Synthesis and Spectroscopic Characterization of the New Sitting-atop Complexes from Reaction of Zirconyl Nitrate and Free Base *meso*-Tetraarylporphyrins in Mild Conditions

Hossein Dehghani[*] and Mohammad Reza Mansournia

Department of chemistry, Faculty of science, University of Kashan, Kashan 87317-51167, Iran
[*]E-mail: Dehghani@kashanu.ac.ir

A series of sitting-atop (SAT) complexes, $[(ZrO)H_2t(X)pp(NO_3)_2]$, have been prepared via the reactions of free base *meso*-tetraarylporphyrins, $H_2t(X)pp$, with zirconyl nitrate hydrate, $ZrO(NO_3)_2 \cdot xH_2O$. The products have been characterized by a variety of methods including ^{1}H NMR, ^{13}C NMR, IR and UV-Vis spectroscopies, elemental analysis and conductance measurements. The data indicate that the *meso*-tetraarylporphyrins coordinate with two pyrrolenine nitrogen atoms to the zirconyl cation located above the distorted porphyrin plane and two protons remain on the pyrrole nitrogens. Such half sandwich-type sitting-atop complexes may be considered as models for the initial steps of the metallation of the macrocycles.

Introduction

In recent years, the development of new strategies to improve the synthesis of functionalized porphyrins, metalloporphyrins and sandwich-type complexes of metal bisporphyrin and metal porphyrin-phthalocyanine have been widely studied due to their applications in various fields such as artificial photosynthesis, photodynamic therapy, molecular electronics, chemical sensors, electrocatalysts, DNA binding agents, electrochromism, thermochromism, optical discs, and magnetic materials.[1-10] In the metallation of porphyrins, depending on size, charge, and spin multiplicity of metal ions, they can fit into the center of the porphyrin ring, forming regular metalloporphyrins, or several of them are located out of the ligand plane, resulting in sitting-atop (SAT) complexes.[11] For the first time, these complexes were indicated as intermediate in the metallation processes of the protoporphyrin dimethyl ester in chloroform, in which two pyrrolenine nitrogens coordinate to the metal ion and two protons on the pyrrole nitrogens remain.[12] Deviating from the regular porphyrins, in the sitting-atop (SAT) complexes, the ligand plane is distorted and its symmetry lowered. This structure is characterized by special photophysical and photochemical features as well as offers the possibility for formation of bi and even trinuclear (bisporphyrin) complexes.[13] Interestingly, in the case of lanthanide ions as metal centers, double and triple decker porphyrin sandwich complexes were also synthesized and studied.[9,10,14]

In the previous study, we presented the formation of sitting-atop complexes from *meso*-tetraarylporphyrins and uranyl nitrate hexahydrate.[15] The high oxidation number of uranium and using of the suitable solvent (chloroform with very weak basicity) caused that we could be prepared the sitting-atop complexes as stable solids. We have synthesized and characterized new half sandwich-type sitting-atop complexes from *meso*-tetraarylporphyrins (Figure 1) and zirconyl as a smaller ion in mild conditions. The spectroscopic similarities between the produced complexes, the SAT complexes of uranyl[15] and molecular complexes of *meso*-tetraarylporphyrins with various acceptors[16-19] suggested a similar structure for the porphyrin core in all of the species. In these SAT complexes, one zirconyl is bonded to only two pyrrolenine nitrogens of the porphyrin and the pyrrole protons are not released.

Results and Discussion

The UV-Vis spectra of the studied *meso*-tetraarylporphyrins show five absorption bands, one soret band (416 - 420 nm) and four Q bands (515 - 653 nm), that upon the sitting-atop complexation with zirconyl nitrate are shifted to red and appear as two new bands at 441 - 453 and 655 - 687 nm, respectively (Table 1, Figure 2). These red shifts are similar to which were observed for uranyl SAT complexes[15] and molecular complexes of the porphyrins with various acceptors,[16-19] and indicate analogous porphyrin cores in all of them. This is related to π-resonance interaction of the aryl rings with the porphyrin core in the sitting-atop complexes.
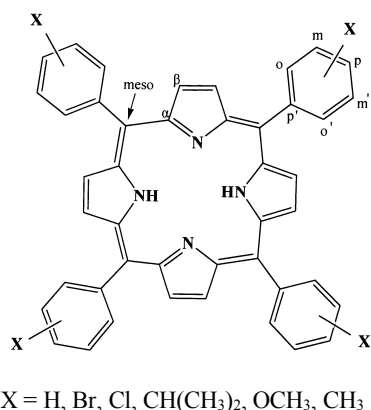

X = H, Br, Cl, CH(CH₃)₂, OCH₃, CH₃

**Figure 1.** *meso*-Tetraarylporphyrins ($H_2t(X)pp$).

Table 1. UV-Vis and ^{1}H NMR spectral results of the various *meso*-tetraarylporphyrins and the related sitting-atop complexes.

entry	*meso*-tetraarylporphyrin sitting-atop complex shifts	λmax(nm)		H_β	N–H
		Soret	Q-bands		
1	H₂tpp	416.7	516.8 , 551.5 , 592.0 , 648.0	8.85	-2.76
	[H₂tpp(ZrO)(NO₃)₂]	441.9	658.3	8.70	-0.43
	Δ	25.2	10.3	-0.15	2.33
2	H₂t(4-Br)pp	418.9	515.3 , 550.7 , 589.6 , 645.9	8.89	-2.82
	[H₂t(4-Br)pp(ZrO)(NO₃)₂]	445.4	658.3	8.65	-0.28
	Δ	26.5	12.4	-0.24	2.54
3	H₂t(4-Cl)pp	418.2	517.4 , 551.0 , 592.1 , 649.2	8.84	-2.75
	[H₂t(4-Cl)pp(ZrO)(NO₃)₂]	442.4	655.7	8.66	-0.28
	Δ	24.2	6.5	-0.18	2.47
4	H₂t(4-CH(CH₃)₂)pp	418.9	518.0 , 553.3 , 592.3 , 648.6	8.87	-2.74
	[H₂t(4-CH(CH₃)₂)pp(ZrO)(NO₃)₂]	447.1	668.5	8.64	-0.39
	Δ	28.2	21.9	-0.23	2.35
5	H₂t(3-OCH₃)pp	418.9	517.0 , 550.3 , 590.3 , 646.6	8.90	-2.75
	[H₂t(3-OCH₃)pp(ZrO)(NO₃)₂]	450.0	659.1	8.72	-0.72
	Δ	31.1	12.5	-0.18	2.03
6	H₂t(4-OCH₃)pp	419.5	520.5 , 557.1 , 596.0 , 653.0	8.86	-2.75
	[H₂t(4-OCH₃)pp(ZrO)(NO₃)₂]	452.6	686.8	8.55	-0.21
	Δ	33.1	33.8	-0.31	2.54
7	H₂t(3-CH₃)pp	418.2	517.5 , 550.6 , 590.0 , 647.2	8.88	-2.75
	[H₂t(3-CH₃)pp(ZrO)(NO₃)₂]	443.6	659.1	8.67	-0.49
	Δ	25.4	11.9	-0.21	2.26
8	H₂t(4-CH₃)pp	418.3	518.4 , 554.0 , 593.0 , 649.0	8.85	-2.77
	[H₂t(4-CH₃)pp(ZrO)(NO₃)₂]	452.6	686.8	8.63	-0.41
	Δ	34.3	37.8	-0.22	2.36

Δ: Shifts in the positions of absorption bands and β and NH protons of the *meso*-traarylporphyrins upon the sitting-atop compexation.

In the ^{1}H NMR spectra, the N−H and the β-protons for the *meso*-tetraarylporphyrins, H₂t(X)pp, are upfield (-2.74 to -2.82 ppm) and downfield (8.84 to 8.90 ppm), respectively. The formation of sitting-atop (SAT) complex of these porphyrins with zirconyl caused downfield shifts for the proton signals of N−H and aryl rings, and upfield shift of the β-hydrogens, Figure 3. These changes are similar to the observed shifts upon the SAT complexation of the *meso*-tetraarylporphyrins with uranyl and so the molecular complexation of them with various acceptors.[15-19] Therefore, the shifts of N−H and β-protons in the SAT complexes are because of the ring current difference between *meso*-teraarylporphyrins and their sitting-atop complexes with zirconyl. In the SAT complexes, the effect of ring current for the porphyrins is lost. This may be related to change of the 22π-electrons system of porphyrin
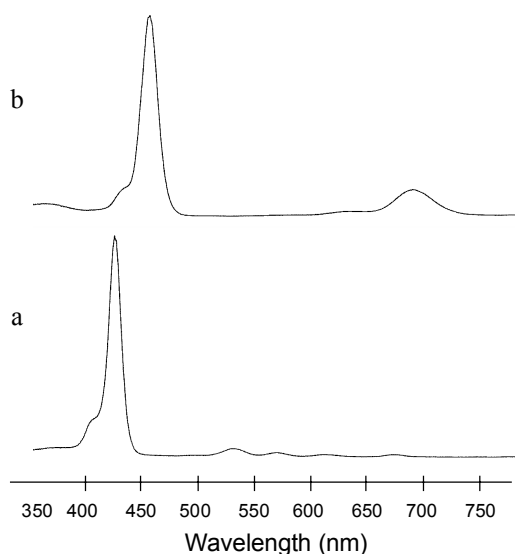
Figure 2. UV-Vis spectra (absorbance-wavelength) of (a) H₂tpp (b)[H₂tpp(ZrO)(NO₃)₂].
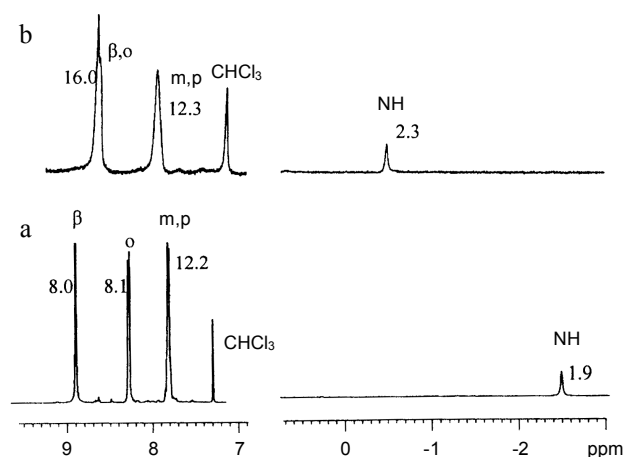
Figure 3. ^{1}H NMR spectra of (a) H₂tpp (b) [H₂tpp(ZrO)(NO₃)₂].

core to 18π-electrons in the sitting-atop complexes. Also, the downfield shifts of the aryl ring hydrogens for the complexes can be because of increasing the ring current of aryl rings and correlate to extension of the aryl π-system in the SAT complexes.[17]

^{13}C NMR spectrum of H$_2$tpp gives rise to six sharp signals (120.5 (C$_{meso}$), 127.1 (C$_{m,m'}$), 128.1 (C$_p$), 131.5 (C$_\beta$), 135.0 (C$_{o,o'}$), 142.6 (C$_{p'}$) ppm) and a very broad signal (145.0 ppm) for α-carbons, whereas the related SAT complex, [H$_2$tpp(ZrO) (NO$_3$)$_2$], shows seven signals at aromatic region, (123.1 (C$_{meso}$), 128.4 (C$_{m,m'}$), 128.8 (C$_p$), 130.1 (C$_\beta$), 138.8 (C$_{o,o'}$), 139.8 (C$_{p'}$), and 146.3 (C$_\alpha$) ppm), Figure 4. The sitting-atop complexes of the *meso*-tetraarylporphyrins with zirconyl nitrate sharpens the α-signals in the ^{13}C NMR spectra of the porphyrins and leads to small shifts in the other lines. These changes are quite similar to that happened in the molecular complexes of *meso*-tetraaryl-porphyrins with SbCl$_3$ and BiCl$_3$ acceptors.[16,17]

The spectral correspondences (UV-Vis, ^{1}H NMR and ^{13}C NMR) for [H$_2$t(X)pp(ZrO)(NO$_3$)$_2$] and [(UO$_2$)H$_2$t(X)pp](NO$_3$)$_2$ SAT complexes[17] and the molecular complexes of the *meso*-tetraarylporphyrins with the various acceptors,[16-19] suggest the similar structure of porphyrin core in all of them. In the proposed structure, the noncoplanar pyrrole rings tilted alternately up and down and the lone pairs of two pyrrolenine nitrogens acted as the electron donors to one zirconyl group in a side of the mean plane of the porphyrin, Figure 5.

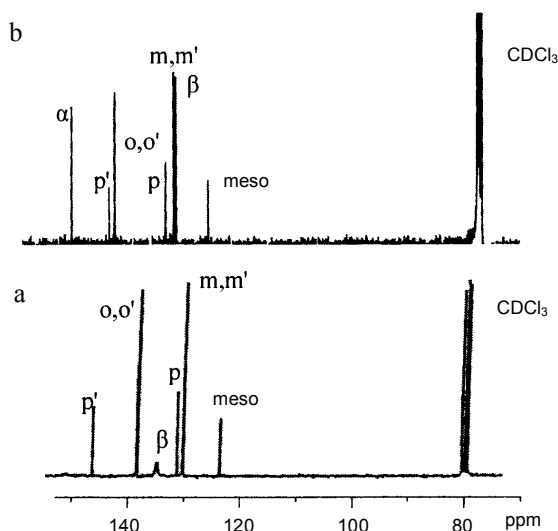In accordance with the occurred changes in the UV-Vis, ^{1}H

NMR and ^{13}C NMR spectra of the *meso*-tetraarylporphyrins on the reaction with zirconyl nitrate, more steric hindrance for *meta*-substituents of the aryl rings in the porphyrins than para-substituents decreases the electron donation of it. Further, the sitting-atop complexes contain *ortho*-substituted *meso*-tetraarylporphyrins were not produced in our reaction system. This is related to steric hindrance in these porphyrins.

In the infrared spectrum of ZrO(NO$_3$)$_2\cdot x$H$_2$O, the intense band at *ca.* 1384 cm^{-1} is attributed to ionic NO$_3^-$, whereas the related SAT complexes with the porphyrins show two additional bands at *ca.* 1280 and 1480 cm^{-1}, suggesting the coordination of the nitrate groups to the zirconyl center.[20,21] Furthermore, the FT-IR spectra show a N−H stretching band at *ca.* 3320 cm^{-1} (without intramolecular or intermolecular hydrogen bonding) for free base porphyrins,[22] that upon the complexation with zirconyl nitrate does not change. On the other hand, conductivity measurements showed that the sitting-atop complexes behaved as electrolytes in methanol and nonelectrolytes in acetonitrile. This indicates that the complexes were dissociated to the nitrates and zirconyl-porphyrin cation in methanol but remained neutral and undissociated in acetonitrile.[23] This is in accordance with the results obtained from the IR studies and proposed formula. Therefore, according to spectroscopic, conductometric and elemental analysis data, the sitting-atop complexation occurred in our reaction system.

Conclusion

The sitting-atop (SAT) complexes can be produced in the metallation process of porphyrins. Deviating from the regular metalloporphyrins, depending on size, charge, and spin multiplicity of metal ions, the metal centers are located out of the ligand plane, distorting it and causing lower symmetry. We have successfully performed the sitting-atop complexation between zirconyl and *meso*-tetraarylporphyrins by grinding in a small amount of methanol at ambient temperature. These mild conditions are caused that the reaction do not progress until the metallation of porphyin and stopped in the intermediate step, in which two pyrrolenine nitrogens coordinate to the metal ion and two protons on the pyrrole nitrogens still remain.

Figure 4. ^{13}C NMR spectra of (a) H$_2$tpp (b) [H$_2$tpp(ZrO)(NO$_3$)$_2$].
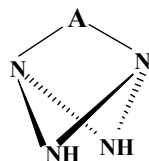

Figure 5. The tetrahedrally tilted pyrrolenine nitrogens of a porphyrin core: two nitrogen atoms of pyrrolenine in one side of the porphyrin plane act as the electron donors to the acceptor (A=ZrO(NO$_3$)$_2$).

Experimental

Benzaldehydes and zirconyl nitrate hydrate, ZrO(NO$_3$)$_2\cdot$xH$_2$O (x is 32% determined gravimetrically), were commercial products obtained from Merck and Fluka, respectively, and were used without further purifications. Pyrrole was purchased from Merck and distilled. Chloroform (Merck) was dried over anhydrous calcium chloride for 3 days and distilled before use. Other solvents that were employed for the synthesis of the porphyrins and sitting-atop complexes were obtained from Merck and were used as received. *meso*-Tetra-phenylporphyrin and its substituted derivatives were prepared and purified by usual methods.[24]

The electronic absorption spectra were obtained in chloroform by an ATI UNICAM-UV\Vis Vision SOFTWARE V-2011 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded

on a Bruker 400 MHz spectrometer in $CDCl_3$. The residual $CHCl_3$ in the conventional 99.8% atom $CDCl_3$ gives a signal at δ = 7.26 ppm, which was used for calibration of the chemical shift scale. The FT-IR spectra were recorded on a Magna 550 Nicolet spectrometer using KBr pellets in the range of 400 - 4000 cm^{-1}. Molar conductivity data of freshly prepared 1×10^{-3} mol/dm^3 solutions in methanol and acetonitrile were measured at room temperature by a METROHM 644 conductometer.

In a typical reaction, 0.4 mmole *meso*-tetraarylporphyrin (presented in Figure 1) and 0.5 mmole $ZrO(NO_3)_2 \cdot xH_2O$ (0.170 g, 25% excess) grinded in a mortar at ambient temperature, with dropwise adding of 1 mL methanol during 20 - 30 minutes, until complexation was complete, that was determined by the disappearance of the Soret band of the related porphyrin in the UV-Vis spectra. The methanol was evaporated and the produced solid dissolved in chloroform and filtered for removing of the unreacted zirconyl nitrate from the SAT complex (zirconyl nitrate is insoluble in chloroform). After the evaporation of the filtrate and drying under vacuum at 60 ^{o}C for 12 h, the sitting-atop complex was obtained as a green solid and was identified by elemental analysis, molar conductivity and spectroscopic data.

[H$_2$tpp(ZrO)(NO$_3$)$_2$]: Found: C, 62.25; H, 3.39; N, 10.06 %. Anal. Calc. for $C_{44}H_{30}N_6O_7Zr$: C, 62.47; H, 3.57; N, 9.93 %. ^{1}H NMR (CDCl$_3$): δ 8.70 (s, 8H, β), δ 8.66 (d, 8H, o, o′), δ 8.03 (m, 8H, m, m′), δ 8.03 (m, 4H, p), δ -0.43 (s, 2H, NH).

[H$_2$t(4-Br)pp(ZrO)(NO$_3$)$_2$]: Found: C, 45.29; H, 2.42; N, 7.45%. Anal. Calc. for $C_{44}H_{26}Br_4N_6O_7Zr$: C, 45.50; H, 2.26; N, 7.23%. ^{1}H NMR (CDCl$_3$): δ 8.65 (s, 8H, β), δ 8.45 (d, 8H, o, o′), δ 7.69 (d, 8H, m, m′), δ -0.28 (s, 2H, NH).

[H$_2$t(4-Cl)pp(ZrO)(NO$_3$)$_2$]: Found: C, 53.49; H, 2.45; N, 8.68%. Anal. Calc. for $C_{44}H_{26}Cl_4N_6O_7Zr$: C, 53.72; H, 2.66; N, 8.54%. ^{1}H NMR (CDCl$_3$): δ 8.66 (s, 8H, β), δ 8.55 (d, 8H, o, o′), δ 8.02 (d, 8H, m, m′), δ -0.28 (s, 2H, NH).

[H$_2$t(4-CH(CH$_3$)$_2$)pp(ZrO)(NO$_3$)$_2$]: Found: C, 66.06; H, 5.18; N, 8.53%. Anal. Calc. for $C_{56}H_{54}N_6O_7Zr$: C, 66.31; H, 5.37; N, 8.29%. ^{1}H NMR (CDCl$_3$): δ 8.64 (s, 8H, β), δ 8.57 (d, 8H, o, o′), δ 7.88 (d, 8H, m, m′), δ -0.39 (s, 2H, NH).

[H$_2$t(3-OCH$_3$)pp(ZrO)(NO$_3$)$_2$]: Found: C, 59.42; H, 4.13; N, 8.59%. Anal. Calc. for $C_{48}H_{38}N_6O_{11}Zr$: C, 59.68; H, 3.96; N, 8.70%. ^{1}H NMR (CDCl$_3$): δ 8.72 (s, 8H, β), δ 8.16 (s, 4H, o), δ 8.16 (d, 4H, o′), δ 7.90 (t, 4H, m), δ 7.52 (d, 4H, p), δ 4.16 (s, 12H, OCH$_3$), δ -0.72 (s, 2H, NH).

[H$_2$t(4-OCH$_3$)pp(ZrO)(NO$_3$)$_2$]: Found: C, 59.45; H, 3.81; N, 8.83%. Anal. Calc. for $C_{48}H_{38}N_6O_{11}Zr$: C, 59.68; H, 3.96; N, 8.70%. ^{1}H NMR (CDCl$_3$): δ 8.55 (s, 8H, β), δ 8.13 (d, 8H, o, o′), δ 7.53 (d, 8H, m, m′), δ 4.17 (s, 12H, OCH$_3$), δ -0.21 (s, 2H, NH).

[H$_2$t(3-CH$_3$)pp(ZrO)(NO$_3$)$_2$]: Found: C, 64.18; H, 4.11; N, 9.13%. Anal. Calc. for $C_{48}H_{38}N_6O_7Zr$: C, 63.91; H, 4.25; N, 9.32%. ^{1}H NMR (CDCl$_3$): δ 8.67 (s, 8H, β), δ 8.44 (s, 4H, o),

δ 8.44 (d, 4H, o′), δ 7.90 (t, 4H, m), δ 7.78 (d, 4H, p), δ 2.82 (s, 12H, CH$_3$), δ -0.49 (s, 2H, NH).

[H$_2$t(4-CH$_3$)pp(ZrO)(NO$_3$)$_2$]: Found: C, 63.69; H, 4.42; N, 9.59%. Anal. Calc. for $C_{48}H_{38}N_6O_7Zr$: C, 63.91; H, 4.25; N, 9.32%. ^{1}H NMR (CDCl$_3$): δ 8.63 (s, 8H, β), δ 8.52 (d, 8H, o, o′), δ 7.82 (d, 8H, m, m′), δ 2.79 (s, 12H, CH$_3$), δ -0.41 (s, 2H, NH).

References

1. Burrell, A. K.; Wasielewski, M. R. J. *J. Porph. Phthal.* **2000**, *4*, 401.
2. Pushpan, S. K.; Venkatraman, S.; Anand, V. G.; Sankar, J.; Parmeswaran, D.; Ganesan, S.; Chandrashekar, T. K. *Curr. Med. Chem.* **2002**, *2*, 187.
3. Li, Q.; Surthi, S.; Mathur, G.; Gowda, S.; Zhao, Q.; Sorenson, T. A.; Tenent, R. C.; Muthukumaran, K.; Lindsey, J. S.; Misra, V. *Appl. Phys. Lett.* **2004**, *85*, 1829.
4. Screen, T. E. O.; Blake, I. M.; Rees, L. H.; Clegg, W.; Borwick, S. J.; Anderson, H. L. *J. Chem. Soc. Perkin Trans. 1* **2002**, 320.
5. Awawdeh, M. A.; Legako, J. A.; Harmon, H. J. *Sensor Actuator B* **2003**, *91*, 27.
6. Araki, K.; Winnischofer, H.; Herbert, H. E. B.; Toyama, M. M.; Engelmann, F. M.; Llldemar, F.; Andre, A. L. B.; Toma, H. E. *J. Electroanal. Chem.* **2004**, *562*, 145.
7. Song, R.; Kim, Y.-S.; Sohn, Y. S. *J. Inorg. Biochem.* **2002**, *89*, 83.
8. Narra, M.; Elliott, P.; Swavey, S. *Inorg. Chim. Acta* **2006**, *359*, 2256.
9. Jiang, J.; Bao, M.; Rintoul, L.; Arnold, D. P. *Coord. Chem. Rev.* **2006**, *250*, 424.
10. Liu, Z.; Yasseri, A. A.; Lindsey, J. S.; Bocian, D. F. *Science* **2003**, *302*, 154.
11. Horvath, O.; Huszank, R.; Valicsek, Z.; Lendvay, G. *Coord. Chem. Rev.* **2006**, *250*, 1792.
12. Fleischer, E. B.; Wang, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 498
13. Hudson, M. F.; Smith, K. M. *Chem. Commun.* **1973**, 515.
14. Wittmer, L. L.; Holten, D. *J. Phys. Chem.* **1996**, *100*, 860.
15. Dehghani, H.; Mansournia, M. R. *Polyhedron* **2008**, *27*, 849.
16. Dehghani, H.; Ansari Sardrood, A. R. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 518.
17. Dehghani, H.; Ansari Sardrood, A. R. *Polyhedron* **2007**, *26*, 4263.
18. Dehghani, H.; Fathi, F. *Dyes and Pigments* **2008**, *77*, 323.
19. Dehghani, H.; Fathi, F. *J. Porph. Phthal.* **2007**, *11*, 849.
20. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Fifth ed.; John Wiley and Sons Inc.: New York, 1997; Part B.
21. Wyllie, G. R. A.; Munro, O. Q.; Schulz, C. E.; Scheidt, W. R. *Polyhedron* **2007**, *26*, 4664.
22. Limbach, H. H.; Hennig, J.; Stulz, J. *J. Chem. Phys.* **1983**, *78*, 5432.
23. Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
24. Gonsalves, A. M. D. A. R.; Varejao, J. M. T. B.; Pereira, M. M. *J. Heterocycl. Chem.* **1991**, *28*, 635.