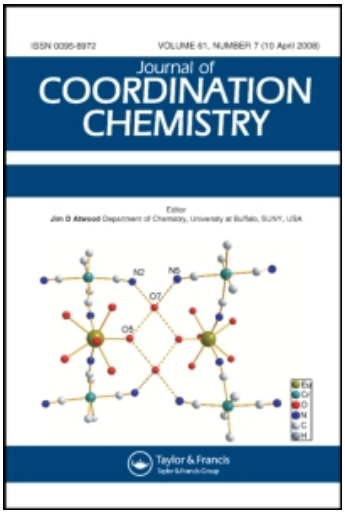


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Structural study of 2-pyridine-derived *N*(4)-*p*-tolyl thiosemicarbazone zinc(II) complexes-DFT analysis

Ralph Puchta[ab]; Shaban Y. Shaban[ac]; Hanaa Mansour[ac]; Basam M. Alzoubi[ad]
[a] Inorganic Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Egerlandstr. 1, 91058 Erlangen, Germany [b] Computer Chemistry Center, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Nägelsbachstr. 25, 91052 Erlangen, Germany [c] Department of Chemistry, Faculty of Science, Kafrelsheikh University, Kafrelsheikh 33516, Egypt [d] Department of Basic Science, Zarka University College, Al-Balqa Applied University, Zarka, Jordan

First published on: 14 June 2010

To cite this Article Puchta, Ralph , Shaban, Shaban Y. , Mansour, Hanaa and Alzoubi, Basam M.(2010) 'Structural study of 2-pyridine-derived *N*(4)-*p*-tolyl thiosemicarbazone zinc(II) complexes-DFT analysis', Journal of Coordination Chemistry, 63: 14, 2879 — 2887, First published on: 14 June 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958972.2010.492428
URL: http://dx.doi.org/10.1080/00958972.2010.492428

Journal of Coordination Chemistry
Vol. 63, Nos. 14–16, 20 July–20 August 2010, 2879–2887

Structural study of 2-pyridine-derived *N*(4)-*p*-tolyl thiosemicarbazone zinc(II) complexes – DFT analysis[#]

RALPH PUCHTA*†‡, SHABAN Y. SHABAN†§, HANAA MANSOUR†§ and BASAM M. ALZOUBI†¶

†Inorganic Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Egerlandstr. 1, 91058 Erlangen, Germany
‡Computer Chemistry Center, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Nägelsbachstr. 25, 91052 Erlangen, Germany
§Department of Chemistry, Faculty of Science, Kafrelsheikh University, Kafrelsheikh 33516, Egypt
¶Department of Basic Science, Zarka University College, Al-Balqa Applied University, Zarka, Jordan

(*Received 18 February 2010; in final form 17 March 2010*)

Zinc complexes of three substituted pyridine thiosemicarbazones, [*N*(4)-*p*-tolyl-2-benzoylpyridine-thiosemicarbazone]zinc(II) (**1**), dichloro[*N*(4)-*p*-tolyl-2-formylpyridine-thiosemicarbazone]-zinc(II) (**2**), and dichloro[*N*(4)-*p*-tolyl-2-acetylpyridine-thiosemicarbazone]zinc(II) (**3**), have been investigated by DFT calculations (B3LYP/6-31G*). The calculated ^{13}C NMR data for **1**–**3** are harmonized with experimental data. The structures are suggested to be distorted tetrahedral for all complexes.

Keywords: Thiosemicarbazones; Zinc(II) complexes; DFT calculation; NMR

1. Introduction

Determination of structures of zinc complexes is essential for a better understanding of their reactivity in chemical and biological systems [1]. Zinc is the second most abundant transition metal in living organisms and plays an important role in structural, catalytic, and enzymatic processes [2, 3]. Zinc enzymes are related to hormonal actions and brain pathologies, and are involved in synthetic, hydrolytic, hydration, and degradation processes [4–6]. Heterocyclic ligands occur in natural products, such as nucleic acids, plant alkaloids, vitamins, proteins, anthocyanins, flavones, heme pigments, and chlorophyll [7]. Complexes of bispyridine and its derivatives are used in photo- and electrochemical devices [8, 9], electro catalysts [10], multicolor luminescent cross-linkers for biological molecules [11], and photo-luminescence [12]. Thiosemicarbazones have a

*Corresponding author. Email: Ralph.Puchta@chemie.uni-erlangen.de
[#]Dedicated to Prof. Rudi van Eldik on the occasion of his 65th birthday.

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.492428

long history and broad spectrum of biological efficacy [13, 14] that includes antimalarial [15], antimicrobial [16], and antitumor activities [17, 18].

The number of coordinated ligands around Zn(II) is flexible. In both zinc-finger proteins and enzymes, zinc is usually tetrahedrally coordinated, but in some catalytic binding sites and in solution it is found to be five coordinate and rarely six coordinate [19, 20]. Thiosemicarbazide (NH_2CSNHN_2) and thiosemicarbazones ($NH_2SNHN=CR_1R_2$) usually react as chelating ligands with transition metal ions by bonding through the sulfur and hydrazinic nitrogen, although in a few cases they behave as monodentate ligands and bond through sulfur only [21]. The thiosemicarbazone ligand coordinates with divalent zinc with different coordination number depending on the type of the chelating ligand [22].

In this study we want to demonstrate that the combination of NMR spectroscopy and standard DFT calculations (B3LYP/6-31G*) is a valuable tool to derive structural data, not only in organic chemistry [23] but also in coordination chemistry. Recently, we have used DFT calculations (B3LYP/6-31G*) in combination with NMR spectroscopic data to solve the structures of new pentadentate zinc complexes containing N_3S_2 [24]. Recently, da Silva *et al.* [25] synthesized three zinc complexes containing pyridine thiosemicarbazone, namely, dichloro[*N*(4)-*p*-tolyl-2-benzoylpyridine-thiosemicarbazone]zinc(II) (**1**), dichloro[*N*(4)-*p*-tolyl-2-formylpyridine-thiosemicarbazone]zinc(II) (**2**), and dichloro[*N*(4)-*p*-tolyl-2-acetylpyridine-thiosemicarbazone]zinc(II) (**3**), and proposed their structures from IR and NMR data (figure 1). In order to gain deeper insight, we investigated these structures using DFT calculations (B3LYP/6-31G*) [26–30] and simulated the NMR by DFT (B3LYP/6-31G*), too, to compare these data with the experimental NMR data.

2. Quantum chemical method

All structures were fully optimized at the B3LYP/6-31G(d) level of theory (DFT) [26] using the Gaussian 03 program [27]. Frequencies were computed at the same level to characterize all structures as local minima to obtain zero-point vibration energies (ZPEs). DFT, in particular B3LYP, was shown to provide accurate geometries and good harmonic vibration frequencies for a broad range of molecules and ions

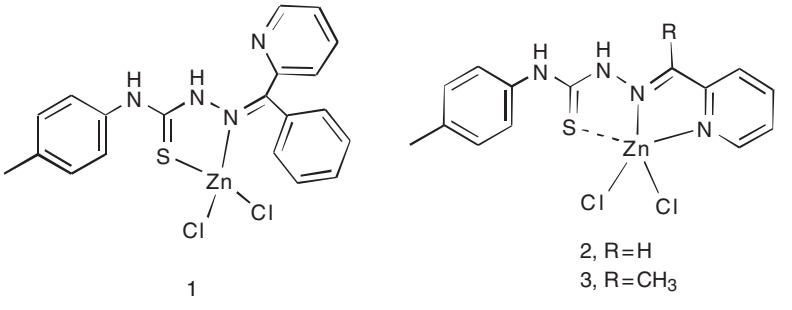


Figure 1. Schematic representatives for zinc complexes **1–3**.

(see, e.g. [28]). The level of theory selected (B3LYP/6-31G(d)) is well-suited for NMR [29] and NICS calculations [30]. Following the approach of van Eikema Hommes and Clark [29a], we converted the calculated magnetic shielding constants (σ) into δ(C) relative to $SiMe_4$ by applying equation (1).

$$\delta = 200.65 + (-1.0715\sigma)(R^2 = 0.9984) \quad (1)$$

3. Results and discussion

Parallel to experimental studies, theoretically orientated chemists model the structures by quantum chemical calculations. In general, there is a good agreement between the experimental information (X-ray structure) and the computed data. In this study, the structure of a series of zinc complexes containing thiosemicarbazones have been investigated using DFT calculations (B3LYP/6-31G*) [26–30] and simulated the NMR by DFT (B3LYP/6-31G*), too, to compare these data with the experimental NMR data. The DFT (B3LYP/6-31G*) calculated structure for dichloro[*N*(4)-*p*-tolyl-2-benzoylpyridine-thiosemicarbazone]zinc(II) (**1**) shown in figure 2 fit with the experimental ^{13}C-NMR data, as well as with the structure suggested by da Silva *et al.* [25] (see table 1). The structure shows that one thiosemicarbazone coordinates to zinc through N(imine), S(thione) and with additional two chlorides to form the four-coordinate zinc(II) complex. The thiosemicarbazone in this case is in the *Z* configuration, as experimentally found.

The coordination of the thione sulfur to zinc is evidenced experimentally [25] by the new absorption in the IR (KBr) spectrum at 344–350 cm^{-1} assigned to ν(Zn–S).

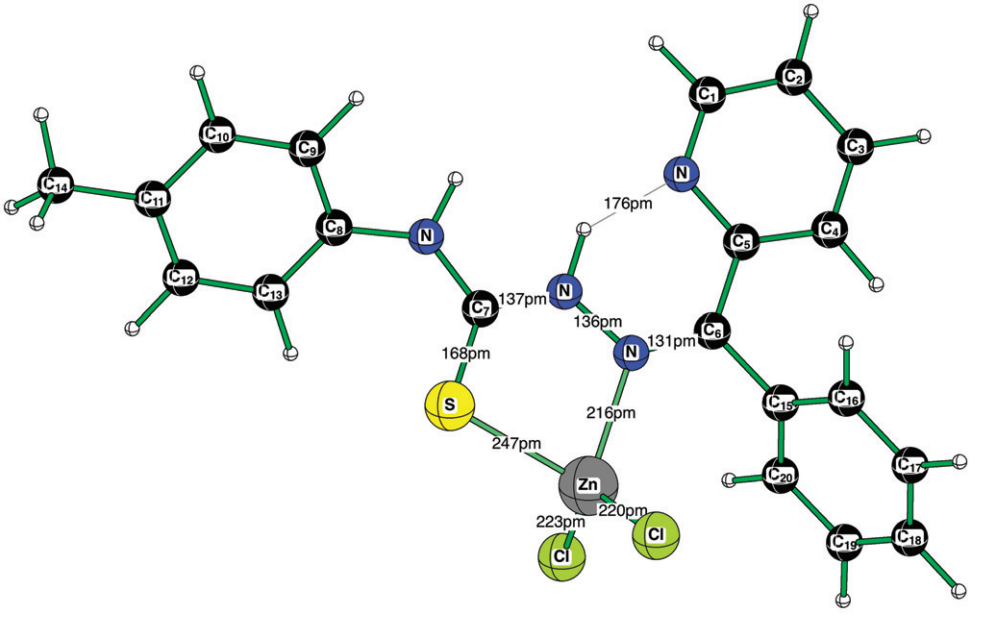


Figure 2. Calculated (B3LYP/6-31G*) structure of dichloro[*N*(4)-*p*-tolyl-2-benzoylpyridine-thiosemicarbazone]zinc(II) complex **1**.

Table 1. Experimental ^{13}C-NMR chemical shifts (δ (ppm) relative to TMS in DMSO [25]) and calculated (B3LYP/6-31G*) shifts of **1**–**3**.

Compound		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)=N	C(7)=S	C(8)–N	C(9,13)	C(10,12)	C(11)	C(14)	C(15)–C(20)
1 Experimental		148.2	124.6	138.2	121.6	151.9	140.9	176.6	136.3	123.0	128.7	134.8	20.5	–
Calculated	A	153.7	125.0	138.0	123.7	147.4	136.4	179.1	131.2	124.4	131.2	139.5	20.6	–
	B	152.3	131.8	145.2	130.1	144.7	142.2	179.0	124.4	123.8	134.1	150.7	21.0	–
2 Experimental		146.4	125.0	140.7	122.9	148.7	147.9	177.4	136.3	126.1	128.8	135.1	20.5	12.8
Calculated	A	154.2	124.3	138.1	120.2	149.3	145.0	180.8	131.5	124.2	131.1	139.2	20.7	9.5
	B	152.0	130.7	145.1	126.0	146.1	154.0	179.1	124.7	124.0	134.1	150.6	20.5	9.1
3 Experimental		148.7	123.9	138.5	126.3	151.2	143.5	176.6	136.3	125.2	128.6	134.8	20.6	136.7, 129.4 129.1, 128.4
Calculated		146.6	123.7	137.7	130.9	156.4	153.7	179.9	133.0	123.5	129.5	137.9	20.9	132.3, 131.9 130.9, 128.8

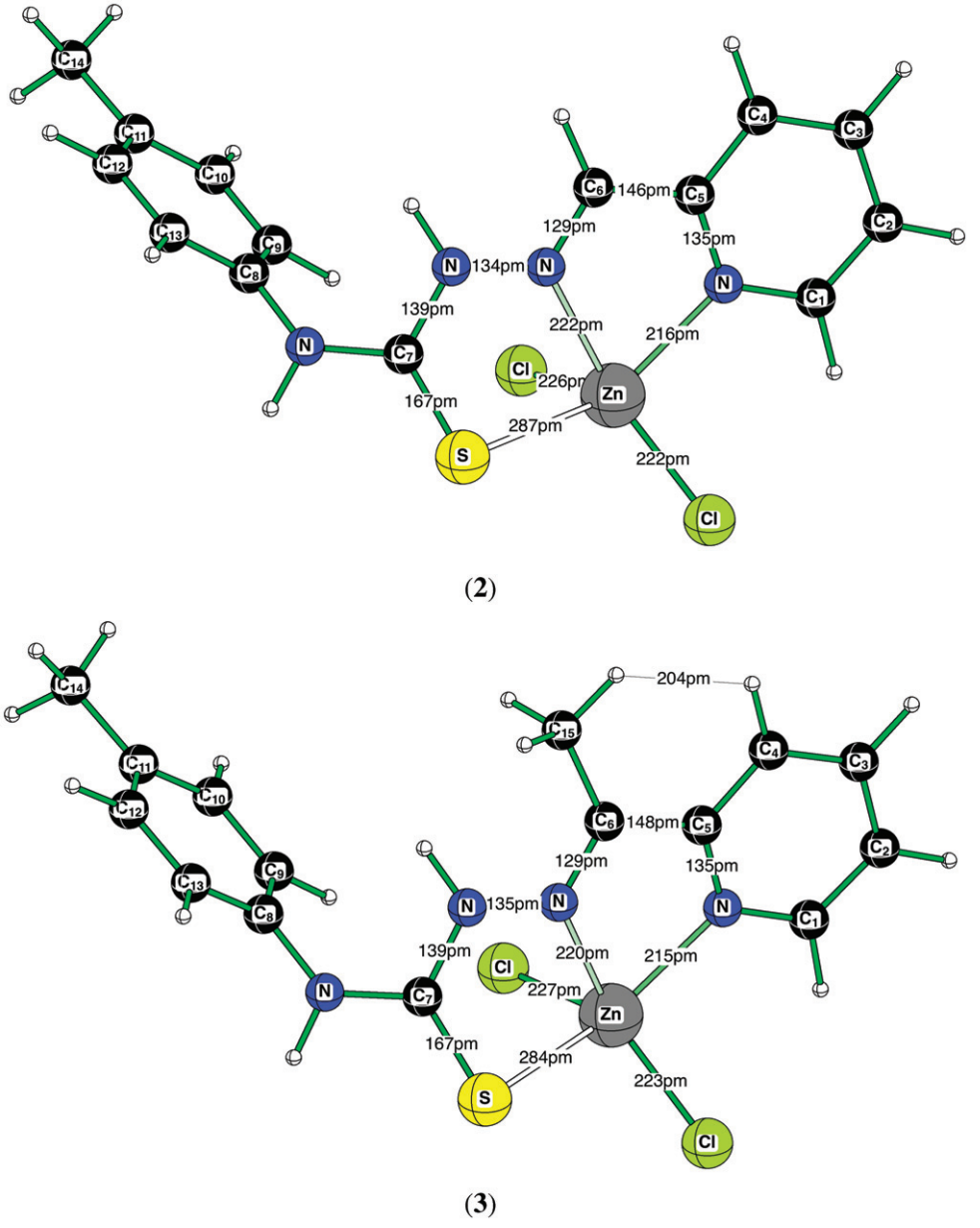
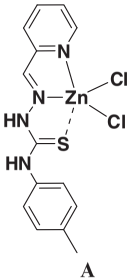
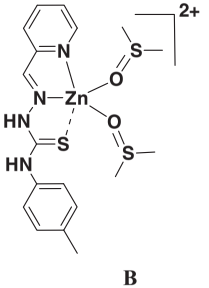
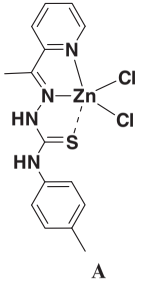
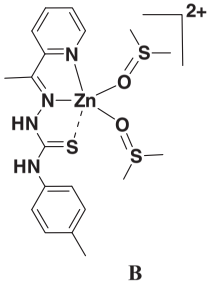
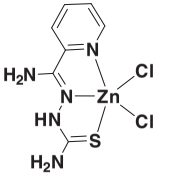
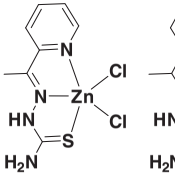
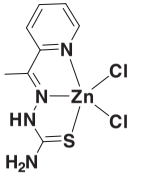
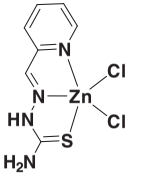


Figure 3. Calculated structures (B3LYP/6-31G*) of dichloro[*N*(4)-*p*-tolyl-2-formylpyridine-thiosemicarbazone]zinc(II) (**2**) and dichloro[*N*(4)-*p*-tolyl-2-acetylpyridine-thiosemicarbazone]zinc(II) (**3**).

The thiosemicarbazone acts in this case as a bidentate ligand because the pyridine is too far away from the zinc center. Formation of hydrogen bonds between the N(pyridine) donor to the NH group may preclude the pyridine moiety from free rotation along the C–C bond. A fifth coordination by the pyridine moiety is prevented by the ligands conformation especially the N = C double bond. The calculated *d*(Zn–S) in **1** (247 pm)

Table 2. Selected bond distances [pm] of the calculated (B3LYP/6-31G*) structural data of **2** and **3** together with X-ray structural data of **4–7**.

	 A	 B	 A	 B				
	2		**3**		**4 [31a]**	**5 [31b]**	**6 [31c]**	**7 [31c]**
d(Zn–N)	222	212.9	220	216	210	214	215	205
d(Zn–N(py))	216	212.9	215	211	217	215	215	221
d(Zn–S)	287	255.1	284	253	245	245	245	243
d(Zn–Cl)	222, 226	–	223, 227	–	230, 232	229, 230	229	230, 234

is within the range of the average d(Zn−S) (av. 244 pm), whereas the d(Zn−Cl) is slightly shorter than in related zinc complexes in general (av. 230 pm) [31].

In the case of dichloro[*N*(4)-*p*-tolyl-2-formylpyridine-thiosemicarbazone] zinc(II) (**2**) and dichloro[*N*(4)-*p*-tolyl-2-acetylpyridine-thiosemicarbazone]zinc(II) (**3**), the DFT (B3LYP/6-31G*) calculated structures are shown in figure 3 and fit with the experimental ^{13}C-NMR data, also. The thiosemicarbazones have the *E* conformation as experimentally found, too.

To the best of our knowledge, no X-ray structures are known for zinc complexes with the investigated ligands but there are a couple of related structures published with the thiosemicarbazone building block in combination with $ZnCl_2$ [31]. A comparison of the bond lengths of the investigated complexes with the related X-ray structures are depicted in table 2. The d(Zn−S) in **2** and **3** (284 pm) fall outside the range of the average d(Zn−S) in general (av. 244 pm) [31], indicating very weak bonding with the central zinc center. This observation is in line with the experimental observation reported by da Silva *et al*. [25]. Upon formation of **2** and **3**, the signals of the pyridine carbons and the signal of the C(6) = N shift, in accord with the coordination of the imine nitrogen and the heteroaromatic nitrogen, whereas the C(7) = S signal stays practically unaffected after complexation [31]. In this case the thiosemicarbazone ligand coordinates to the central metal ion through N(imine), N(pyridine) donor as well as two chlorides and the zinc center is four coordinate. If this is the case, a question may arise why the thione function cannot coordinate to the zinc center? To answer this question one should compare these structures with the reported X-ray structures (table 2). One observation is that all reported complexes do not have a substituent at the amino group at position 4, which is much closer to the thione function. The steric hindrance, as a result of replacing one of the amine hydrogens by *p*-tolyl may prevent the thione function from coordination. Additionally, the basicity of the thiourea may be important. The basicity and, therefore, the electron density increases from the amino (in **4**–**7**) to the *p*-tolyl-amino (in **2** and **3**) and as a result the electron density of the thione sulfur to the metal increases, too. This may lead to destabilization of the zinc–sulfur bond and in this case the zinc center becomes four coordinate. The effect of the electron-donating group at the C(6) is insignificant in **3** due to the weak interaction between sulfur and the central ion. Another possibility is DMSO could replace chlorides. For this reason the structures of **2** and **3** have been calculated (B3LYP/6-31G*) after replacing both chloride with DMSO (table 2). The d(Zn−S) in both complexes are slightly longer than the d(Zn−S) in general but the calculated data do not fit nicely with the experimental data and ^{13}C-NMR signals for coordinated DMSO have not been mentioned in the reported data [25]. In conclusion, the calculated data show that the zinc centers in **1**–**3** are four coordinate with a distorted tetrahedral. The thiosemicarbazone moieties in all complexes act as bidentate ligands.

Acknowledgments

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft. We would like to thank Prof. Tim Clark for hosting this work at the CCC and the Regionales Rechenzentrum Erlangen (RRZE) for a generous

allotment of computer time. B.M. Alzoubi thanks Al-Balqa Applied University for its support.

References

[1] (a) D. Jantz, B.T. Amann, G.J. Gatto Jr, J.M. Berg. *Chem. Rev*., **104**, 789 (2004); (b) J. Elflein, F. Platzmann, N. Burzlaff. *Eur. J. Inorg. Chem*., 5173 (2007); (c) L. Peters, N. Burzlaff. *Polyhedron*, **23**, 245 (2004); (d) I. Hegelmann, A. Beck, C. Eichhorn, B. Weibert, N. Burzlaff. *Eur. J. Inorg. Chem*., 339 (2003); (e) G. Schürer, T. Clark, R. van Eldik. In *The Chemistry of Organozinc Compounds* Z. Rappoport, I. Marek (Eds), Chap. 1, part 1, John Wiley & Sons, England (2006); (f) N. Burzlaff. In *Concepts and Models in Bioinorganic Chemistry*, H.B. Kraatz, N. Metzler-Nolte (Eds), Wiley-VCH Verlag GmbH & Co. KcaA, Weinheim (2006).

[2] J.M. Berg, H.A. Godwin. *Annu. Rev. Biophys. Biomol. Struct*., **26**, 357 (1997).

[3] (a) R.L. Wilson, C.F. Mills (Eds.), *Zinc in Human Biology*, *ILS Human Nutrition Reviews*, Vol. 10, Springer-Verlag, Berlin, (1989); (b) A. Beck, B. Weibert, N. Burzlaff. *Eur. J. Inorg. Chem*., 521 (2001); (c) H. Vahrenkamp. *Acc. Chem. Res*., **32**, 589 (1999); (d) M. Bräuer, E. Anders, S. Sinnecker, W. Koch, M. Rombach, H. Brombacher, H. Vahrenkamp. *J. Chem. Soc., Chem. Commun*., 647 (2000); (e) M. Tesmer, M. Shu, H. Vahrenkamp. *Inorg. Chem*., **40**, 4022 (2001); (f) G.P. Miscione, M. Stenta, D. Spinelli, E. Anders, A. Bottoni. *Theor. Chem. Acc*., **118**, 193 (2007).

[4] M.E.P. Murphy, S. Turley, M. Kukimoto, M. Nishiyama, S. Horinouchi, H. Sasaki, M. Tanokura, E.T. Adam. *Biochemistry*, **34**, 12107 (1995).

[5] K. Haensson, M. Carlsson, L.A. Svensson, A. Liljas. *J. Mol. Biol*., **227**, 1192 (1992).

[6] Y. Kim, S.H. Eom, J. Wang, D.-S. Lee, S.W. Suh, T.A. Steitz. *Nature*, **376**, 612 (1995).

[7] (a) J.D. Cartledge, J. Midgley, D. Shanson, B.G. Gazzard. *J. Antimicrob. Chemother*., **40**, 517 (1997); (b) A.R. Katritzky, A.F. Pozharskii. *Handbook of Heterocyclic Chemistry*, 2nd Edn, Elsevier Ltd, London (2003); (c) A.R. Katritzky. *Chem. Rev*., **104**, 2125 (2004).

[8] B. Mondal, V.G. Puranik, G.K. Lahiri. *Inorg. Chem*., **41**, 5831 (2002).

[9] N. Chanda, B. Mondal, V.G. Puranik, G.K. Lahiri. *Polyhedron*, **21**, 2033 (2002).

[10] J.A. Barron, S. Glazier, S. Bernhard, K. Takada, P.L. Houston, H.D. Abruna. *Inorg. Chem*., **42**, 1448 (2003).

[11] K.K.W. Lo, C.K. Chung, N.Y. Zhu. *Chem. Eur. J*., **9**, 475 (2003).

[12] D.R. McMillin, J.J. Moore. *Coord. Chem. Rev*., **229**, 113 (2002).

[13] (a) K.C. Agrawal, A.C. Sartorelli. *Prog. Med. Chem*., **15**, 321 (1978); (b) D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonawane, A.S. Kumbhar, R.G. Yerande. *Coord. Chem. Rev*., **123**, 49 (1993); (c) M.-C. Liu, T.-S. Lin, A.C. Sartorelli. *Prog. Med. Chem*., **32**, 1 (1995).

[14] (a) J.S. Casas, M.S. Garcia-Tasende, J. Sordo. *Coord. Chem. Rev*., **209**, 197 (2000); (b) J. Li, L.-M. Zheng, I. King, T.W. Doyle,; S.-H. Chen. *Front. Biotechnol. Pharm*., **1**, 314 (2000); (c) A.G. Quiroga, C. Navarro Ranninger. *Coord. Chem. Rev*., **248**, 119 (2004).

[15] (a) D.C. Greenbaum, Z. Mackey, E. Hansell, P. Doyle, J. Gut, C.R. Caffrey, J. Lehrman, P.J. Rosenthal, J.H. McKerrow, K. Chibale. *J. Med. Chem*., **47**, 3212 (2004); (b) A. Walcourt, M. Loyevsky, D.B. Lovejoy, V.R. Gordeuk, D.R. Richardson. *Int. J. Biochem. Cell Biol*., **36**, 401 (2004); (c) C. Biot, B. Pradines, M.-H. Sergeant, J. Gut, P.J. Rosenthal, K. Chibale. *Bioorg. Med. Chem. Lett*., **17**, 6434 (2007).

[16] (a) D. Kovala-Demertzi, M.A. Demertzis, J.R. Miller, C. Papadopoulou, C. Dodorou, G. Filousis. *J. Inorg. Biochem*., **86**, 555 (2001); (b) N.C. Kasuga, K. Sekino, M. Ishikawa, A. Honda, M. Yokoyama, S. Nakano, N. Shimada, C. Koumo, K. Nomiya. *J. Inorg. Biochem*., **96**, 298 (2003); (c) N.C. Kasuga, K.Onodera, S. Nakano, K. Hayashi, K. Nomiya. *J. Inorg. Biochem*., **100**, 1176 (2006).

[17] (a) S. Padhye, Z. Afrasiabi, E. Sinn, J. Fok, K. Mehta, N. Rath. *Inorg. Chem*., **44**, 1154 (2005); (b) A. Perez-Rebolledo, J.D. Ayala, G.M. de Lima, N. Marchini, G. Bombieri, C.L. Zani, E.M. Souza-Fagundes, H. Beraldo. *Eur. J. Med. Chem*., **40**, 467 (2005); (c) S. Adsule, V. Barve, D. Chen, F. Ahmed, Q.P. Dou, S. Padhye, F.H. Sarkar. *J. Med. Chem*., **49**, 7242 (2006); (d) W.-X. Hu, W. Zhou, C.-N. Xia, X. Wen. *Bioorg. Med. Chem. Lett*., **16**, 2213 (2006).

[18] (a) F. Bisceglie, M. Baldini, M. Belicchi-Ferrari, E. Buluggiu, M. Careri, G. Pelosi, S. Pinelli, P. Tarasconi. *Eur. J. Med. Chem*., **42**, 627 (2007); (b) I. Dilovic, M. Rubcic, V. Vrdoljak, S.K. Pavelic, M. Kralj, I. Piantanida, M.Cindric. *Bioorg. Med. Chem*., **16**, 5189 (2008).

[19] (a) Y. Marcus. *Chem. Rev*., **88**, 1475 (1988); (b) U. Brand, R. Burth, H. Vahrenkamp. *Inorg. Chem. Soc*., **35**, 1083 (1996); (c) B.M. Alzoubi, R. Puchta, R. van Eldik. *Z. Anorg. Allg. Chem*., **635**, 1536 (2009).

[20] (a) I.L. Alberts, K. Nadassy, S.J. Wodak. *Protein Sci*., **7**, 1700 (1998); (b) S.Y. Shaban, M.M. Ibrahim, F.W. Heinemann. *Inorg. Chim. Acta*, **360**, 2929 (2007); (c) B.M. Alzoubi, R. Puchta, R. van Eldik.

Aust. J. Chem., **63**, 236 (2010); (d) B.M. Alzoubi, R. Puchta, R. van Eldik. *Chem. Eur. J.*, **16** (2010) (in press).
[21] M.J.M. Campbell. *Coord. Chem. Rev.*, **15**, 279 (1975).
[22] P. Souza, L. Sanz, V. Fernández, A. Arquero, E. Gutierrez, A. Monge. *Z. Naturf. Teil b*, **46**, 767 (1991); (b) M.A. Yampol'skaya, P.N. Bouroshch, Y.A. Simonov, N.V. Gerbeleu. *Russ. J. Inorg. Chem.*, **32**, 984 (1987); (c) M.B. Ferrari, G.G. Fava, C. Pelizzi, P. Tarasconi. *J. Chem. Soc., Dalton Trans.*, 2153 (1992).
[23] (a) R. Puchta, T. Clark, W. Bauer. *J. Mol. Mod.*, **12**, 739 (2006); (b) M. Klisch, P. Richter, R. Puchta, D.-P. Häder, W. Bauer. *Helv. Chim. Acta*, **90**, 488 (2007); (c) C.A. France, S.B. Etcheverry, R.P. Diez, P.A.M. Williams. *J. Raman Spectrosc.*, **40**, 1296 (2009); (d) K. Krohn, S.F. Kouam, G.M. Kuigoua, H. Hussain, S. Cludius-Brandt, U. Flörke, T. Kurtán, G. Pescitelli, L. Di Bari, S. Draeger, B. Schulz. *Chem. Eur. J.*, **15**, 12121 (2009).
[24] S.Y. Shaban, R. Puchta, R. van Eldik. *Z. Natur forsch.*, **65b**, 251 (2010).
[25] J.G. da Silva, S.M.S.V. Wardell, J.L. Wardell, H. Beraldo. *J. Coord. Chem.*, **62**, 1400 (2009).
[26] (a) C. Lee, W. Yang, R.G. Parr. *Phys. Rev. B*, **37**, 785 (1988); (b) P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch. *J. Phys. Chem.*, **98**, 11623 (1994); (c) W.J. Hehre, L. Radom, P. von R. Schleyer, J. Pople. *Ab initio Molecular Orbital Theory*, Wiley-Interscience, Wiley, New York (1986).
[27] 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, V. Bakken, 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, Revision C.02, Gaussian Inc.*, Wallingford, CT (2004).
[28] (a) W. Koch, M.C. Holthausen, at *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim (2000); (b) C. Dosche, M.U. Kumke, F. Ariese, A.N. Bader, C. Gooijer, P.I. Dosa, S. Han, O.S. Miljanic, K.P.C. Vollhardt, R. Puchta, N.J.R. van Eikema Hommes. *Phys. Chem. Chem. Phys.*, **5**, 4563 (2003); (c) C. Dosche, M.K. Kumke, H.-G. Löhmannsröben, F. Ariese, A.N. Bader, C. Gooijer, O.S. Miljanic, M. Iwamoto, K.P.C. Vollhardt, R. Puchta, N.J.R. van Eikema Hommes. *Phys. Chem. Chem. Phys.*, **6**, 5476 (2004) and literature cited therein.
[29] (a) N.J.R. van Eikema Hommes, T. Clark. *J. Mol. Model.*, **11**, 175 (2005); (b) R. Puchta, T. Clark, W. Bauer. *J. Mol. Model.*, **12**, 739 (2006).
[30] (a) P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N.J.R. van Eikema Hommes. *J. Am. Chem. Soc.*, **118**, 6317 (1996); (b) P. von R. Schleyer, H. Jiao, N.J.R. van Eikema Hommes, V.G. Malkin, O.L.J. Malkina. *J. Am. Chem. Soc.*, **119**, 12669 (1997); (c) P. von R. Schleyer, M. Manoharan, Z.-X. Wang, B. Kiran, H. Jiao, R. Puchta, N.J.R. van Eikema Hommes. *Org. Lett.*, **3**, 2465 (2001); (d) Z. Chen, C.S. Wannere, C. Corminboeuf, R. Puchta, P. von R. Schleyer. *Chem. Rev.*, **105**, 3842 (2005).
[31] (a) A. Castineiras, I. Garcia, E. Bermejo, D.X. West. *Z. Naturf., B: Chem. Sci.*, **55**, 511 (2000); (b) N.C. Kasuga, K. Sekino, M. Ishikawa, A. Honda, M. Yokoyama, S. Nakano, N. Shimada, C. Koumo, K. Nomiya. *J. Inorg. Biochem.*, **96**, 298 (2003); (c) D. Kovala-Demertzi, P.N. Yadav, J. Wiecek, S. Skoulika, T. Varadinova, M.A. Demertzis. *J. Inorg. Biochem.*, **100**, 1558 (2006).