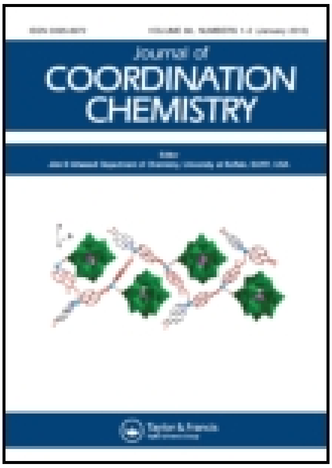


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

NMR and theoretical study on the coordination interaction between peroxovanadium(V) complexes and 5-amino-1,10-phenanthroline

Xianyong Yu[abc], Lin Deng[a], Hongwen Tao[a], Bingfei Jiang[a] & Xiaofang Li[a]

[a] Key Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education, Hunan Province College Key Laboratory of QSAR/QSPR, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, China

[b] State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, PR China

[c] Key Laboratory of Computational Physical Sciences, Fudan University, Ministry of Education, Shanghai, PR China

To cite this article: Xianyong Yu, Lin Deng, Hongwen Tao, Bingfei Jiang & Xiaofang Li (2014) NMR and theoretical study on the coordination interaction between peroxovanadium(V) complexes and 5-amino-1,10-phenanthroline, Journal of Coordination Chemistry, 67:2, 315-322, DOI: 10.1080/00958972.2014.880783

To link to this article: http://dx.doi.org/10.1080/00958972.2014.880783

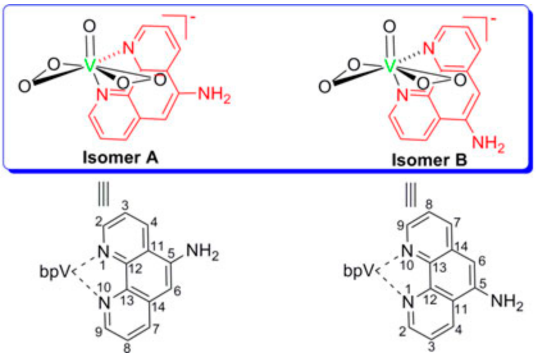
Journal of Coordination Chemistry, 2014
Vol. 67, No. 2, 315–322, http://dx.doi.org/10.1080/00958972.2014.880783

NMR and theoretical study on the coordination interaction between peroxovanadium(V) complexes and 5-amino-1,10-phenanthroline

XIANYONG YU*†‡§, LIN DENG†, HONGWEN TAO†, BINGFEI JIANG† and XIAOFANG LI*†

†Key Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education, Hunan Province College Key Laboratory of QSAR/QSPR, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, China
‡State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, PR China
§Key Laboratory of Computational Physical Sciences, Fudan University, Ministry of Education, Shanghai, PR China

(*Received 4 October 2013; accepted 16 December 2013*)



To understand the coordination modes and the solution structure of 5-amino-1,10-phenanthroline (5-NH_2-phen), the coordination reaction between peroxovanadium(V) complex $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(HOD)]^-$ and 5-NH_2-phen has been investigated by multinuclear (^{1}H, ^{13}C, and ^{51}V) magnetic resonance with variable temperature NMR, COSY, and HSQC. The experimental results indicate a pair of isomers in solution, which are attributed to different coordination modes between vanadium and 5-NH_2-phen. The solution structures of these newly formed peroxovanadate species were proposed based on experimental NMR information and confirmed by theoretical calculations. Moreover, the results of density functional calculations indicate that solvation plays an important role in these interactions.

Keywords: Peroxovanadate; 5-Amino-1,10-phenanthroline; Coordination reaction; NMR; DFT-calculation

---

*Corresponding authors. Email: yu_xianyong@163.com (X. Yu); lixiaofang@iccas.ac.cn (X. Li)

1. Introduction

Vanadium complexes, particularly vanadate(V) and more recently heteroligand peroxidovanadate(V) complexes (pVs), have attracted attention because of their implication in many biological processes and therapeutic applications as the inhibitors of cancerous tumor growth, insulin mimetics, etc. [1–6]. Therefore, coordination chemistry and biological mechanism of vanadium compounds are of increasing interest. For example, coordination reactions between peroxovanadate complexes and a series of amino acids or peptides through NMR spectroscopic methods were explored by Tracey and co-workers [7]. A new series of vanadium complexes containing imidazole-like ligands have been prepared by Crans' group [8]. Kanamori and co-workers studied the physiological effects of peroxidovanadate complexes and their results indicate that both the toxicity and the physiological effects of pVs can be controlled by selecting an appropriate ancillary ligand [9]. Three supramolecular oxovanadium complexes containing oxalate have been prepared and characterized by Xing's group, who studied the catalytic bromination activity for conversion of phenol red to bromophenol blue at pH 5.8 [10]. Shan and co-workers have synthesized two vanadium-amino acid hydroxylamido complexes and explored their PTP1B inhibitory activities [11]. Several peroxidovanadate complexes containing two bidentate heteroligands were used to study DNA damage induction and antiproliferative activity by Andrezálová's group [12]. Adão and co-workers reported the synthesis and characterization of several vanadate complexes containing amino alcohol-derived reduced Schiff base ligands, which can be catalysts for asymmetric sulfoxidation of thioanisole [13]. Similarly, coordination interactions between peroxovanadate complexes and organic ligands were explored through spectroscopic investigations in our previous study [14].

Ligands containing the 1,10-phenanthroline unit, such as 5-nitro-1,10-phenanthroline, 5-methyl-1,10-phenanthroline, and 5,6-dimethyl-1,10-phenanthroline, are important building blocks and have been used to form many transition metal complexes [15]. Studies indicate that 5-amino-1,10-phenanthroline (5-NH_2-phen) could coordinate to metal ions such as Ag^+, Ru^{2+}, Mn^{2+}, Fe^{2+}, Pt^{2+}, Cu^{2+}, Pd^{2+}, and Ir^{3+} [16]. Therefore, in this work, the interaction system NH_4VO_3/H_2O_2/5-NH_2-phen was also studied using multinuclear (^{1}H, ^{13}C, and ^{51}V) magnetic resonance, variable temperature NMR, COSY, and HSQC. Theoretical calculations were performed to provide a reasonable explanation for the reaction system and the ^{13}C NMR peak assignment of the newly formed peroxovanadate complexes. Through combined use of these methods, solution structures and coordination modes of all species in the interaction system could be determined and a better understanding of the coordination reaction was achieved.

2. Experimental

2.1. *Spectroscopies*

All spectra were recorded on a Bruker AV-II 500 MHz NMR spectrometer. DSS (3-(trimethylsilyl)-propanesulfonic acid sodium salt) was used as an internal reference for ^{1}H and ^{13}C chemical shifts. The ^{51}V chemical shift was measured relative to the external standard $VOCl_3$ with upfield shifts considered as negative.

2.2. *Materials and preparations*

D_2O, H_2O_2, NaCl, NH_4VO_3, and 5-NH_2-phen (shown in scheme 1) were commercial products (Sinopharm Chemical Reagent Co., Ltd.) used without purification. The ionic medium was chosen to represent the physiological condition, 0.15 M/L NaCl/D_2O solution in all NMR experiments. To form the ternary system of NH_4VO_3/H_2O_2/5-NH_2-phen, NH_4VO_3, and H_2O_2 were first mixed in D_2O to produce $[OV(O_2)_2(D_2O)]^-/[OV(O_2)_2(HOD)]^-$ (bpV) followed by addition of the ligand.

2.3. *Computational method*

The geometries of the complexes were optimized using the B3P86 method [17–20]. The Wadt and Hay core-valence effective core potential [21] was used for the metal center (13 explicit electrons for neutral V) with the valence double zeta contraction of the basis functions (denoted as Lanl2dz in Gaussian [22]). For O, N, C, and H, the standard 6–31 + G* basis sets developed by Hariharan and Pople were used [23]. The solvation energy and the solvation effects of the chemical shieldings were calculated using polarizable continuum models at each optimized gas phase geometry [24, 25]. Vibrational frequencies were calculated to ensure that each minimum is a true local minimum (only real frequencies). All calculations were carried out with the Gaussian 03 program suite [22].

3. Results and discussion

3.1. *^{51}V NMR studies on the coordination reaction*

The starting sample is a mixture of NH_4VO_3 and H_2O_2 with 1 : 5 molar ratio in D_2O solution (0.1 M/L vanadate concentration). Its ^{51}V NMR spectrum has a peak at −692 ppm, shown in figure 1, which was assigned to the peroxovanadate species bpV according to previous reports [14]. After 5-NH_2-phen was added to the bpV solution, a pair of peaks appeared at −744 and −748 ppm, assigned to $[OV(O_2)_2(5\text{-}NH_2\text{-phen})]^-$ (**Isomers A** and **B**). Its intensity increases with increasing quantity of 5-NH_2-phen (from 0 to 0.5, 1, and finally

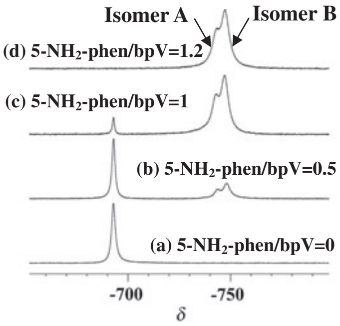


Figure 1. ^{51}V NMR spectra for the interaction system NH_4VO_3/H_2O_2/5-NH_2-phen. The total concentration of vanadate species was 0.1 M/L and the bpV refers to $[OV(O_2)_2(D_2O)]^-/[OV(O_2)_2(HOD)]^-$. Peaks of the newly formed $[OV(O_2)_2(5\text{-}NH_2\text{-phen})]^-$ species are indicated by arrows.

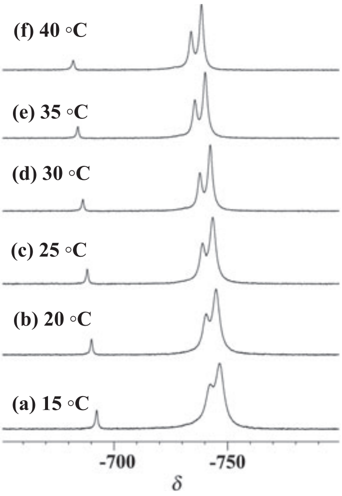


Figure 2. Variable temperature ^{51}V NMR spectra of the coordination reaction system between bpV and 5-NH_2-phen with a 1 : 1 molar ratio in aqueous solution.

1.2 equivalents) before reaching a maximum, as shown in figure 1(a)–(d). Moreover, with the addition of 5-NH_2-phen, the peak at −744 or −748 ppm hardly moves. When the molar ratio between 5-NH_2-phen and bpV reached 1.2 : 1, it was not possible to observe the peak of bpV in the ^{51}V NMR spectrum anymore.

To explore the influence of temperature on the coordination equilibrium, variable temperature ^{51}V NMR spectra were used to study the coordination reaction system between bpV and 5-NH_2-phen from 15 to 40 °C. The experimental results shown in figure 2 indicate: (1) with increasing temperature all the peaks in the spectra move to low field. The chemical shift of bpV moves about 4.2 ppm every 10 °C and that of **Isomers A** or **B** move about 3.2 or 3.1 ppm every 10 °C, respectively. (2) With increasing temperature, the quantity of the $[OV(O_2)_2(5\text{-}NH_2\text{-phen})]^-$ decreases and converts into bpV. At the same time, the ratio between **Isomers A** and **B** reduces (1 : 1.25 at 15 °C and 1 : 1.5 at 40 °C). This implies that with increasing temperature, besides $[OV(O_2)_2(5\text{-}NH_2\text{-phen})]^-$ gradually converting back to bpV, **Isomer A** also converts into **Isomer B**.

Table 1. NMR data for the bpV and 5-NH_2-phen coordination reaction system with a 1 : 1 molar ratio.

	Chemical shifts	
Species	^{1}H (ppm)	^{13}C (ppm)
$[OV(O)_2(5\text{-}NH_2\text{-phen})]^-$ **(Isomer A)**	6.12(s, 1H), 7.13(dd, *J* = 8.0, 4.6 Hz, 1H), 7.49(dd, *J* = 8.3, 5.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.86(d, *J* = 4.6 Hz, 1H); 8.08(d, *J* = 8.3 Hz, 1H), 9.43(d, *J* = 5.0 Hz, 1H)	153.8, 144.0, 142.2, 140.3, 136.0, 134.3, 134.2, 129.7, 124.4, 123.6, 122.6, 105.3
$[OV(O)_2(5\text{-}NH_2\text{-phen})]^-$ **(Isomer B)**	5.94(s, 1H), 7.28–7.35(m, 2H), 7.55(d, *J* = 8.0 Hz, 1H), 7.94(d, *J* = 8.2 Hz, 1H), 8.14(d, *J* = 4.2 Hz, 1H), 9.14(d, *J* = 4.6 Hz, 1H)	150.0, 145.6, 141.2, 140.9, 138.8, 137.1, 131.6, 131.2, 130.7, 124.5, 123.6, 103.6

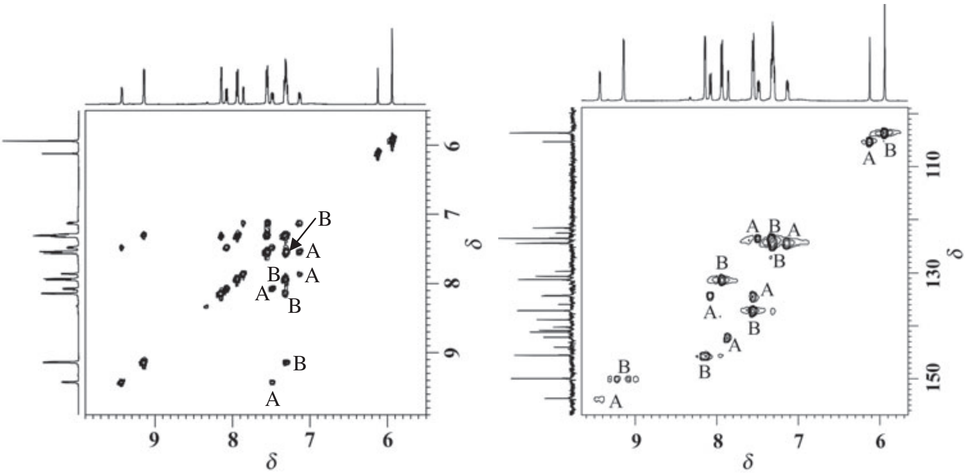


Figure 3. COSY (left) and HSQC (right) spectra of the coordination reaction system between bpV and 5-NH$_2$-phen with a 1 : 1 molar ratio in aqueous solution. A or B indicates the cross peaks of the **Isomers A** or **B**.

3.2. *Assignments of ^{1}H and ^{13}C NMR data*

^{1}H and ^{13}C NMR spectral data for the interaction system of bpV (0.1 M/L) and 5-NH$_2$-phen in sodium chloride deuterium oxide solution are listed in table 1.

For 5-NH$_2$-phen, there are two groups of peaks in every ^{1}H and ^{13}C NMR spectrum. One group was assigned to **Isomer A**, the other to **Isomer B**. According to the assignments of the ^{1}H and ^{13}C NMR signals of the bpV-5-NH$_2$-phen coordination reaction system, the NMR signals can also be assigned through the COSY and HSQC spectra, which are displayed in figure 3. Based on the chemical shifts and/or the relative areas of the ^{1}H, ^{13}C, and ^{51}V peaks, we suggest that the newly formed $[OV(O_2)_2L]^-$ (L = 5-NH$_2$-phen) is seven coordinate. According to NMR or X-ray diffraction, these *N,N′*-chelating bihetero-aromatic ligands should form the seven coordinate $[OV(O_2)_2L]^-$ (L = 5-NH$_2$-phen) as exemplified by $[OV(O_2)_2(\text{py-im})]^-$, $[OV(O_2)_2(\text{pprd})]^-$, or $[OV(O_2)_2(2\text{-NH}_2\text{-pprd})]^-$ [14(a–c)].

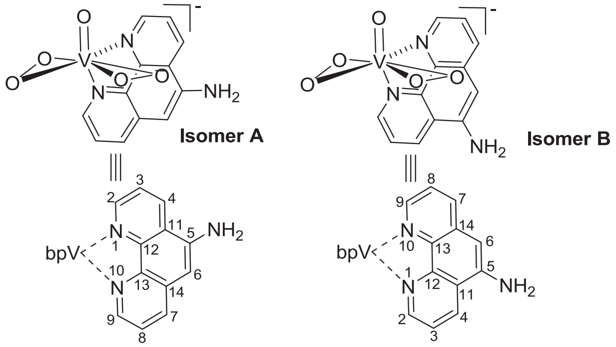
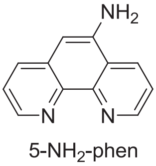


Figure 4. The structures of **Isomer A** (left) and **Isomer B** (right).



Scheme 1. Structure of 5-NH_2-phen.

Table 2. Selected bond lengths for **Isomers A** and **B** as well as those for other biperoxovanadate complexes.

	Isomer A	**Isomer B**	bpV(pprd)	bpV(2-NH_2-pprd)	bpV(py-im)	bpV(bipy)
V=O	1.604	1.603	1.611	1.606	1.614	1.619
V–$O_{peroxido(trans)}$	1.858	1.861	1.895	1.882 1.878	1.891 1.879	1.883 1.880
V–$O_{peroxido(cis)}$	1.881	1.882	1.887	1.912 1.901	1.918 1.899	1.911 1.909
$(O–O)_{peroxido}$	1.422	1.421	1.472	1.473 1.465	1.462 1.449	1.471 1.465
V–$N_{equatorial}$	2.194	2.191	2.142	2.128	2.102	2.149
V–N_{axial}	2.433	2.416	2.332	2.400	2.356	2.288
Ref.	This work		[14c]	[14c]	[14b]	[26]

3.3. *Theoretical study on the reaction products*

The NMR spectra of the coordination reaction indicated that **Isomers A** and **B** are seven coordinate. The bpV-5-NH_2-phen coordination reaction system was explored by density functional calculations. The structures of the newly formed species were optimized using the B3P86 method. Compared to the free energy, one isomer is 0.73 kcal/M more stable than the other. Based on the NMR results, **Isomer B** is the main product. Therefore, their structures are shown in figure 4. Based on the DFT calculations, the important bond distances of **Isomers A** and **B** are listed in table 2.

According to the data in table 2, the bond length variance is within the range of that reported for biperoxovanadate complexes [14, 26]. Compared to typical bond distances in different peroxovanadate species, the V=O or V–O bond lengths are typically found for a double bond between V and O and are within the range observed in similar geometries such as those of $[OV(O_2)_2(py\text{-}im)]^-$ or $[OV(O_2)_2(2\text{-}NH_2\text{-}pprd)]^-$ [14(b, c)]. The V–$O_{peroxido}$ bond lengths (1.858−1.882 Å) are also within the range of the normal V–$O_{peroxido}$ bond distances reported in $[OV(O_2)_2(pprd)]^-$ and $[OV(O_2)_2(py\text{-}im)]^-$ [14(c), 26]. The lengths of the $(O–O)_{peroxido}$ bonds are 1.421−1.422 Å, similar to the corresponding values in $[OV(O_2)_2(py\text{-}im)]^-$ [26]. The bond lengths for both V–$N_{equatorial}$ (2.194 Å for **Isomer A**, 2.191 Å for **Isomer B**) and V–N_{axial} (2.433 Å for **Isomer A**, 2.416 Å for **Isomer B**) are in agreement with the corresponding values reported for other peroxidovanadate complexes such as $[OV(O_2)_2(bipy)]^-$, $[OV(O_2)_2(pprd)]^-$, and $[OV(O_2)_2(py\text{-}im)]^-$ [14(b, c), 26]. Shorter V–N bond lengths in **Isomer B** may indicate that **Isomer B** is more stable than **Isomer A**. The reactivity of 5-NH_2-phen in solution depends on the intrinsic bonding strength between $[OV(O_2)_2]^-$ and 5-NH_2-phen and solvation effects. The free energies of the two reactions studied here are:

$$\text{5-NH}_2\text{-phen} + \left[\mathrm{OV(O_2)_2(H_2O)}\right]^- \longrightarrow \left[\mathrm{OV(O_2)_2}(\text{5-NH}_2\text{-phen})\right]^- \ (\textbf{Isomer A}) \ + \ \mathrm{H_2O} \tag{1}$$

$$\Delta G\ (298\ \mathrm{K}) = 11.15\ \text{kcal/M (in gas phase) and} - 6.73\ \text{(in solution)}$$

$$\text{5-NH}_2\text{-phen} + \left[\mathrm{OV(O_2)_2(H_2O)}\right]^- \longrightarrow \left[\mathrm{OV(O_2)_2}(\text{5-NH}_2\text{-phen})\right]^- \ (\textbf{Isomer B}) \ + \ \mathrm{H_2O} \tag{2}$$

$$\Delta G\ (298\ \mathrm{K}) = 10.14\ \text{kcal/M (in gas phase) and} - 7.46\ \text{(in solution)}$$

These results indicate that the reactions are unfavorable in the gas phase but thermodynamically favorable in solution. The free energy changes for these two reactions resulting from solvation effects are 17.88 and 17.60 kcal/M, respectively. Comparison of the free energies of reactions (1) and (2) in solution shows that:

$$\Delta G(\text{reaction } 2) < \Delta G(\text{reaction } 1)$$

This order is in agreement with the relative affinity between 5-NH_2-phen and bpV observed experimentally.

4. Conclusion

Multinuclear NMR spectroscopy and density functional calculations were employed to study the formation of coordination complexes between biperoxovanadate $[OV(O_2)_2(D_2O)]^-/[OV(O_2)_2(HOD)]^-$ and 5-NH_2-phen. The NMR experiments indicate a pair of isomers in solution, which are due to the different types of coordination for 5-NH_2-phen. The solution structures of **Isomers A** and **B** were proposed based on NMR experimental information and confirmed by the theoretical calculations. The density functional calculations indicate solvation effects play an important role in these interactions. Similarly, the peroxovanadium(V) complex and bisubstituted pyridine reaction systems were also reported previously by NMR measurements along with density functional calculations. Both the solvent and the substitution effect of ligands affected the coordination equilibrium [14(d)]. Due to the amino groups being far from the metal center in 5-NH_2-phen, the solvation mainly affects the coordination reaction equilibrium. Therefore, the ratio between **Isomers A** and **B** is determined by the free energies of reactions (1) and (2) in solution.

Funding

This work was supported by Hunan Provincial Natural Science Foundation of China [14JJ7049]; Scientific Research Fund of Hunan Provincial Education Department [12K101]; The Opening Project of State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University [grant number 201309]; and Aid program for Science and Technology Innovative Research Team in Higher Educational Institutions of Hunan Province.

References

[1] K.H. Thompson, C. Orvig. *Science*, **300**, 936 (2003).

[2] K.H. Thompson, C. Orvig. *J. Inorg. Biochem.*, **100**, 1925 (2006).

[3] K.H. Thompson, J.H. McNeill, C. Orvig. *Chem. Rev.*, **99**, 2561 (1999).

[4] A. Butler, J.V. Walker. *Chem. Rev.*, **93**, 1937 (1993).

[5] D.C. Crans, J.J. Smee, E. Gaidamauskas, L. Yang. *Chem. Rev.*, **104**, 849 (2004).

[6] J.H. Hwang, R.K. Larson, M.M. Abu-Omar. *Inorg. Chem.*, **42**, 7967 (2003).

[7] (a) J.S. Jaswal, A.S. Tracey. *J. Am. Chem. Soc.*, **115**, 5600 (1993); (b) A.S. Tracey, J.S. Jaswal. *Inorg. Chem.*, **32**, 4235 (1993).

[8] D.C. Crans, A.D. Keramidas, S.S. Amin, O.P. Anderson, S.M. Miller. *J. Chem. Soc., Dalton Trans.*, 2799 (1997).

[9] H. Sugiyama, S. Matsugo, H. Misu, T. Takamura, S. Kaneko, Y. Kanatani, M. Kaido, C. Mihara, N. Abeywardana, A. Sakai, K. Sato, Y. Miyashita, K. Kanamori. *J. Inorg. Biochem.*, **121**, 66 (2013).

[10] C. Chen, F.Y. Bai, R. Zhang, G. Song, H. Shan, N. Xing, Y.H. Xing. *J. Coord. Chem.*, **66**, 671 (2013).

[11] H.Q. Zhang, Q.Y. Zhang, J. Li, D. Liu, X.F. Wu, Y.K. Shan. *Chem. J. Chinese U.*, **33**, 243 (2012).

[12] L. Andrezálová, H. Gbelcová, Z. Ďuračková. *J. Trace Elem. Med. Biol.*, **27**, 21 (2013).

[13] P. Adão, M.L. Kuznetsov, S. Barroso, A.M. Martins, F. Avecilla, J.C. Pessoa. *Inorg. Chem.*, **51**, 11430 (2012).

[14] (a) X.Y. Yu, S.H. Cai, X. Xu, Z. Chen. *Inorg. Chem.*, **44**, 6755 (2005); (b) X.Y. Yu, S.H. Cai, Z. Chen. *J. Inorg. Biochem.*, **99**, 1945 (2005); (c) X.Y. Yu, P.G. Yi, D.H. Ji, B.R. Zeng, X.F. Li, X. Xu. *Dalton Trans.*, **41**, 3684 (2012); (d) B.S. Zheng, L. Deng, H.T. Liu, X.Y. Yu, Z.X. Wang, X.C. Yang, P.G. Yi. *J. Coord. Chem.*, **66**, 2558 (2013).

[15] (a) R. Takjoo, J.T. Mague, A. Akbari, S.Y. Ebrahimipour. *J. Coord. Chem.*, **66**, 2852 (2013); (b) J.J. Wang, Q.L. Bao, J.X. Chen. *J. Coord. Chem.*, **66**, 2578 (2013); (c) X.L. Wang, M. Jiang, Y.T. Li, Z.Y. Wu, C.W. Yan. *J. Coord. Chem.*, **66**, 1985 (2013); (d) S.R. Maqsood, N. Islam, S. Bashir, B. Khan, A.H. Pandith. *J. Coord. Chem.*, **66**, 2308 (2013).

[16] (a) H.H. Li, J.X. Wu, H.J. Dong, Y.L. Wu, Z.R. Chen. *J. Mol. Struct.*, **987**, 180 (2011); (b) S.M. Ji, H.M. Guo, X.L. Yuan, X.H. Li, H.D. Ding, P. Gao, C.X. Zhao, W.T. Wu, W.H. Wu, J.Z. Zhao. *Org. Lett.*, **12**, 2876 (2010); (c) C.R. Goldsmith, W.C. Jiang. *Inorg. Chim. Acta*, **384**, 340 (2012); (d) C. Loechel, A. Basran, J. Basran, N.S. Scrutton, E.A. Hall. *Analyst*, **128**, 889 (2003); (e) S. Kemp, N.J. Wheate, D.P. Buck, M. Nikac, J.G. Collins, J.R. Aldrich-Wright. *J. Inorg. Biochem.*, **101**, 1049 (2007); (f) N. Marino, O.F. Ikotun, M. Julve, F. Lloret, J. Cano, R.P. Doyle. *Inorg. Chem.*, **50**, 378 (2011); (g) D. Wesselinova, M. Neykov, N. Kaloyanov, R. Toshkova, G. Dimitrov. *Eur. J. Med. Chem.*, **44**, 2720 (2009); (h) K.W. Huang, I.W. Bulik, A.A. Marti. *Chem. Commun.*, **48**, 11760 (2012).

[17] A.D. Becke. *Phys. Rev. A*, **38**, 3098 (1988).

[18] A.D. Becke. *J. Chem. Phys.*, **98**, 5648 (1993).

[19] (a) J.P. Perdew. *Phys. Rev. B*, **33**, 8822 (1986); (b) J.P. Perdew. *Phys. Rev. B*, **34**, 7406 (1986).

[20] M. Bühl, C. Reimann, D.A. Pantazis, T. Bredow, F. Neese. *J. Chem. Theory Comput.*, **4**, 1449 (2008).

[21] P.J. Hay, W.R. Wadt. *J. Chem. Phys.*, **82**, 299 (1985).

[22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople. *Gaussian 03*, Gaussian Inc., Pittsburgh, PA (2003).

[23] P.C. Hariharan, J.A. Pople. *Theor. Chim. Acta*, **28**, 213 (1973).

[24] S. Miertus, E. Scrocco, J. Tomasi. *J. Chem. Phys.*, **55**, 117 (1981).

[25] V. Barone, M. Cossi, J. Tomasi. *J. Chem. Phys.*, **107**, 3210 (1997).

[26] S. Helga, S. Rolf. *Acta Chem. Scand.*, **A37**, 553 (1983).