Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gsch20>

Binding ability of Zn-tetraarylporphyrins with two, four and eight 4-(4-(3,6-bis(t-butyl)carbazol-9-ylphenyl)-1,2,3-triazole end groups towards N-containing substrates of different nature

Nguyen Tran Nguyen^a, Galina Mamardashvili^b, Matvey Gruzdev^b, Nugzar Mamardashvili^b & Wim Dehaen^a

^a Molecular Design and Synthesis, KU Leuven, Celestijnenlaan 200F, B-3001, Leuven, Belgium

^b Coordination Chemistry of Macrocyclic Compounds, G.A. Krestov Institute of Solution Chemistry of Russian Academy of Sciences, Akademicheskaya St. 1, 153045, Ivanovo, Russia
Published online: 12 Dec 2012.

To cite this article: Nguyen Tran Nguyen, Galina Mamardashvili, Matvey Gruzdev, Nugzar Mamardashvili & Wim Dehaen (2013): Binding ability of Zn-tetraarylporphyrins with two, four and eight 4-(4-(3,6-bis(t-butyl)carbazol-9-ylphenyl)-1,2,3-triazole end groups towards N-containing substrates of different nature, *Supramolecular Chemistry*, 25:3, 180-188

To link to this article: <http://dx.doi.org/10.1080/10610278.2012.741687>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

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.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Binding ability of Zn-tetraarylporphyrins with two, four and eight 4-(4-(3,6-bis(*t*-butyl)carbazol-9-ylphenyl)-1,2,3-triazole end groups towards N-containing substrates of different nature

Nguyen Tran Nguyen^a, Galina Mamardashvili^b, Matvey Gruzdev^b, Nugzar Mamardashvili^{b*} and Wim Dehaen^{a*}

^aMolecular Design and Synthesis, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium; ^bCoordination Chemistry of Macrocyclic Compounds, G.A. Krestov Institute of Solution Chemistry of Russian Academy of Sciences, Akademicheskaya St. 1, 153045 Ivanovo, Russia

(Received 8 August 2012; final version received 16 October 2012)

The binding ability of Zn-tetraarylporphyrins with two, four and eight 4-carbazolylphenyl-1,2,3-triazole end groups towards 1,4-diazabicyclo[2.2.2]octane, pyridine and 1,2,3-triazole in toluene was studied by spectrophotometric and ¹H NMR titration. It was determined that due to a good geometric match of the ligand size to the size of the intramolecular cavities of the porphyrinic receptor, and by the existence of additional π – π and/or hydrogen bonding interactions between the ligand and the triazole fragments of the porphyrin, the Zn-tetraarylporphyrin with eight 4-carbazolylphenyl-1,2,3-triazole end groups could be used as an effective receptor for 1,2,3-triazole and other small heterocycles such as pyridine. Taking into account the fact that binding is accompanied by a clear and easily identifiable response in the UV–vis spectra of the reaction mixture, this metalloporphyrin could be considered as a molecular optical sensing device for small heterocyclic substrates.

Keywords: porphyrin; spectrophotometric titration; binding ability; receptor; sensing device

1. Introduction

Metalloporphyrins (MPs) with coordinatively unsaturated metals cations have the ability to bind organic bases as additional axial ligands with the formation of porphyrin–ligand complexes (MP–L) in a 1:1 ratio (1–8).

[2.2.2]octane (DABCO), piperazine and pyrazine), the formation of the complexes in a ratio of either 1:1 (ZnPorph–L') or 2:1 (ZnPorph–L'–ZnPorph) is possible (9, 10). Porphyrins containing nitrogen atoms at the periphery of the macrocycle due to multipoint binding are able to form linear or cyclic associates, the composition and

Upon interaction of Zn-porphyrins with bifunctional nitrogen-containing ligands ($L' = 1,4$ -diazabicyclo

structure of which depends on the structure of the macrocycle (11–13).

*Corresponding authors. Emails: ngm@isc-ras.ru; wim.dehaen@chem.kuleuven.be

Thus, a number of pyridyl- and imidazolyl-substituted porphyrins exist in solutions in the form of dimeric supramolecular complexes [$(\text{ZnPy})_2$ and $(\text{ZnIm})_2$] having a

‘slipped’ orientation (14, 15). The stronger the $\text{Zn}-\text{N}_L$ bond, the greater the degree of the dimerisation.

This paper investigates the binding ability of Zn-tetraarylporphyrins with two (**ZnP1**), four (**ZnP2**) and eight (**ZnP3**) 4-carbazolylphenyl-1,2,3-triazole end groups towards DABCO (**L1**), pyridine (**L6**) and 1,2,3-triazole (**L9**) in toluene. These porphyrins were previously synthesised (16) as new fluorescent switches and photoactive devices for the detection of substrates of different nature.

2. Experimental

The porphyrins **ZnP1**, **ZnP2** and **ZnP3** were obtained using the click reaction (17), using different azide core porphyrins and carbazole branches prepared in adaptation of earlier work from our laboratories. The details of the synthesis will be communicated together with the forthcoming spectroscopic studies (16). DABCO (**L1**), pyridine (**L6**) and 1,2,3-triazole (**L9**) from Sigma–Aldrich were used without further purification. ¹H NMR spectra were recorded on a Bruker VC-500 (500.17 MHz) in CDCl₃ using tetramethylsilane (TMS) as the internal standard. UV–vis spectra of the porphyrins and their evolution upon addition of the ligands were measured on a Carry 100 spectrophotometer and are depicted in Table 1.

The UV–vis absorption spectral studies reveal red-shifted Soret and visible bands upon addition of the ligands to a solution of the investigated receptor porphyrins

confirming that the N-containing entity of the ligands binds to the Zn-cation of the coordination centre of the tetrapyrrolic macrocycle.

The stability constants of the MP complexes with the ligands in a ratio of 2:1 ($K_{\text{assoc.1}}$) and 1:1 ($K_{\text{assoc.2}}$) according to the literature (18) were calculated based on spectrophotometric data at two wavelengths (decreasing and increasing) using the following relationships (1) and (2):

$$K_{\text{assoc.1}} = \frac{[A - B - A]}{[A]^2 \cdot [B]}$$

$$= \frac{1}{[A][B]} \left(\frac{\Delta A_i, \lambda_1}{\Delta A_o, \lambda_1} \cdot \frac{\Delta A_o, \lambda_2}{\Delta A_i, \lambda_2} \right), \quad M^{-2}, \quad (1)$$

$$K_{\text{assoc.2}} = \frac{[A - B]}{[A] \cdot [B]}$$

$$= \frac{1}{[B]} \left(\frac{\Delta A_i, \lambda_1}{\Delta A_o, \lambda_1} \cdot \frac{\Delta A_o, \lambda_2}{\Delta A_i, \lambda_2} \right), \quad M^{-1}, \quad (2)$$

where λ_1 is the decreasing wavelength, λ_2 is the increasing wavelength, $[A]$ is the Zn-porphyrin concentration, $[B]$ is the ligand concentration, ΔA_o is the maximal change of the optical density at the given wavelength and ΔA_i is the change of the optical density of the solution at a given wavelength at a given concentration.

Table 1. UV-vis spectra [$\lambda_{\max}$, nm ($\log \epsilon$)] of **ZnP1**, **ZnP2** and **ZnP3** and their complexes with **L1**, **L6** and **L9** in toluene; $C_{\text{ZnPorph.}} \approx 1.5 \times 10^{-5}$ M.

	$\lambda_{\max}$, nm ($\log \epsilon$)			
ZnP1	399 (4.57)	418 (5.30)	548 (4.25)	—
ZnP1-L1	408 (4.56)	428 (5.29)	563 (4.21)	603 (3.97)
ZnP1-L1-ZnP1	—	423 (5.29)	555 (4.23)	603 (3.83)
ZnP1-L6	—	428 (5.30)	561 (4.21)	602 (3.98)
ZnP1-L9	—	422 (5.30)	559 (4.22)	601 (3.98)
ZnP2	401 (4.50)	424 (5.37)	550 (4.31)	—
ZnP2-L1	410 (4.49)	431 (5.36)	562 (4.28)	603 (4.10)
ZnP2-L1-ZnP2	—	427 (5.31)	556 (4.23)	603 (3.93)
ZnP1-L6	—	430 (5.38)	562 (4.26)	602 (4.08)
ZnP2-L9	—	427 (5.37)	561 (4.26)	602 (4.03)
ZnP3	—	418 (5.25)	560 (4.41)	604 (3.84)
ZnP3-L1	—	423 (5.25), 450 (br.)	572 (4.42)	603 (4.19)
ZnP1-L6	—	422 (5.24)	563 (4.49)	612 (4.18)
ZnP3-L9	—	422 (5.23)	565 (4.49)	614 (4.18)

3. Results and discussions

The ability of Zn-porphyrins for axial coordination depends on the nature and structure of the porphyrinate itself, the nature of the additional ligand and the environment in which this process occurs. As seen from the stability constants of the 1:1 complexes between Zn-porphyrins and nitrogen-containing bases (Table 2), the strength of the complexes formed, in general, depends on the basicity of the additional ligand.

basic, azole nitrogen atom greatly increases the ability of the heterocycle to be coordinated on the Zn-porphyrins, especially if the second nitrogen atom is substituted at the β -position of the cycle (the binding constant increases by two orders of magnitude).

At the same time, the introduction of two extra nitrogen atoms into the pyrrole molecule only slightly increases the binding ability of the heterocycle compared with unsubstituted pyrrole, due to the inductive effect of

Pyrrole is an NH-acid rather than a base and its binding ability towards ZnP is the weakest among all the nitrogen-containing organic heterocycles listed in Table 2. Introduction into the molecule of a second, much more

the nitrogens on the basicity, as also seen for the pyrazole molecule.

Chemical modification of the porphyrin macrocycle has a significant influence on the process of axial coordination

Table 2. Stability constants of 1:1 complexes between the **ZnP** and the different nitrogen-containing organic molecules in toluene.

Extra ligand		Solvent	Basicity of a ligand	$K_{\text{assoc.}}$ (M^{-1})	Literature
DABCO	L1	Toluene	10.9 ($\text{p}K_{\text{a1}}$)	190,000	(19)
Piperidine	L2	Toluene	11.3 ($\text{p}K_{\text{a}}$)	80,900	(4)
Piperazine	L3	Toluene	9.9 ($\text{p}K_{\text{a1}}$)	80,000	(19)
Ethylenediamine	L4	Toluene	9.6 ($\text{p}K_{\text{a1}}$)	26,000	(19)
Imidazole	L5	Toluene	6.9 ($\text{p}K_{\text{a}}$)	24,000	(4)
Pyridine	L6	CHCl_3	5.2 ($\text{p}K_{\text{a}}$)	5800	(4)
				2525	(19)
Pyrazole	L7	CHCl_3	2.5 ($\text{p}K_{\text{a}}$)	1500	(19)
Pyrazine	L8	Toluene	0.6 ($\text{p}K_{\text{a1}}$)	980	(19)
1,2,3-Triazole	L9	Toluene	—	480	
Pyrrole	L10	Toluene	— 2 ($\text{p}K_{\text{a}}$)	200	(4)

Note: The error in determining the stability constants was 5–7%.

Table 3. Stability constants of 1:1 and 1:2 complexes of **ZnP**, **ZnP1**, **ZnP2** and **ZnP3** with **L1**, **L6** and **L9** in toluene, $C_{\text{ZnPorph}} \approx 1.1/1.6 \times 10^{-5} \text{ M}$.

	ZnPorph–L9 , $K_{\text{assoc.2}}$ (M^{-1})	ZnPorph–L1–ZnPorph , $K_{\text{assoc.1}}$ (M^{-2})	ZnPorph–L1 , $K_{\text{assoc.2}}$ (M^{-1})	ZnPorph–L6 , $K_{\text{assoc.2}}$ (M^{-1})
ZnP	480	5.0×10^9	1.9×10^5	5.8×10^3
ZnP1	90	1.7×10^8	2.3×10^4	1.2×10^3
ZnP2	240	1.3×10^9	9.7×10^4	3.9×10^3
ZnP3	6.6×10^5	–	1.3×10^6	1.1×10^5

Note: The error in determining the stability constants was 5–7% (for 1:1 complexes) and 10% (for 1:2 complexes).

if a change of electron density on the nitrogen atoms and of the charge of the Zn^{2+} cation in the coordination centre of the macrocycle occurs. Introduction of bulky substituents into the porphyrin macrocycle, in most cases, reduces the ability of Zn-porphyrins to coordinate additional axial ligands. Firstly, the presence of bulky substituents usually leads to a deformation of the macrocycle, which results in a decrease in charge on the cation Zn^{2+} (6–8). Secondly, the bulky substituents may block the reaction centre of the tetrapyrrole macrocycle.

In this work, we have studied the ability of Zn-tetraarylporphyrins with two (**ZnP1**), four (**ZnP2**) and eight (**ZnP3**) 4-carbazolylphenyl-1,2,3-triazole end groups for self-aggregation and their binding ability towards DABCO (**L1**), pyridine (**L6**) and 1,2,3-triazole (**L9**) (Table 3). Since these porphyrins contain triazole fragments, there is a possibility of formation of porphyrin dimers or polymers through multipoint binding of the molecules (Figure 1). To clear up the matter, the binding ability of **ZnP1**, **ZnP2** and **ZnP3** towards **L9** has been studied.

Initially, we studied the complexation of **L9** with the model porphyrinic system (**ZnP**) which does not contain any triazole fragments. The study of the complexation of **ZnP** with **L9** by spectrophotometric titration showed that over a wide concentration range of the ligand

($C_{\text{L9}} = 0/8 \times 10^{-2} \text{ M}$), changes in the UV–vis spectra of the reaction mixture occur with the formation of one family of spectral curves with one set of isosbestic points (Figure 2(a)). The titration curve (Figure 2(b)) has one step, which indicates the formation of a single type of complexes in a ratio of 1:1. Stability constants of the complexes are presented in Table 3.

In the next step, the complexation of **ZnP1**, **ZnP2** and **ZnP3** with **L9** was investigated in comparable conditions. It was determined that, as in the case of the interaction between **ZnP** and **L9**, changes in the UV–vis spectra of the mixtures **ZnP1–L9**, **ZnP2–L9** and **ZnP3–L9** occur with the formation of one family of spectral curves, and the titration curves of the processes have a single step. As an example, Figure 3(a),(b) shows the data for the system **ZnP1–L9**.

The same features were obtained for the complexation of **ZnP**, **ZnP1**, **ZnP2** and **ZnP3** with **L6**. The dependence of the complexation stability constants on the nature of the porphyrinate and ligand is presented in Table 3 and is depicted in Figure 4. From the data, we can clearly see that the stabilities of the complexes **ZnP3–L9** and **ZnP3–L6** are much higher as compared with the complexes of **ZnP**, **ZnP1** and **ZnP2** with the same ligands.

The significant increase in the affinity of **L6** and **L9** to **ZnP3** can be explained by a good geometric match

Figure 1. Possible structure of the **ZnP1** dimers.

Figure 2. (a) Changes in the UV-vis spectra of the system **ZnP-L9** in toluene at 20°C, $C_{\text{ZnP}} = 1.1 \times 10^{-5}$ M. (b) The binding isotherm of the system **ZnP-L9** in toluene at 20°C, $C_{\text{ZnP}} = 1.1 \times 10^{-5}$ M.

Figure 3. (a) The changes in the UV-vis spectra of the system **ZnP1-L9** in toluene at 20°C, $C_{\text{ZnP1}} = 1.5 \times 10^{-5}$ M. (b) The binding isotherm of the system **ZnP1-L9** in toluene at 20°C, $C_{\text{ZnP1}} = 1.5 \times 10^{-5}$ M.

Figure 4. Dependence of the stability constants of the complexes of **ZnP**, **ZnP1**, **ZnP2** and **ZnP3** with **L1**, **L6** and **L9** on the nature of the porphyrinate and the ligand.

between the size of the ligands and the intramolecular cavities of **ZnP3**. If in the case of porphyrinates **ZnP1** and **ZnP2**, the 4-carbazolylphenyl-1,2,3-triazole end groups due to rotation of the phenyl fragments can occupy an arbitrary position relative to the tetrapyrrolic macrocycle, the porphyrinate **ZnP3** due to the *meso*-mesityl fragments is fixed relative to the porphyrin plane, and the porphyrin can be seen as a 'picket-fence' porphyrins with intramolecular cavities formed by the 4-carbazolylphenyl-1,2,3-triazole end groups emanating from both sides of the porphyrin core (Figure 5).

The presence of the intramolecular cavities increases the strength of the axial coordination, probably due to the ligand's incorporation in the cavity and formation of additional $\pi-\pi$ interactions between the ligand and the triazole fragments. So in the systems **ZnP3-L6** and **ZnP3-L9**, multipoint binding of the ligand by the porphyrinic receptor may be due to (i) coordination interactions between the Zn^{2+} cation of the metaloporphyrin reaction

centre with the ligand N-atom and (ii) $\pi-\pi$ or hydrogen bonding interactions between the ligand and the triazole fragments of the intramolecular cavity of **ZnP3**.

However, the fact that porphyrinates **ZnP1**, **ZnP2** and **ZnP3** are able to react with **L9** with the formation of 1:1 complexes suggests that the porphyrins are in the form of monomers in toluene solution. The matter also is confirmed by a concentration dependent on the UV-vis measurement: the Soret band of the Zn-porphyrins does not change its shape, and a plot of absorbance coefficient dependence from the concentration is constant. The absence of splitting and the high intensities of the Soret bands in the UV-vis spectra of the Zn-porphyrins indicate the absence of a dimerisation due to the coordination of the triazole fragments of one molecule with the Zn^{2+} cation of the another molecule.

According to our interests in the supramolecular chemistry of porphyrins (8, 10, 13), we also investigated the binding ability of **ZnP**, **ZnP1**, **ZnP2** and **ZnP3** towards **L1**. The study of complex formation of **ZnP1** and **ZnP2** with **L1** using the method of spectrophotometric titration showed that these processes in toluene, similar to the system **ZnP-L1**, proceed in two stages as apparent by the two steps on the corresponding titration curve (Figure 6(a),(b)). Each step on the titration curve corresponds to its own family of spectral curves with a set of isosbestic points. Existence of the two steps in the complexation is also confirmed by the graphical dependence of $\log [(A_o - A_i)/(A_i - A_k)]$ from $\log C_L$ for the system.

There are characteristic shifts of signals of the ligand protons in the ^1H NMR spectra of the complexes. Thus, in the spectrum of the complex **ZnP2-L1**, formed at low concentrations of the ligand [up to a molar ratio of reagents of 1:(0/0.5)], protons of **L1** appear at ~ -3.5 ppm. The equivalence of the protons of $-\text{CH}_2\text{CH}_2-$ fragments of **L1** in the ^1H NMR spectra indicates the formation of

Figure 5. Possible structure of **ZnP3**.

Figure 6. (a) Changes in the UV-vis spectra (a) and binding isotherm (b) of the system **ZnP2-L1** in the first step in toluene at 20°C, $C_{\text{ZnP2}} = 1.2 \times 10^{-5}$ M. (b) Changes in the UV-vis spectra (a) and binding isotherm (b) of the system **ZnP2-L1** in the second step in toluene at 20°C, $C_{\text{ZnP2}} = 1.2 \times 10^{-5}$ M.

Figure 7. Illustration of various types of protons of the ligand in the investigated 2:1 and 1:1 complexes between the Zn-porphyrinates and the **L1**.

so-called sandwich complexes between **ZnP2** and **L1** in a ratio of 2:1, when the bidentate ligand is located between the two molecules of the Zn-porphyrins.

In the ^1H NMR spectra of the complexes formed at the higher concentrations of the ligand [molar ratio of reagents 1:(0.5/10.0)], the protons of **L1** appear as two signals of equal intensity, which indicates the formation of 1:1 complexes. The protons of $-\text{CH}_2\text{CH}_2-$ fragments of **L1**, which are closer to the tetrapyrrole macrocycle (Figure 7),

undergo the shielding effect of its π -electron system and appear at high field (-3.3 ppm). The other protons, which are more distant from the macrocycle, appear at relatively lower field but still observe some shielding (0.5 ppm). The stability constants of the considered complexes are presented in Table 3. It should be noted that in comparison to **ZnP2**, the complexation of **ZnP1** with **L1** with the formation of the complexes in a ratio of 1:1 occurs at the higher concentrations of the ligand.

The study of complex formation of **ZnP3** with **L1** using the spectrophotometric titration method showed that this process in toluene proceeds in a single step with the formation of only one type of complex in a ratio of 1:1. The presence of bulky substituents above the coordination centre of the porphyrin, obviously, prevents two-centred coordination of **L1**. At the same time, the association constant of the 1:1 complex increases somewhat when compared to the smaller MP (Table 3).

4. Conclusion

Thus, Zn-tetraphenylporphyrin substitution by two, four and eight bulky triazole-containing fragments does not lead to the dimerisation or self-aggregation of the macrocycles. This fact could be explained by the steric hindrance to the multipoint self-binding of the macrocycles and the low basicity of 1,2,3-triazole. At the same time, the chemical modification of the tetrapyrrolic macrocycle by eight 4-carbazolylphenyl-1,2,3-triazole end groups increases the strength of the axial coordination of the ligands (**L6** and **L9**) containing π -electronic systems in their composition. In the case of non-aromatic **L1**, probably due to the absence of the effect of π - π interactions between the molecules of the substrate and the porphyrin, the difference in the stability constants in going from **ZnP-L1** to **ZnP3-L1** is less pronounced.

An increase in the stability of the axial coordination of **L9** by **ZnP3** could be explained by a good geometric match of the ligand size to the size of the intramolecular cavities of the porphyrinic receptor, and by the existence of additional π - π and/or hydrogen bonding interactions between the ligand and the triazole fragments of the porphyrin. On the base of the experimental data, we can conclude that the Zn-tetraarylporphyrin with eight 4-carbazolylphenyl-1,2,3-triazole end groups could be used as an effective receptor for 1,2,3-triazole. Taking into account the fact that binding is accompanied by a clear and easily identifiable response in the UV-vis spectra of the reaction mixture, this MP could be considered as a molecular optical sensing device for small heterocyclic substrates. Further research will be directed towards this goal.

Acknowledgements

This work was financially supported by the Seventh Framework Programme of the European Community for Research, Technological Development and Demonstration Activities, IRSES-GA-2009-247260 and the Programme of the Presidium of Russian Academy of Sciences No. 24 'Fundamental basics of nanostructures and nanomaterials technologies', research

direction – 'Nanomedicines and their targeted delivery'. NTN and WD thank the support of the KU Leuven, the 'Ministerie voor Wetenschapsbeleid' and the FWO-Vlaanderen.

References

- (1) Sessler, J.W.; Karnas, E.; Sedenberg, E. In *Supramolecular Chemistry: From Molecules to Nanomaterials*; Gale, P.A., Steed, J.W., Eds.; Wiley: Chichester, 2012; vol. 3, pp. 1045–1074.
- (2) Sprafke, J.K.; Odell, B.; Claridge, T.D.W.; Anderson, H.L. *Angew. Chem. Int. Ed.* **2011**, *50*, 5572–5575.
- (3) Hunter, C.A.; Anderson, H.L. *Angew. Chem. Int. Ed.* **2009**, *48*, 7488–7499.
- (4) Berezin, B.D. *Metalloporphyrins*; Science: Moscow, 1988.
- (5) Beletskaya, I.P.; Tyurin, V.S.; Tsivadze, A.Y. *Chem. Rev.* **2009**, *109*, 1659–1713.
- (6) Grozema, F.C.; Houarner-Rassin, C.; Prins, P.; Siebbeles, L.D.A.; Anderson, H.L. *J. Am. Chem. Soc.* **2007**, *129*, 13370–13371.
- (7) Ogoshi, H.; Mizutani, T.; Hayashi, T.; Kuroda, Y. In *The Porphyrin Handbook*; Kadish, K.M., Smith, K.M., Guillard, R., Eds.; Academic Press: New York, 2000; vol. 6, Chapter 46, pp. 279–339.
- (8) Mamardashvili, G.M.; Mamardashvili, N.Zh.; Koifman O.I. *Uspekhi Khimii* **2005**, *74*, 839–855; Mamardashvili, G.M.; Mamardashvili, N.Zh.; Koifman O.I. *Russ. Chem. Rev.* **2005**, *74*, 765–780.
- (9) Hunter, C.A.; Meah, M.N.; Sanders, J.K.M. *J. Am. Chem. Soc.* **1990**, *112*, 5773–5780.
- (10) Mamardashvili, G.M.; Mamardashvili, N.Zh.; Koifman, O.I. *Zhur. Neorg. Khimii* **2007**, *52*, 1299–1303; Mamardashvili, G.M.; Mamardashvili, N.Zh.; Koifman, O.I. *Russ. J. Inorgan. Chem.* **2007**, *52*, 1215–1219.
- (11) Imamura, T.; Fukushima, K. *Coord. Chem. Rev.* **2000**, *198*, 133–156.
- (12) Wojaczyński, J.; Latos-Grazhynski, L. *Coord. Chem. Rev.* **2000**, *204*, 113–171.
- (13) Mamardashvili, G.M.; Mamardashvili, N.Zh.; Koifman, O.I. *Uspekhi Khimii* **2008**, *77*, 60–77; Mamardashvili, G.M.; Mamardashvili, N.Zh.; Koifman, O.I. *Russ. Chem. Rev.* **2008**, *77*, 59–76.
- (14) Kobuke, Y.; Miyaji, H. *J. Am. Chem. Soc.* **1994**, *116*, 4111–4112.
- (15) Stibrany, R.T.; Vasudevan, J.; Knapp, S.; Potenza, J.A.; Emge, T.; Schugar, H.J. *J. Am. Chem. Soc.* **1996**, *118*, 3980–3981.
- (16) (a) Hameurlaine, A.; Dehaen, W. *Tetrahedron Lett.* **2003**, *44*, 957–959. (b) McClenaghan, N.D.; Passalacqua, R.; Loiseau, F.; Campagna, S.; Verheyde, B.; Hameurlaine, A.; Dehaen, W. *J. Am. Chem. Soc.* **2003**, *125*, 5356–5365. (c) Loiseau, F.; Campagna, S.; Hameurlaine, A.; Dehaen, W. *J. Am. Chem. Soc.* **2005**, *127*, 11352–11363.
- (17) Morton, M.; Wenzel, C.W. *Chem. Rev.* **2008**, *108*, 2952–3015.
- (18) Meites, L. *Introduction to Chemical Equilibrium and Kinetics*; Pergamon: Oxford, 1981.
- (19) Bonar-Law, R.P.; Sanders, J.K.M. *J. Am. Chem. Soc.* **1995**, *117*, 259–271.