans.* **1996**, *6*, 961–968.
20. Chakraborty, J.; Ray, A.; Pilet, G.; Chastanet, G.; Luneau, D.; Ziessel, R. F.; Charbonniere, L. J.; Carrella, L.; Rentschler, E.; El Fallah, M. S.; Mitra, S. *Dalton Trans.* **2009**, *46*, 10263–10272.
21. Chakraborty, J.; Pilet, G.; El Fallah, M. S.; Ribas, J.; Mitra, S. Synthesis, characterization and cryomagnetic studies of a novel homonuclear Nd(III) Schiff base dimmer. *Inorg. Chem. Commun.* **2007**, *10*, 489–493.
22. Chakraborty, J.; Thakurta, S.; Samanta, B.; Ray, A.; Pilet, G.; Batten, S. R.; Jensen, P.; Mitra, S. Synthesis, characterisation and crystal structures of three trinuclear cadmium(II) complexes with multidentate Schiff base ligands. *Polyhedron* **2007**, *26*, 5139–5149.
23. Luna-Garcia, R.; Damian-Murillo, B. M.; Barba, V.; Hopfl, H.; Beltran, H. I.; Zamudio-Rivera, L. S. Structural relationship between a host included chain of spirocyclic water hexamers and bulk water: the role of water clusters in self assembly and crystallization processes. *Chem. Commun.* **2005**, *44*, 5527–5529.
24. Geary, W. J. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coord. Chem. Rev.* **1971**, *7*, 81–122.
25. Root, C. A.; Hoeschele, J. D.; Cornman, C. R.; Kampf, J. W.; Pecoraro, V. L. Structural and spectroscopic characterization of dioxovanadium(V) complexes with asymmetric Schiff-base ligands. *Inorg. Chem.* **1993**, *32*, 3855–3861.
26. Rayati, S.; Wojtczak, A.; Kozakiewicz, A. One step preparation of $[(VO(\mu\text{-}O)L)]_2$: a 2D supramolecular network directed by intermolecular interaction. *Inorg. Chim. Acta* **2008**, *361*, 1530–1533.