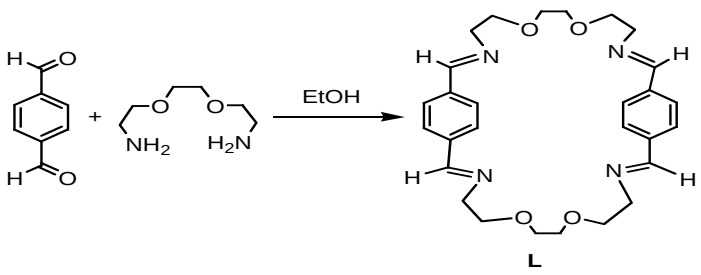
Synthesis, Complexation and Antifungal, Antibacterial Activity Studies of a New Macrocyclic Schiff Base

H. Ibrahim Ugras*, Ismet Basaran, Turgut Kilic, Umit Cakir

Balıkesir University, Faculty of Science and Arts, Department of Chemistry, 10145, Balıkesir, Turkey

Received December 13, 2005



Scheme 1. Synthesis of New Macrocyclic Ligand **L**

A new macrocyclic ligand, **L** was synthesized using the high dilution condition with condensation of triethylene glycol diamine and terephtalaldehyde in ethanol. The obtained product, **L** was identified by FT-IR, ^{1}H-NMR, ^{13}C-NMR and Mass spectroscopy. The extraction equilibrium constants were estimated using dichloromethane/water membranes transfer with ICP-AES and AES spectroscopy. Biological studies of this compound was determinated with disc diffusion method. The biological activity results showed that the synthesized ligand **L** has high activity against the studied microorganisms and high complexation ability against the Fe^{2+} cation.

J. Heterocyclic Chem., **43**, 1679 (2006).

Introduction.

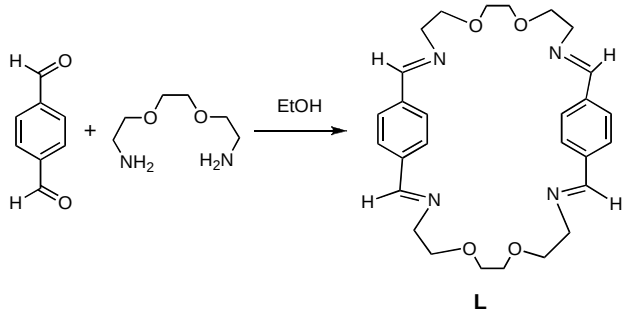
The synthesis of macrocyclic ligands as synthetic receptors for organic or inorganic cations, anions or neutral molecules has been attracting increasing interest in a number of areas in chemistry as well as biochemistry [1-4]. Interest in multidentate macrocyclic compounds is increasing continuously because of their unique properties and use in the synthesis of polynuclear metal complexes. The aza-crown ethers have complexation properties that are intermediate between those of the all-oxygen crowns, which strongly complex alkali and alkaline earth metal ions, and those of the all-nitrogen cyclams, which strongly complex heavy metal cations. These mixed complexation properties make the aza-crowns interesting to researchers in many areas [5-7]. Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most transition metals [8-9]. They are also important in diverse field's chemistry owing to their biological activities [10-16]. There has been a remarkable interest in the synthesis and study of aza-oxomacrocyclic ligand complexes with transition metal cations [17-24].

In many Schiff base macrocyclization process, reaction products were easily obtained in high yields with using metal template [25-33]. But it is often difficult to choose the correct template metal ion for obtaining desired compound and after this step that contain template effect, removing of the template ion have been difficult in some cases [25,26,34,35].

Macrocyclic Schiff bases can be formed without metal templates [25,36-42]. Nontemplate macrocyclic Schiff base synthesis process requires the use of rigid starting carbonyl groups and high dilution conditions. This process is very efficient and the metal-free product can be obtained in excellent yield [43-50].

In the present work, a new type macrocyclic ligand, 1,8,17,24-tetraaza-11,14,27,30-tetraoxa-3,4,5,6;19,20,21,22-dibenzo–1,7,17,23-cyclodotricontatetraene, $C_{28}H_{36}N_4O_4$ (**L**), was synthesized by the high dilution condensation of diamino compound (triethylene glycol diamine) with dicarbonyl compound (terephtalaldehyde) in ethanol (Scheme I).

Scheme I

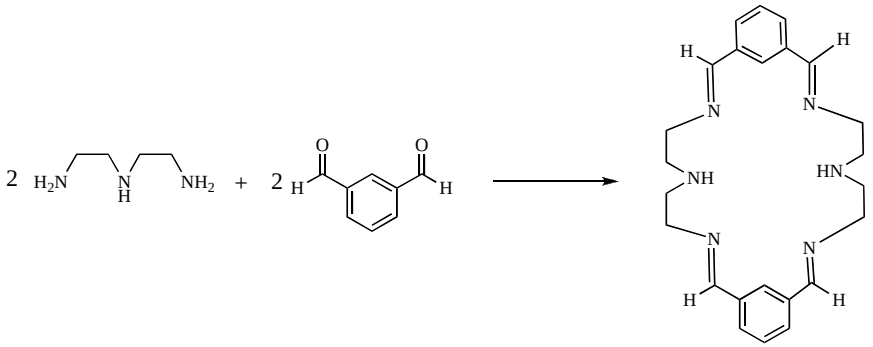


Results and Discussion.

The problem for synthesis of macrocyclic Schiff bases is the reversibility due to the presence of imine in the reaction media. If the metal cation resulting in template effect is not used, the high dilution technique at the high temperature should increase the product yield. There are many diareno azacrown ether synthesis which consist of 2:2 condensation ratios, were achived in high yields by using Schiff base reaction and high dilution technique [32,34,36-50]. Lehn and Jazwinski have reported macrocyclic Schiff bases using nontemplate method [44]. Izatt *et al*. have reported new types of Schiff bases prepared by a nontemplate condensation of 1,10-phenanthroline-2,9-dicarbaldehyde with diamino compounds [32].

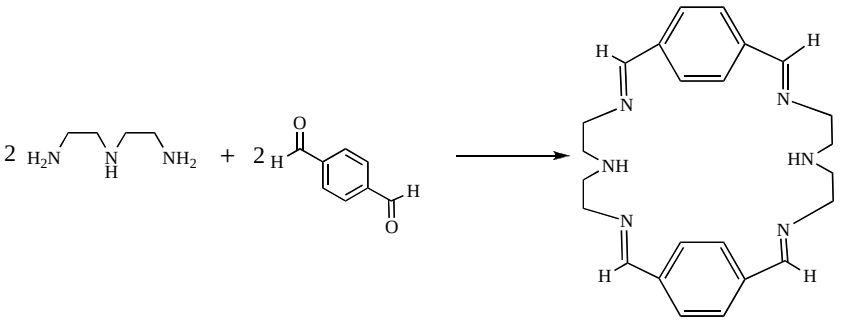
Menif and co-workers have synthesized a series of azacrown ethers using same method with isophtalaldehyde and diethylenetriamine (Scheme II) [48-50].

Scheme II



The same compounds were prepared by Habibi and Izadkhah using terephtalaldehyde and diethylene triamine in high dilution conditions (Scheme III) [47].

Scheme III



This synthetic method was employed in this research for the condensation terephtalaldehyde with triethylene glycol diamine to produce, in a single step the macrocyclic Schiff base **L** in high yield. Our ligand, **L** was synthesized using high dilution conditions in order to inhibit the relevant polymer formation. This is an exceptionaly high yield for a dipodal (2:2) reaction for cyclic Schiff base condensations. As a rationalization of why cyclic condensation predominates so strongly over the normaly excepted linear condensation to produce polymeric Schiff bases, it is suggested that the cyclic product is thermodynamically preferred over the polymer and that the long period of time allowed for the reaction makes possible the redistribution of Schiff base species from the oligomers (which may be kinetically favored) to the more thermodynamically stable cyclic Schiff bases [50].

Hence, the facile synthesis of a new macrocyclic Schiff base as a stable solid were achieved successfully with high yield.

The antifungal, antibacterial activity and complexation properties of this macrocyclic ligand was studied using disc diffusion method and ICP-AES, AES measurements. The cation-complexing ability of the macrocyclic Schiff base under experimental conditions showed that very high selectivity was observed between ligand **L** and Fe^{2+} cation with all studied cations. The antifungal and antibacterial activity results expressed that the synthesized ligand **L** has high activity against the studied microorganisms. The **L** and its derivatives could be used a potential antifungal agent.

Synthesis of Macrocycles.

Template effects are widely applied on synthesises of macrocycle Schiff bases and give good results [25-33]. However, as described at the start of paper, difficulties of finding suitable metals for the macrocycle and removing metals from the macrocycles were encountered in some cases [25,26,34,35]. Hence, transmetallation processes are used to prepare the desired macrocycles in these cases [51]. We didn't use template effect in this study, so we choose the high dilution method. To synthesize the macrocyclic ligand, the method of macrocyclization consisting in the reaction of diamino with dicarbonyl compound was chosen. Macrocyclic ligand was synthesized by the high dilution one-to-one [2:2] condensation of diamino compound with dicarbonyl compound in ethanol. The synthesis of macrocyclic Schiff bases using metal-free condensations of primary or diamines with dialdehydes were first published by Tasker *et al* [52] and Fenton *et al* [53]. This method has also been studied in literature [25-50]. The yields are high for the condensation reactions.

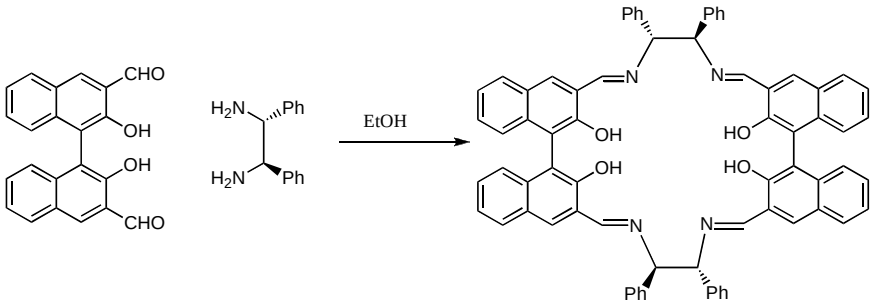
Jazwinski [44] method has been widely used in many studies. Each reactant (dialdehyde and diamine) are dropped into acetonitrile over a time period of 24-28 hours according to this method. On the contrary, Izatt and Bradshaw achieved this reaction in methanol at 16 hours [32]. The other macrocyclization reaction in THF and acetonitrile were done by Habibi between 24 and 48 hours time periods (Scheme II) [47]. Martel performed the cyclization reaction in acetonitrile-methanol in 12 hours [50]. However, Brunner and Schiessling prepared macrocycles having optical activity with high yield at reflux temperature in ethanol (Scheme IV) [37,42]

On the other hand, Chandra and Gupta synthesized macrocycle compounds starting from 2,3-hexanedione and *m*-phenylenediamine with HCl catalysis with refluxing in ethanol (Scheme V) [39].

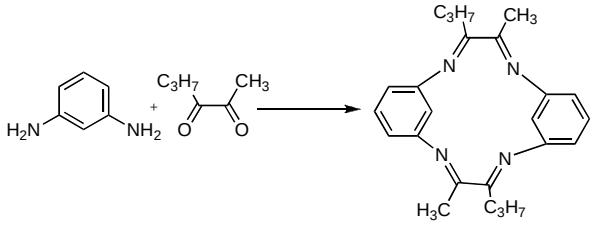
Hence, we prepared the macrocyclic compound, **L** by adding ethanol solutions of dialdehyde and daimine dropwise into ethanol after which the reaction media was refluxed for 25 hours. The yield of reaction (79%) is almost same as that of high dilution reaction given in the literature Bradshaw *et al*. 56-71%; Lehn *et al*. 65-85%; Llobet *et al*. 66%; Habibi *et al*. 70-75%; Gupta and Chandra 68%).

IR spectroscopy shows a band corresponding to C=N at 1570 cm^{-1} and does not show a band corresponding to C=O. Peaks at 7.6 ppm (s, 8H) and 8.2 ppm (s, 4H) in the ^{1}H-NMR verify the formation of a symmetrical imine macrocycle. Specific C-O-C etheric peaks were observed at 1220 cm^{-1} in the IR spectrum and resonances at 3.1 ppm (t, 8H), 3.6 ppm (t, 8H), 3.7 ppm (t, 8H) in ^{1}H-NMR. Also, the peak at m/z 493 in the mass spectrum clearly indicates the (2+2) addition. (1+1) Addition does not occur because of the high dilution method and the dropwise addition of the reagents. The ^{13}C-NMR results are consistent with the ^{1}H-NMR results.

Scheme IV



Scheme V



Complexation Studies.

We studied in the present work with a common formalism of equations (1-3), K_{ex} is extraction equilibrium constant; $[M^{+m}]$ and $[MLA_m]$ are the concentrations of metal cation in aqueous phase and organic phase, respectively. $K_{D,L}$ denotes a distribution constant of ligand between organic solvent and water [54-56]. Extraction values, complexation and distribution constants of synthesized ligand **L** are collected in Table 1.

$M^{+m}_{(aq)} + L_{(org)} + mA^-_{(aq)} \rightleftharpoons^{K_{ex}} (MLA_m)_{(org)}$	Eq.1
$K_{ex} = \dfrac{[MLA_m]_{(org)}}{[M^{+m}]_{(aq)}[L]_{(org)}[A^-]^m_{(aq)}}$	Eq.2
$K_{D,L} = [L]_{(org)} / [L]_{(w)}$	Eq.3

Table 1

$K_{D,L}$, % Ext and Log K_{ex} values for extraction of **L** ligand in CH_2Cl_2 with Ca^{2+}, Mg^{2+}, Fe^{2+}, Pb^{2+}, K^+ and Na^+ ions at 25 ± 0.1 °C($^\theta$).

Ligand	Value	Cations					
		Ca^{2+}	Mg^{2+}	Fe^{2+}	Pb^{2+}	K^+	Na^+
L	$K_{D,L}$	0.03	0.23	>100.00	3.92	0.57	$9.3x10^{-3}$
	% Ext	3.32	18.48	100.00	79.67	36.38	0.92
	Log K_{ex}	5.36	6.33	>20.00	8.77	6.95	4.77

($^\theta$) Corr.Coefficient 0.999

There are different complexations that have occured between our ligand and alkaline, transition metals. The complexation of Fe^{2+} ion with **L** compound, which contains oxygen and nitrogen atom was 100 %.

Determination of Minimum Inhibitory Concentration (MIC).

A broth microdilution susceptibility assay was performed using NCCLS methods for the determination of the MIC (NCCLS, 2000). All tests were performed in Mueller Hinton broth (MHB, Oxoid) but the test for yeast was performed in Sabouraud dextrose broth (SDB, Oxoid). Bacterial strains were cultured overnight at 37°C in MHB and the yeast was cultured overnight at 30°C in SDB. Geometric dilutions ranging from 60 mg/ml to 0.47 mg/ml of the compounds with dichloromethane (CH_2Cl_2), were prepared in a 96-well microlitre plate, volume being 20 µl. Then 160 µl of MHB and the same amount of SDB for the yeast were added onto microplates. Finally, 20 µl of 10^6 colony forming units (cfu/ml) (according to Mc Farland turbidity standards) of standardized microorganism suspensions were inoculated onto microplates and the test was performed in a volume of 200 µl. Plates were incubated at 37°C for 24 h for bacteria and at 30°C for 48 h for the yeast. The same tests were performed simultaneously for growth control (MHB + CH_2Cl_2+ test organisms) and sterility control (MHB + CH_2Cl_2 + test compounds). Gentamycine and flucanozole were used as reference compounds for antibacterial and antifungal activity assays. The MIC was calculated as the highest dilution showing complete inhibition of the tested strain [57,58]. The biological activity results of **L** are displayed in Table 2.

Table 2
Antibacterial and antifungal activities of **L***.

Microorganisms	L (mg/ml)	Gentamycine (μg/ml)	Fluconazole (μg/ml)
E.coli ATCC 29998	0.94	0.97	nt
S. epidermidis ATCC 12228	0.94	7.80	nt
B.subtilis ATCC 6633	0.94	0.97	nt
S. aureus 6538 P	0.94	0.48	nt
S. typhimirum CCM 583	1.88	0.48	nt
K.pneumonia CCM 2318	0.94	0.48	nt
P. aeruginosa ATCC 27853	0.94	0.97	nt
E. feacalis ATCC 29212	0.94	3.10	nt
C. albicans ATCC 10239	<0.029	nt	15.60

*Gentamycine and flucanozole were used as positive controls. nt: not tested

There is an interesting result that synthesized oxo-azamacrocyclic ligand **L** showed moderate activity against *E.coli S. Epidermidis, B.subtilis, S. Aureu, S. Typhimirum, K.pneumonia, P. aeruginosa* and *E. feacalis* and the compound showed high antifungal activity against *C. albicans* with a 29 μg/ml MIC value (The MIC value of Flucanozole is 15.6 μg/ml, Table 2). Our ligand has high activity aganist the studied microorganisms

EXPERIMENTAL

General.

The starting chemicals were purchased from Aldrich or Merck unless otherwise cited. $Ca(NO_3)_2$, KNO_3, $Mg(NO_3)_2$, $Zn(NO_3)_2$, $NaNO_3$, $FeSO_4$, $Pb(NO_3)_2$ are analytical grade reagents from Fluka dried over P_2O_5 for 48 h at 0.1 torr. The CH_2Cl_2 used was of analytical reagent grade. FT-IR spectrum has been taken as a KBr pellet using a Perkin Elmer Spectrum spectrometer, model BX-II, High resolution EI mass spectrum has been obtained with Agilent 1100 LC/MSD, NMR spectrum has been obtained with a Bruker-Specrospin Avance DPX-400 Ultra-Shield ^{1}H: 400MHz ^{13}C: 100 MHz. CPX and TMS was the initial standard. The melting point reported is uncorrected.

The concentrations of metal ions in the aqueous phases have been determined spectroscopically: ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy : Perkin Elmer Optima 3100 XL) and AES (Atomic Emission Spectroscopy : Unicam 929 AA Spectrometer).

1,8,17,24-Tetraaza-11,14,27,30-tetraoxa-3,4,5,6;19,20,21,22-dibenzo-1,7,17,23-cyclodotricontatetraene (**L**).

Terephtalaldehyde, (7.5 mmol) in ethanol (75 ml) and triethylene glycol diamine, (7.5 mmol) in ethanol (75 ml) were added dropwise over 1 hour to ethanol (500 ml). After addition, mixture was refluxed for 24 h. A part of ethanol (about 500 ml) was evaporated. After cooling, the solution was filtered, dried at room temparature and recrystalized from ethanol. Yellow solid, mp 105-106°. Yield: 79%; ir (potassium bromide): 2935 (C-H), 2770 (C-H), 1570 (C=N), 1455 (Ar), 1220 (C-O-C) cm^{-1}; ^{1}H-nmr: δ ($CDCl_3$, 400 MHz) 3.1 (t, 8H, N-CH_2), 3.6 (t, 8H, N-CH_2-CH_2-O), 3.7 (t, 8H, O-CH_2-CH_2- O), 7.6 (s, 8H, Ar-*H*), 8.2 (s, 4H, *H*-C=N); ^{13}C-nmr: δ ($CDCl_3$, 100 MHz) δ 162 (*C*=N), 138 (C_{Ar}-C=N), 128(Ar*C*), 71 (O-*C*H_2), 61 (*C*H_2-CH_2-N), 55 (CH_2-*C*H_2-N); ms: m/z : M^+ :493 ($M+1^+$, 80%)

Anal. Calcd. for $C_{28}H_{36}N_4O_4$: C, 68.27; H, 7.37; N, 11.37; O, 12.99. Found: C, 68.23; H, 7.35; N, 1141; O, 13.01.

Extraction Procedure.

The extraction measurements were done in 100 ml glass thermostated cell compartment with a mechanical stirrer where a 25 ml solution of an aqueous salt ($4x10^{-4}$ *M*) and ligand in CH_2Cl_2 organic solvent in appropriate concentration were placed and stirred for 120 min at 25±0.1°C and subsequently allowed to stand for 60 min to complete the phase separation. The optimum concentrations of the ligands were determined by extracting the alkali salts with 10 ml of various concentrations of the ligands ($4x10^{-4}$ *M*).

After extraction, the Ca^{2+}, Mg^{2+}, Zn^{2+}, Fe^{2+}, Pb^{2+} concentrations in the aqueous phase were determined using ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy) and Na^+, K^+ concentration in the aqueous phase was determined using AES (Atomic Emission Spectroscopy). Each value was the average of three subsequent measurements. Complexation and distribution constants are summarized in Table 1.

Biological Activity: Disc Diffusion Method.

The compounds **L** was tested against standard bacterial strains; *E. coli* ATCC 29998, *S. epidermidis* ATCC 12228, *B. subtilis* ATCC 6633, *S. aureus* 6538 P, *S. typhimirum* CCM 583, *K. pneumonia* CCM 2318, *P. aeruginosa* ATCC 27853, *E. feacalis* ATCC 29212 and a fungi *C. albicans* ATCC 10239. Disc diffusion method was applied for the determination of antimicrobial activities of the samples (NCCLS, 2000). Extracts were dissolved in dichloromethane (CH_2Cl_2), then filter-sterilized using a 0.20 μm membrane filter. A suspension of the tested microorganism (0.1 ml of 10^8 cells/ml) was spread over the surface of agar plates (MHA and SDA). Filter papers having a diameter of 6 mm, soaked with 10 μl of extract samples and 8 μl of essential oils were placed on the inoculated agar plates. Before incubation all petri dishes were kept in the refrigerator (4 ºC) for 2 hours. Then they were incubated at 37 ºC for 24 h for bacteria and at 30 ºC for 48 h for the yeasts. The diameters of the inhibition zones were measured in millimeters 50.

Acknowledgement.

The authors thanks to The Scientific and Technical Research Council of Turkey (TUBITAK) for the financial support (TBAG-AY311) and thanks to Assoc. Prof. Dr. Ahmet Ceyhan GOREN for his contribute.

REFERENCES

* Corresponding author: Tel: +90-266-6121278; Fax: +90-266-6121215; *E-mail address*: hugras@balikesir.edu.tr (H.I. Ugras).

[1] C. J. Pedersen, *J. Am. Chem. Soc*., **89**, 7017 (1967).
[2] J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.
[3] J. M. Lehn, *Science*, **227**, 849 (1985).
[4] J. M. Lehn, P. Vierling, *Tetrahedron Lett*., **21**, 1323 (1980).
[5] J. K. Nag, S. Pal, C. Sinha, *Trans. Met. Chem.* **26**, 237 (2001).
[6] R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christiensen, D. Sen, *Chem. Rev*., **85**, 271 (1985).
[7] T. Lorenzo, A. J. Blake, A. Bencini, B. Valtancoli, C. Wilson, M. Schröder,. *Inorganica Chimica Acta*, **337**, 59 (2002)
[8] D. E. Fenton, P. A. Vigato, *Chem. Soc. Rev*., **17**, 69 (1988).
[9] C. Jayabalakrishnan, R. Karvembu, K. Natarajan, *Trans. Met. Chem*., **27**, 790 (2002).
[10] R. Lozier, R. A. Bogomolni, W. Stoekenius, *J. Biophys*., **15**, 955 (1975).
[11] A. D. Garnovskii, A. L. Nivorozkhin, V. I. Minkin, *Coord. Chem. Rev*., **126**, 1 (1993).
[12] J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, G. Mena, *Coord. Chem. Rev*., **119**, 67 (1992).
[13] C. T. Walsh, W. H. Orme-Johnson, *Biochemistry*, **26**, 4901 (1987).
[14] S. K. Chattopadhyay, S. Ghosh, *Inorg. Chim. Acta*, **15**, 131 (1987).
[15] S. K. Chattopadhyay, S. Ghosh, *Inorg. Chim. Acta*, **163**, 245 (1989).
[16] F. Bregant, S. Pacor, S. Ghosh, S. K. Chattopadhyay, G. Sava, *Anti Cancer Res*., **13**, 1007 (1993).
[17] K. E. Bradshaw, J. S. Bradshaw, D. J. Zamecka-Krakowiak, *Chem. Rev*., **89**, 929 (1989).
[18] D. Kong, J. Reibenspies, J. Mao, A. Clearfield, A. E. Martell, *Inorg. Chim. Acta*, **342**, 158 (2003).
[19] D. Kong, J. Mao, A. E. Martell, A. Clearfield, *Inorg. Chim. Acta*, **342**, 260 (2003).
[20] D. Kong, J. Mao, A. E. Martell, A. Clearfield, *Inorg. Chim. Acta*, **335**, 7 (2002).
[21] Y. Sun, Q. Zeng, S. Gou, W. Huang, C. Duan, J. Yao, *J. Incl. Phen*., **42**, 131 (2002).
[22] Y. V. Korovin, R. N. Lozitskaya, L. V. Rusakova, *Rus.J. Gen. Chem*., **73**, 1641 (2003).
[23] C. Lodeiro, R. Bastida, E. Bertolo, A. Macias, A. Rodriguez, *Trans. Met. Chem*., **28**, 388 (2003).
[24] G. Das, P. Tripathi, A. Tripathi and P. K. Bharadwaj, *Tetrahedron*, **56**, 1501 (2000).
[25] A. J. Blake, D. M. J. Doble, W. -S. Li, M. Schröder, *J. Chem. Soc. Dalton Trans.,* 3655 (1997).
[26] L. Tei, G. Baum., A. J. Blake, D. Feuske, M. Schroder, *J. Chem. Soc. Dalton Trans*., 2793 (2000).
[27] D. M. J. Doble, C. H. Benison, A. J. Blake, D. Fenske, M.S. Jackson, R.D. Kay, W-S. Li, M. Schröder*, Angew. Chem. Int. Ed*. **38**, 1915 (1999).
[28] A. J. Atkins, A. J. Blake, M. Schröder, *J. Chem. Soc. Chem. Commun*,. 1662 (1993).
[29] V. B. Arion, V. C. Kravtsov, J. I. Gradinaru, Y. A. Simonov, N. V.Gerbeleu, J. Lipkowski, J.-P. Wignacourt, H. Vezin, O. Mentre, *Inorg. Chim. Acta,* **328**, 123 (2002).
[30] S. Broker, *Coord. Chem. Rev*., **222**, 33 (2001)
[31] S. Broker, *Eur. J. Inorg. Chem*., 2535 (2002).
[32] K. E Krakowiak, J. S. Bradshaw, W. Jiang, N. K Dalley, G. Wu, R. M. Izatt, *J. Org. Chem*., **56**, 2675 (1991).
[33] F. Cabral, B. Murphy, J. Nelson, *Inorg. Chem. Acta*. **90**, 169 (1984).
[34] N. A. Bailey, M. M. Eddy, D. E. Fenton, S. Moss, A. Mukhopadhyay, G. Jones, *J. Chem. Soc. Dalton Trans*., 2281 (1984)
[35] M. G. B. Drew, C. P. Waters, S. G. Mcfall, S. M. Nelson, *J. Chem. Res*., 360 (1979).
[36] B. P. Clark, J. R. Harris, G. H. Timms, J. L. Olkowski, *Tetrahedron Lett.,* **36**, 3889 (1995).
[37] H. Brunner, H. Schiessling, *Angew. Chem. Int. Ed. Engl*., **33**, 125 (1994).
[38] M. Pietraszkiewicz, R. Gasiorowski, *Chem. Ber*., **123**, 405 (1990)
[39] S. Chandra, L. K. Gupta, *Spect. Chim.Acta Part A,* **61**, 1181 (2005).
[40] A. Llobet, J. Reisbenpies, A. E. Martell, *Inorg. Chem.,* **33**, 5946 (1994).
[41] Z. B. Li, J. Lin, H. C. Zhang, M. Sabat, M. Hyacinth, l. Pu, *J. Org. Chem*., **69**, 6284 (2004).
[42] H. Brunner, H. Schiessling, *Bull. Soc. Chim. Belg*., **103**, 119 (1994).
[43] Q. Zeng, J. Sun, S. Gou, K. Zhou, J. Fang, H. Chen, *Trans. Met. Chem*., **23**, 371 (1998).
[44] J. Jazwinski, J. M. Lehn, R. Meric, J. P. Vigneron, M. Cesario, J. Guilhem, C. Pascard, *Tetrahedron Lett.,* **28**, 3489 (1987).
[45] T. Sone, Y. Ohba, R. Watanabe, *Bull. Chem. Soc. Jpn.,* **62**, 1346 (1989).
[46] D. McDowell, J. Nelson, *Tetrahedron Lett*., 385 (1988).
[47] D. Habibi, V. Izadkhah, *Phosphorus, Sulfur and Silicon,* **179**, 1197 (2004).
[48] R. Menif, A. E. Martell, *J. Chem. Soc. Chem. Commun*., 1521 (1989).
[49] R. Menif, A. E. Martell, *J. Am. Chem. Soc.,* 1522 (1989).
[50] R. Menif, A. E. Martell, P. J. Squattrito, A. Clearfield, *Inorg. Chem.,* **29**, 4723 (1990).
[51] S. Brooker, D. J. de Geest, R. J. Kelly, P. G. Plieger, B. Moubaraki, K. S. Murray, G. B. Jameson, *J. Chem. Soc. Dalton Trans*., 2080 (2002).
[52] P. G. Owston, R. Peters, E. Ramsammy, P. A. Tasker, J. Trotter,. *J. Chem. Soc. Chem. Comm*., 1218 (1980).
[53] N. A. Bailey, M. M. Eddy, D. E. Fenton, G. Jones, S. Moss, A. Mukhopadhyay, *J. Chem. Soc. Chem. Comm. Dalton Trans*., 628 (1981)
[54] Y. Takeda, H. Kato, *Bull. Chem. Soc. Jpn*., **52**, 1027 (1979).
[55] L. F. Lindoy, The Chemistry of Macrocyclic Ligand Complexes, 1989, pp 106-107.
[56] U. Cakir, M. Ozer, M. A. Icen, H. I. Ugras, M. Bulut, *Dyes and Pigments,* **60**, 177 (2004).
[57] T. Kilic, T. Dirmenci, F. Satil, G. Bilsel, T. Kocagöz, M. Altun, A. C. Gören, *Chem. Nat. Comp*., **41**, 276 (2005).
[58] H.İ. Uğraş, Ü. Çakır, A. Azizoğlu, T. Kılıç, and Ç. Erk; *J. Inc. Phen. and Mol. Recog*., **55**, 159 (2006).