Contents lists available at ScienceDirect



Inorganic Chemistry Communications



journal homepage: www.elsevier.com/locate/inoche

Embrace interlocking of dipyrazinylpyridine complexes involving N^{\cdot} π interactions

Jing-Wei Dai, Ben-Zhen Li, Ying-Lin Chen, Guang Huang, Bin Cai, Ying Yu, Jian-Zhong Wu*

School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

ARTICLE INFO

Article history: Received 21 December 2009 Accepted 2 March 2010 Available online 9 March 2010

Keywords: Crystal structure $N \cdot \pi$ interaction C-H·· π hydrogen bond Electronic absorption Fluorescence

ABSTRACT

Fe(II) and Ni(II) complexes of 4-*p*-tolyl-2,6-di(2-pyrazinyl)pyridine (tdpzpy) have been synthesized and characterized. The N·· π interaction involving the uncoordinated pyrazinyl N atom, which is stronger than the corresponding C–H·· π hydrogen bonding in a similar 4-*p*-tolyl-2,2':6',2"-terpyridine complex, was distinguished as a supramolecular motif. It acts as an edge-to-face force in assembling cations of [Fe (tdpzpy)₂]²⁺ or [Ni(tdpzpy)₂]²⁺ into chains via embrace interlocking. C–H·· π hydrogen bonds further link the chains into higher dimension net. The electronic absorption and emission properties of [Fe(tdpzpy)₂]²⁺ are largely ligand-centered. [Fe(tdpzpy)₂]²⁺ displays an MLCT absorption at 567 nm. The fluorescence of [Ni(tdpzpy)₂]²⁺ is different markedly in methanol and acetonitrile. The ligand-based fluorescence is quenched to some extent by coordination to the d-orbital unfulfilled Fe(II) or Ni(II) atom. © 2010 Elsevier B.V. All rights reserved.

2,2':6',2"-Terpyridine (terpy) and its substituted analogues are among the most studied tridentate ligands for a wide range of transition metal ions.[1] One of the studying areas of terpy type ligands is their application in supramolecular assembly. Dance and his coworkers have identified a crystal supramolecular motif which was termed "terpy embrace" in a number of octahedral meridional [M (terpy)₂]ⁿ⁺ complexes.[2] The terpy embrace involves one offsetface-to-face (OFF) and two edge-to-face (EF) interactions among the outer pyridyl rings of the ligand between neighbored complex cations. This phenomenon has been found not only in complexes of terpy ligands, but also in some other terimine tridentate ligands, and depending on the ligand's structure, some other motifs may also exist in the crystal packing structures.[3] For example, the pendant phenyl, [3] pyridine [3] or tolyl [3] groups bring additional π - π or hydrogen bonding interactions.

It is some surprising that 2,5-di(2-pyrazinyl)pyridine (dpzpy, Scheme 1), the isoelectronic species of terpy, and other dipyrazinylpyridines have received much scarce attention. Up to now only five papers appeared concerning this family of compounds.[4] The ligand 4-*p*-tolyl-2,6-di(2-pyrazinyl)pyridine (tdpzpy, Scheme 1) was first obtained in 2001 in a short communication, but the synthetic details and characterization data (except crystal analysis) were not given.[4] The ligation investigation of tdpzpy was limited to [Ru(tdpzpy)_2] (PF₆)₂·2CH₃CN [4] and the essential coordinate data of this complex were unavailable either in that paper or in the CSD database (Refcode EFUREC). In order to further investigate the coordination behaviour of the dipyrazinylpyridine ligands, here we present the synthesis [5] of tdpzpy and two of its complexes [Fe(tdpzpy)_2]Cl₂·3.5H₂O (1) and [Ni $(tdpzpy)_2](NO_3)_2 \cdot 4H_2O$ (2). Interestingly, the crystal analysis [6] reveals that an N $\cdot \pi$ interaction between the pyrazinyl moieties can be distinguished which has never been reported before.

Comparing to its isoelectronic species 4-*p*-tolyl-2,2':6',2"terpyridine (ttpy, Scheme 1) (m.p. 168 °C),[4,7] the melting point of tdpzpy is 90 °C higher, reflecting enhancement of intermolecular interaction by replacement of the two peripherical pyridyl rings with pyrazinyls. The iron complex **1** was obtained hydrothermally. Although FeCl₃ was used as the metal source, in the product the iron atom is divalent and in low-spin state, clearly proved by that ¹H NMR signals of **1** are sharp and well-resolved in regular range (chemical shifts 0–10 ppm), indicative of diamagnetic property. Reduction of Fe(III) to Fe(II) in the presence of an aromatic N ligand was ever reported in another case.[8] In contrast, the ¹H NMR spectrum of the nickel complex **2** demonstrates it is paramagnetic, similar to that found for Ni(II)-terpy type complexes.[9]

1 and 2 are virtually isostructural, with the same symmetry (triclinic P-1) and similar cells. [6] They are analogous in the coordination cation structure and the inter-cationic interaction dominates the whole molecular packing as will be described in detail below. The counter anions (chloride and nitrate in 1 and 2, respectively) and water molecules possess the void spaces and have no remarkable effects on the crystal packing, similar to a number of [M $(\text{terpy})_2$ ^{*n*+} complexes with small counter anions.[2] Each Fe(II) or Ni (II) atom is hexa-coordinated by two orthogonal tridentate tdpzpy ligands. The outer $M-N_{pz}$ bonds (averaged 1.966 and 2.104 Å for Fe and Ni-N_{pz}, respectively) are longer than the central M-N_{py} bonds (averaged 1.87 and 1.973 Å for Fe and Ni–N_{py}, respectively). Due to the low-spin state of the Fe(II) atom in 1, the Fe-N bonds in 1 are markedly shorter than the corresponding Ni-N bonds in 2. The twisting of the pendant tolyl moieties with respect to the connected central pyridine rings is very similar for 1 and 2 (twisting angles 19.2

^{*} Corresponding author. *E-mail address:* wujzh@scnu.edu.cn (J.-Z. Wu).

^{1387-7003/\$ -} see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2010.03.004



Scheme 1. Structures of relevant ligands, with ring and atom labelling in tdpzpy used for NMR characterisation.

(2) and $48.0(2)^\circ$ in **1**, 19.2(1) and $46.6(1)^\circ$ in **2**, Fig. 1b and c). The dihedral angle between the two tolyl moieties is not large, 14.5(2) and $16.3(1)^\circ$ for **1** and **2** respectively.

Like the bis(terpy) type complexes, the "terpy embrace", or more generally embrace interlocking, is the dominant interaction between adjacent $[Fe(tdpzpy)_2]^{2+}$ or $[Ni(tdpzpy)_2]^{2+}$ cations, as illustrated in Fig. 1b and c, respectively. The embrace of $[Fe(ttpy)_2]^{2+}$ cations in [Fe (ttpy)_2][PF₆]_2·2.2MeCN,[3] drawn based on the CIF file (Refcode KOGLAU) is shown in Fig. 1a for comparison, where one of the two sets of disordered positions adopted. There are obvious OFF stacking between adjacent pyrazine rings in $[Fe(tdpzpy)_2]^{2+}$ or $[Ni(tdpzpy)_2]^{2+}$,

in which the pyrazine π system acts as either a π Lewis acid or a π Lewis base. This is quite similar to the OFF stacking between pyridine rings in $[Fe(ttpy)_2]^{2+}$. As regards the EF interaction, the difference is much remarkable. In $[Fe(ttpy)_2]^{2+}$ and other bis(terpy) type complexes, the EF interaction between two nearly perpendicular pyridine rings involves $(sp^2)C-H-\pi$ hydrogen bonds. But in $[Fe(tdpzpy)_2]^{2+}$ or $[Ni(tdpzpy)_2]^{2+}$, the EF interaction between two pyrazine rings utilizes the uncoordinated N atom in a pyrazine ring. The N-pyrazine distances in $[Fe(tdpzpy)_2]^{2+}$ are comparable to the H-pyridine distances in $[Fe(tdpzpy)_2]^{2+}$, as shown in Fig. 1a and b.

In order to quantitatively compare the novel N- π interaction with the C-H- π interaction, preliminary theoretical calculations based on crystal structural data of $[Fe(tdpzpy)_2]^{2+}$ and $[Fe(ttpy)_2]^{2+}$ were carried out, taking the embracing pyrazine–pyrazine or pyridine– pyridine moieties as the simplified models, respectively. The DFT method in Guaussian 03 program with B3LYP/6-31G* basis set and 50% basis set superposition error (BSSE) correction was used for the calculation.[10] Since the anions have little influence on the embrace interlocking as mentioned above, they were ignored in the calculation. The interaction energies for the actual N- π or H- π distances are compiled in Table 1. It is clear that the interaction energies of N- π



Fig. 1. Assembling of the cations into a chain by linkage of alternating $[Fe(ttpy)_2]^{2+}(a), [Fe(tdpzpy)_2]^{2+}(b), or [Ni(tdpzpy)_2]^{2+}(c)$ via OFF (green bold lines) and EF (red bold lines) interactions. For clarity, most of the H atoms are omitted. The values are the corresponding centroid ··· centroid, N–centroid or H–centroid distances in angstrom.

Table 1
Comparison of the interaction energies of N $\cdot\pi$ and C–H $\cdot\pi$ interactions

Complex	Interaction type	N (or H)…π/Å	Energy/kcal mol ⁻¹
[Fe(tdpzpy) ₂] ²⁺	N _{pz} <i>π</i> _{pz}	3.120	1.537
		3.067	1.753
$[Fe(ttpy)_2]^{2+}$	$C_{pv}H \cdot \pi_{pv}$	2.872	1.006
		2.992	0.948
		3.103	0.563
		3.124	0.694

interactions are stronger than those of C-H· π hydrogen bonds, although the values are almost in the same magnitude. As C-H· π hydrogen bonds have remarkable effects in the supramolecular assembly,[11] the N· π interaction would likely play some important role, as demonstrated in this paper. **1** and **2** represent two rare examples involving the N· π interaction. Searching the CSD database gives several organic or coordination compounds (Refcodes GALTES, VUDMEM, SIBDAJ, YIDTAH, TISWOI and TISWOI01) with analogous aromatic N· π contacts, which were not definitely indicated by the authors.[12] In [Ni(tdpzpy)₂]²⁺, the EF and OFF interactions are some weaker than those in [Fe(tdpzpy)₂]²⁺ as judged from the N· π and π · π related structural data (Fig. 1), consistent with the larger coordination sphere of [Ni(tdpzpy)₂]²⁺ as indicated above.

For the prototype $[M(terpy)_2]^{n+}$ complexes, normally each complex cation forms eight EF and four OFF interactions with its four neighbours and hence there is a 4-fold two-dimensional net of these embraces.[2] But when the terpy is replaced by a terimine ligand having pendant substituents the situation may become different. $[Fe(ttpy)_2]^{2+}$, for example, forms four EF and two OFF interactions with two neighbours. [3] The similar embrace pattern in $[Fe(tdpzpy)_2]^{2+}$ and $[Ni(tdpzpy)_2]^{2+}$ leads the cations align alternately to form one-dimensional chains, as illustrated in Fig. 1. The metal atoms inside a chain are



Fig. 3. Electronic absorption spectra of tdpzpy and its complexes in methanol (concentration 10 µM) at room temperature.

almost colinear, with the M···M···M angle being 167.2(1) and 168.9(1)° for [Fe(tdpzpy)₂]²⁺ and [Ni(tdpzpy)₂]²⁺ respectively, close to 174.5(1)° for [Fe(ttpy)₂]²⁺. The substituent tolyl groups are aligned orthogonal to the metal line pointing towards two opposite directions. These tolyl groups also have some structural contribution for the supramolecular assembling. As shown in Fig. 2, the intermolecular sp³-C-H··*π* interactions involving the methyl C–H and the pyrazine ring in [Fe(tdpzpy)₂]²⁺ link the chains into two-dimensional layers. Other sp²-C-H··*π* interactions involving the phenyl and pyrazine rings further connect the layers into a three-dimensional network.

It is some regretful that the X-ray crystallographic data for **1** and **2** were not good enough to assure the exact positioning of the water proton atoms. So it is not very safe to describe accurately the water involved hydrogen bonds. But the water molecules and the anions



Fig. 2. Chains of $[Fe(tdpzpy)_2]^{2+}$ expand to a layer by methyl involved C-H- π hydrogen bonds. Only relevant H atoms are shown. Green and cyan lines represent OFF and C-H- π interactions, respectively.

have little influence on the crystal packing comparing to the cationic embrace interlocking as described above. Thermogravity analysis implys that the water involved hydrogen bonding is not strong enough to markedly increase the temperature for complete water removing (below 130 °C).

The electronic absorption spectra of complexes **1** and **2**, as well as the ligand in methanol are shown in Fig. 3. Below 310 nm there are several strong ligand-centered absorption bands for the complexes. The coordination induced new absorption was observed around 335 nm for both complexes. The Fe(II) complex **1** displays a moderately intense metal-to-ligand charge-transfer (MLCT) band at 567 nm and is responsible for the dark purple colour of this complex, supporting the supposed low-spin state of Fe(II), analogous to the Fe(II)-terpyridine type complexes.[13] The absorption spectra of the compounds in acetonitrile are essentially the same as those in methanol. Excitation of the MLCT transition of complex **1** could not trigger off photoemission. But when excited with UV light, both **1** and **2** in methanol exhibited



Fig. 4. Luminescence spectra of tdpzpy and its complexes in methanol and acetonitrile (concentration 10 μ M, excited at 285 nm) at room temperature.



Fig. 5. Luminescence spectra of tdpzpy and its complexes in solid state (excited at 285 nm) at room temperature.

fluorescence around 400 nm and weaker fluoroscence around 320 nm, attributable to the ligand-based transition by comparison with the ligand, as illustrated in Fig. 4. In another solvent acetonitrile the weak bands disappeared, while the strong bands decreased to some extent. The emission of the Ni(II) complex **2** is more likely to be affected by the solvent, as the 410 nm emission in methanol dramatically shifted blue to 390 nm in acetonitrile, accompanied by a remarkable intensity decrease (36%). Comparing the fluorescence intensities in the same solvent (Fig. 4) suggests that coordination to Fe(II) or Ni(II) leads to slight quenching of the emission from tdpzpy, implying some charge-transfer from the ligand to the *d*-orbital unfulfilled metal atom. Such quenching becomes more drastic for the solid state fluorescence (Fig. 5).

In summary, the Fe(II) and Ni(II) complexes with a rarely utilized dipyrazinylpyridine ligand have been synthesized. The supramolecular embrace interlocking between the coordination cations dominates the whole crystal packing. The rarely seen $N \cdot \pi$ interaction, stronger than C–H·· π hydrogen bonding, has been found participating the embrace motif. The electronic absorption and emission properties of the complexes have been preliminarily investigated.

Acknowledgement

Financial support from the National Natural Science Foundation of China (grant no. 20975041), the Guangdong Natural Science Foundation (grant no. 5005935) and the SRFROCS program, State Education Ministry of China, are gratefully acknowledged.

Appendix A. Supplementary data

CCDC 745109 and 745110 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www. ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j. inoche.2010.03.004.

References

- (a) U.S. Schubert, H. Hofmeier, G.R. Newkome, Modern Terpyridine Chemistry, Wiley-VCH, Weinheim, Germany, 2006;
 - (b) E.C. Constable, Chem. Soc. Rev. 246 (2007).
- [2] (a) J. McMurtrie, I. Dance, Cryst. Eng Commun. 7 (2005) 216;
- (b) M.L. Scudder, H.A. Goodwin, I.G. Dance, New J. Chem. 23 (1999) 695.
- [3] (a) J. McMurtrie, I. Dance, Cryst. Eng. Commun. 11 (2009) 1141;
 (b) J. McMurtrie, I. Dance, Cryst. Eng. Commun. 7 (2005) 230;
- (c) R. Pritchard, C.A. Kilner, M.A. Halcrow, Chem. Commun. (2007) 577;
 - (d) C. Carbonera, C.A. Kilner, J.F. Letard, M.A. Halcrow, Dalton Trans. (2007) 1284;
- (e) M.L. Scudder, D.C. Craig, H.A. Goodwin, Cryst. Eng. Commun. 7 (2005) 642;

- (f) E.C. Constable, C.E. Housecroft, E.A. Medlycott, M. Neuburger, F. Reinders, S. Reymann, S. Schaffner, Inorg. Chem. Commun. 11 (2008) 805;
- (g) E.C. Constable, C.E. Housecroft, E. Medlycott, M. Neuburger, F. Reinders, S. Reymann, S. Schaffner, Inorg. Chem. Commun. 11 (2008) 518;
- (h) J.E. Beves, P. Chwalisz, E.C. Constable, C.E. Housecroft, M. Neuburger, S. Schaffner, J.A. Zampese, Inorg. Chem. Commun. 11 (2008) 1009;
- J.E. Beves, E.C. Constable, C.E. Housecroft, C.J. Kepert, M. Neuburger, D.J. Price, S. Schaffner, Cryst. Eng. Commun. 9 (2007) 1073;
- (j) E.C. Constable, C.E. Housecroft, M. Neuburger, S. Schaffner, F. Schaper, Inorg. Chem. Commun. 9 (2006) 433.
- [4] (a) F.A. Al-mutlaq, P.G. Potvin, A.I. Philippopoulos, P. Falaras, Eur. J. Inorg. Chem. (2007) 2121;
 - (b) M. Darabantu, L. Boully, A. Turckb, N. Ple, Tetrahedron 61 (2005) 2897;
 - (c) S. Vaduvescu, P.G. Potvin, Eur. J. Inorg. Chem. (2004) 1763;
 - (d) R. Liegghio, P.G. Potvin, A.B.P. Lever, Inorg. Chem. 40 (2001) 5485;
 (e) U. Ziener, E. Breuning, J.-M. Lehn, E. Wegelius, K. Rissanen, G. Baum, D.
- Fenske, G. Vaughan, Chem.-Eur. J. 6 (2000) 4132. [5] Synthesis of tdpzpy: 2-Acetylpyrazine (4.15 g, 34 mmol) and p-tolualdehyde 2 ml, 17 mmol) in MeOH (20 ml) was stirred at room temperature for 2 hours and 5 g NaOH in 10 ml water was added. Then 50 ml ammonia was added slowly. After continuous stir for 12 hours, the precipitate was collected and washed with water, cold ethanol and diethyl ether and recrystallized from chloroform. Yellow block crystals, yield 61%, m.p. 258.2 °C. $\delta_{\rm H}/\rm ppm$ (400 MHz, CDCl₃): 9.86 (d, 2 H, H^{A1}), 8.76–8.75 (m, 4 H, H^{A2/A3}), 8.67 (d, 2 H, H^{B1}), 7.78 (d, 2 H, H^{C1}), 7.34 (d, 2 H, H^{C2}), 9.86 (d, 2 2.44 (s, 3 H, CH₃). ESI-MS: m/z = 326.51 ([tdpzpy + H]⁺). Synthesis of 1: tdpzpy (0.1368 g, 0.42 mmol) and FeCl₃·6H₂O (0.0615 g, 0.23 mmol) were mixed with water (10 ml) and sealed in a 15 ml stainless steel bomb with a Teflon liner and heated at 170 °C for 72 h. After cooling to room temperature at a rate of 5 °C h⁻¹ $\begin{array}{l} purple-black \ block-shaped \ crystals \ were \ obtained, \ yield \ 68.7\% \ based \ on \ tdpzpy. \\ \delta_{H}/ppm \ (d^{6}-DMSO) \ 10.08 \ (s, 4 \ H, \ H^{A3}), 9.75 \ (s, 4 \ H, \ H^{B3}), 8.44 \ (d, 4 \ H, \ H^{A6}), 8.32 \ (d, 4 \ H, \ H^{A5}), 7.63 \ (d, 4 \ H, \ H^{C2}), 7.43 \ (d, 4 \ H, \ H^{C3}), 2.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H, \ H^{A5}), 8.41 \ (d, 4 \ H, \ H^{C2}), 7.43 \ (d, 4 \ H, \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H, \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ (s, 6 \ H, \ H^{Me}). \ Synthesis \ of 2: \ 10.04 \ H^{C3}), 1.52 \ H^{C3}), 1.52 \ H^{C3}$ $Ni(NO_3)_2\cdot 6H_2O~(0.0301~g,~0.1~mmol)$ and tdpzpy (0.0662 g, 0.2 mmol) were added to MeOH (10 ml) and stirred for a 5 h period under reflux. A yellow precipitate formed, which was removed by filtration, and the X-ray quality crystals of 2 were obtained by slow evaporation of the solution, yield 43% based on tdpzpy. δ_H/ppm (d⁶-DMSO) 75, 66, 51, 12, 10, 9-0.
- [6] Crystallographic data for 1: triclinic *P*-1, a = 12.1633(2), b = 12.6856(2), c = 15.085(2), Å, $\alpha = 77.588(3)$, $\beta = 69.440(3)$, $\gamma = 64.511(3)^\circ$, V = 1961.6(5) Å³, Z = 2, T = 298 K, 10652 reflections collected. Refinement of 7600 reflections (525 parameters) with $I > 2\sigma(I)$ converged at final $R_1 = 0.0776$, $wR_2 = 0.2063$,

GOF = 1.002. CCDC-745109. Crystallographic data for 2: triclinic *P*-1, *a* = 12.472 (3), *b* = 12.745(3), *c* = 15.445(4) Å, α = 78.103(3), β = 71.123(3), γ = 64.150 (3)°, *V* = 2084.5(9) Å³, *Z* = 2, *T* = 298 K, 10982 reflections collected. Refinement of 7602 reflections (570 parameters) with *I*>2 σ (*I*) converge0d at final *R*₁ = 0.0672, *wR*₂ = 0.1797, GOF = 1.012. CCDC-745110.

- [7] J.P. Collin, S. Guillerez, J.P. Sauvage, F. Barigelletti, L. De Cola, L. Flamigni, V. Balzani, Inorg. Chem. 30 (1991) 4230.
- [8] Y. Xu, L. Han, Z.-Z. Lin, C.-P. Liu, D.-Q. Yuan, Y.-F. Zhou, M.-C. Hong, Eur. J. Inorg. Chem. (2004) 4457.
- [9] (a) N.W. Alcock, P.R. Barker, J.M. Haider, M.J. Hannon, C.L. Painting, Z. Pikramenou, E.A. Plummer, K. Rissanen, P. Saarenketo, J. Chem. Soc., Dalton Trans. (2000) 1447;
 - (b) E.C. Constable, R. Martinez-Manez, A.M.W.C. Thompson, J.V. Walker, J. Chem. Soc., Dalton Trans. (1994) 1585.
- [10] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J. J. A. Montgomery, 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. Hrtchian, 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, Revision B.03, Gaussian Inc., Pittsburgh PA, 2003.
- [11] (a) M. Nishio, Cryst. Eng. Commun. 6 (2004) 130;
 - (b) M. Nishio, Y. Umezawa, K. Honda, S. Tsuboyama, H. Suezawa, Cryst. Eng. Commun. 11 (2009) 1757.
- [12] (a) Z.P. Deng, S. Gao, S.W. Ng, Acta Cryst. E 63 (2007) M1650;
 - (b) S.C. Shoner, P.P. Power, Inorg. Chem. 31 (1992) 1001;
 - (c) J.Q. Tao, Z.G. Gu, T.W. Wang, Q.F. Yang, J.L. Zuo, X.Z. You, Inorg. Chim. Acta 360 (2007) 4125;
 - (d) Y. Yamashita, K. Saito, T. Suzuki, C. Kabuto, T. Mukai, T. Miyashi, Angew. Chem. Int. Ed. Engl. 27 (1988) 434;
- (e) Y.Y. Zhang, J.S. Li, X.L. Zhou, X.P. Fan, Acta Cryst. E 63 (2007) o1285.
 [13] (a) J.E. Beves, E.C. Constable, C.E. Housecroft, C.J. Kepert, M. Neuburger, D.J. Price,
 - S. Schaffner, J.A. Zampese, Dalton Trans. (2008) 6742; (b) P.S. Braterman, J.-I. Song, R.D. Peacock, Inorg. Chem. 31 (1992) 555.
 - (D) P.S. DIALEIIIIAII, J.-I. SOUG, K.D. PEACOCK, IIIOIG. CHEIII. 51 (1992) 553