ICC

Iranian Chemical Communication

Original Research Article

Payame Noor University *http://icc.journals.pnu.ac.ir*

Synthesis, spectroscopic investigation and coductometry of a new hexadentate symmetric Schiff base ligand containing $N_2O_2S_2$ donor atoms and related complexes with Cd(II),Zn(II),Co(II) and Mn(II) metal ions

Reza Golbedaghi*, Ehsan Alavipour

Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran

Received: 11 September 2015, Accepted: 3 October 2015, Published: 1 April 2016

Abstract

In this paper, we report the synthesis and characterization of a new symmetric macroacyclic Schiff base ligand (H_2L) and related complexes with different metals. (H_2L) was synthesized by the one pot condensation reaction of 2-[2-(2-formyl phenoxy)ethoxy]benzaldehyde and 2-aminobenzenethiol in a 1:2 molar ratio. The acyclic Schiff base was characterized by IR, NMR spectroscopy and elemental analysis. Also, the resulting synthesized metal complexes in this work were characterized by elemental analysis, IR and molar conductivity in all cases and NMR spectroscopy for the case of Cd(II) complex.

Keywords: Schiff base; macroacyclic; symmetric; hexadentate; donor atoms; complex.

Introduction

Various polydentate chelating ligands have been prepared in the past and successfully used in the selective coordination of metalations. The properties arising from this aggregation were investigated in detail by different physicochemical procedures and adequately reviewed [1–18]. These systems were acyclic or cyclic in nature, planer or tridimensional in their framework, and depend on the designed structure (discrete, ordered, porous, helicoidal, 1D, 2D or 3D polymeric, etc.) to which they give rise, the specific functions they must perform or the peculiar properties they must achieve. Compartmental ligands, i.e. compounds with two(or more) coordination chambers in close proximity, represented a relevant evolution, owing to their capability

---

*Corresponding author: Reza Golbedaghi
Tel: +98 (813) 2542400, Fax: +98 (813) 2542400
E-mail: golbedaghi82@gmail.com

of providing different, well selective recognition of charged and/or neutral species at their adjacent chambers. These systems quite often are Schiff bases (or the related reduced derivatives), obtained by condensation of appropriately designed and prepared formyl (or keto-) and primary amine precursors. The synthesis and properties of these ligands and related complexes have been reviewed up to 2002 [18]. Furthermore, a more recent paper reviewed the results published on related macrocyclic compartmental systems up to 2005 [19].

Schiff bases issued from salicylaldehyde and amines have been largely investigated owing to their capacity to append various substituents [20–22]. Because of the versatility to adopt various modes, this chemistry is able to generate stable framework [23,24] the combination of veracity of the binding modes and the nature of the metal ion is expected to generate new compounds. In the course of our studies on the chemistry of transition metal compounds, we have prepared and characterized a number of chelates containing N and O donor sites [25, 26].

We have observed the synthesis of a new acyclic Schiff base. We have recently reported the synthesis and characterization of a number of metals Schiff base complexes [27, 28]. Herein, we report the synthesis and characterization of some new acyclic complexes from a synthesized symmetric linear diamine ligand, H_2L.

In the recent past, a large variety of acyclic compartmental Schiff bases have been successfully proposed and extensively studied owing to their relatively easy synthesis and their versatility in the formation of stable complexes. The symmetric acyclic compartmental ligand (H_2L) derive from the one pot condensation reaction of 2-[2-(2-formyl phenoxy)ethoxy]benzaldehyde and appropriate amine C_6H_7NS in a 1:2 molar ratio.

The acyclic Schiff base was characterized by IR, NMR spectroscopy and elemental analysis. The resulting complexes in this work were characterized by elemental analysis, IR, mass and NMR spectroscopy.

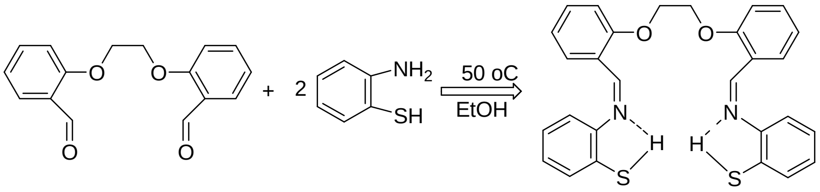
Experimental

Materials and measurements

Solvents were dried and purified before being used according to published procedures. Other reagents were purchased from Sigma–Aldrich and Merck and used as received. IR spectra were recorded on a STOE IPDS-II as KBr pallets. Mass spectra were measured on a Bruker micro TOFQ. NMR spectra were measured on Bruker DPX 300 and 400 spectrometers and the conductivity measurements were carried out in acetonitrile at room temperature using a Hanna Conductometer Metrohm 712 instrument.

Synthesis of Schiff base ligand (H_2L)

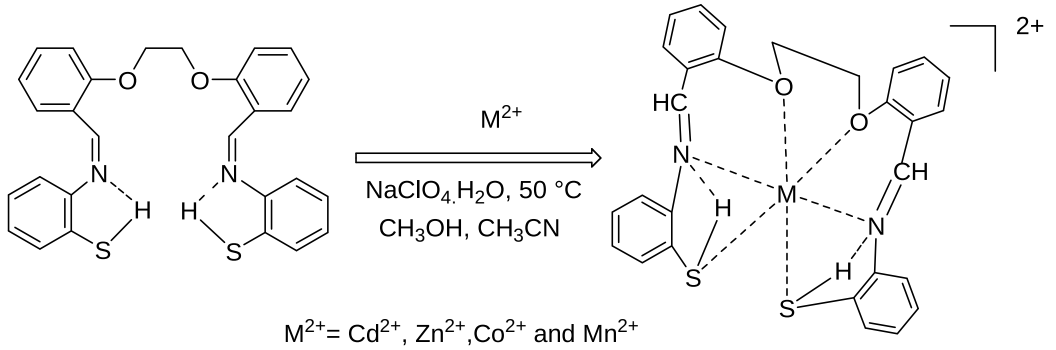
2-[2-(2-formyl phenoxy)ethoxy]benzaldehyde (0.270 gr, 1 mmol) and 2-aminobenzenethiol (0.250 gr, 2mmol) were mixed and heated to 60°C under reflux for 24 hours in EtOH (100 mL) then cooled at 0 °C. The cream colored solid product was recrystallized. The resulting crystals were collected by filtration and dried in a vacuum desiccator over P_4O_{10}. Yield: 86%, m.p. 82-84. Anal. Calc. for $C_{28}H_{24}N_2O_2S_2$: C, 69.39; H, 4.99; N, 5.78. Found: C, 69.04; H, 4.45; N, 5.37%. IR (KBr, cm^{-1}): 1584, (νC=N Schiff base), 3394, (νNH) This band was assigned to the stretching frequency of the NH group, due to the presence of the intramolecular hydrogen bond (N–SH) in the molecule[29-31]. ^1H NMR (DMSO-d_6, ppm, 300 MHz,): 8.44 (s, 2H, HC=N); 7.13–8.02 (m, 16H, ArH) ; 4.88 (s, 4H, CH_2-CH_2); 4.27 (s, 2H, NS-H). ^{13}C NMR (DMSO-d_6, ppm, 300 MHz,): 67.57, 113.21, 116.84, 121.74, 124.05, 126.78, 127.23, 128.15, 130.59, 131.35, 132.12, 157.86, 158.47 and 159.53 (Scheme 1).



Scheme 1. The synthetic route of macroacyclic H_2L

Synthesis of complex [Cd (H_2L)](ClO_4)$_2$, 1

H_2L (0.121 g, 0.25 mmol) and $CdCl_2.4H_2O$ (0.064 g, 0.25 mmol) were mixed and heated under reflux for 30 min in acetonitrile (25 mL). Then $NaClO_4.H_2O$ (0.07 g, 0.50 mmol) was added and stirred for 10 min then cooled at 0 °C. The solution was filtered and the filtrate was reduced to ca 10 cm^3. A White-colored purified powder was obtained by slow diffusion of Et_2O vapor into this solution. Yield: 52%. Anal. Calc. for $C_{28}H_{24}CdCl_2N_2O_{10}S_2$: C, 42.25; H, 3.04; N, 3.52. Found: C, 41.99; H, 2.98; N, 3.48%. IR (KBr, cm^{-1}): 1599, (νC=N Schiff base), 3366, (νN+ H) This band was assigned to the stretching frequency of the N+ H group, due to the presence of the intramolecular hydrogen bond (N–SH) in the molecule[29–31], 1244, (νC-O). ^1HNMR (DMSO-d_6, ppm, 300 MHz,): 8.48 (s, 2H, HC=N); 7.08–8.14 (m, 16H, ArH); 4.66 (t, 4H, $2CH_2$); 4.40; (s, 2H, NS-H) (Scheme 2).



Scheme 2. Preparation of complexes of ligand H_2L

Synthesis of complex [Zn (H_2L)](ClO_4)$_2$, 2

H_2L (0.121 g, 0.25 mmol) and $ZnCl_2.6H_2O$ (0.061 g, 0.25 mmol) were mixed and heated under reflux for 30 min in acetonitrile (25 mL). Then $NaClO_4.H_2O$ (0.07 g, 0.50 mmol) was added and stirred for 10 min then cooled at 0 °C. The solution was filtered and the filtrate was reduced to ca 10 cm^3. A yellow-colored purified powder was obtained by slow diffusion of Et_2O vapor into this solution. Yield: 49%. Anal. Calc. for $C_{28}H_{24}ZnCl_2N_2O_{10}S_2$: C, 44.90; H, 3.23; N, 3.74. Found: C, 44.88; H, 3.27; N, 3.69%. IR (KBr, cm^{-1}): 1586, (νC=N Schiff base), 3396, (νN+ H) This band was assigned to the stretching frequency of the N+ H group, due to the presence of the intramolecular hydrogen bond (N–SH) in the molecule[29–31], 1240, (νC-O).

Synthesis of complex [Co (H_2L)](ClO_4)$_2$, 3

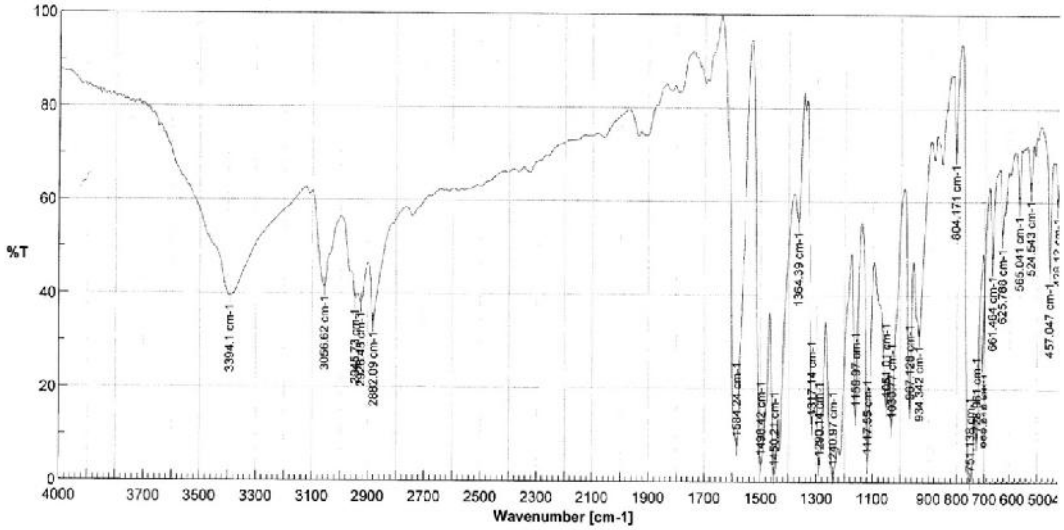
H_2L (0.121 g, 0.25 mmol) and $CoCl_2.6H_2O$ (0.059 g, 0.25 mmol were mixed and heated under reflux for 30 min in acetonitrile (25 mL) then $NaClO_4.H_2O$ (0.07 g, 0.50 mmol) was added and stirred for 10 min then cooled at 0 °C. The solution was filtered and the filtrate was reduced to ca 10 cm^3. A blue-colored purified powder was obtained by slow diffusion of Et_2O vapor into this solution. Yield: 57%. Anal. Calc. for $C_{28}H_{24}CoCl_2N_2O_{10}S_2$: C, 45.29; H, 3.26; N, 3.77. Found: C, 45.27; H, 3.21; N, 3.74%. IR (KBr, cm^{-1}): 1598, (νC=N Schiff base), 3423, (νN+ H) This band was assigned to the stretching frequency of the NH group, due to the presence of the intramolecular hydrogen bond (N–SH) in the molecule[29–31], 1241, (νC-O).

Synthesis of complex [Mn (H_2L)](ClO_4)$_2$, 4

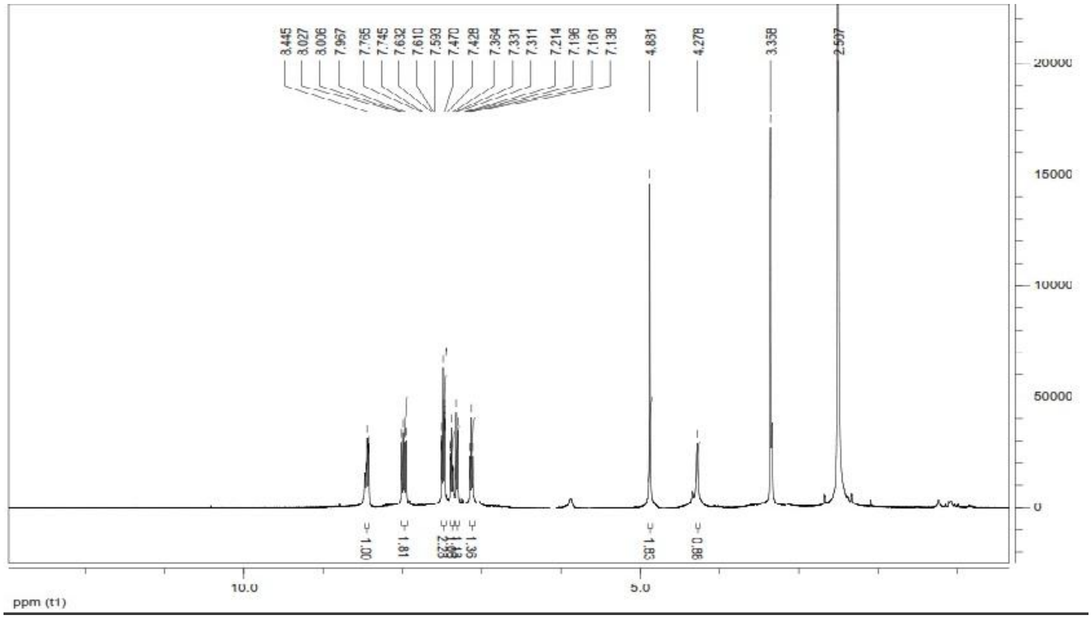
H_2L (0.121 g, 0.25 mmol) and $MnCl_2.6H_2O$ (0.051 g, 0.25 mmol) were mixed and heated under reflux for 30 min in acetonitrile (25 mL) then $NaClO_4.H_2O$ (0.07 g, 0.50 mmol) was added and stirred for 10 min then cooled at 0° C. The solution was filtered and the filtrate was reduced to ca 10 cm^3. A brown-colored purified powder was obtained by slow diffusion of Et_2O vapor into this solution. Yield: 47%. Anal. Calc. for $C_{28}H_{24}MnCl_2N_2O_{10}S_2$: C, 45.54; H, 3.28; N, 3.79. Found: C, 45.44; H, 3.25; N, 3.91%. IR (KBr, cm^{-1}): 1588, (νC=N Schiff base), 3397, (νN+ H) This band was assigned to the stretching frequency of the N+ H group, due to the presence of the intramolecular hydrogen bond (N–SH) in the molecule[29–31], 1239, (νC-O).

Results and discussion

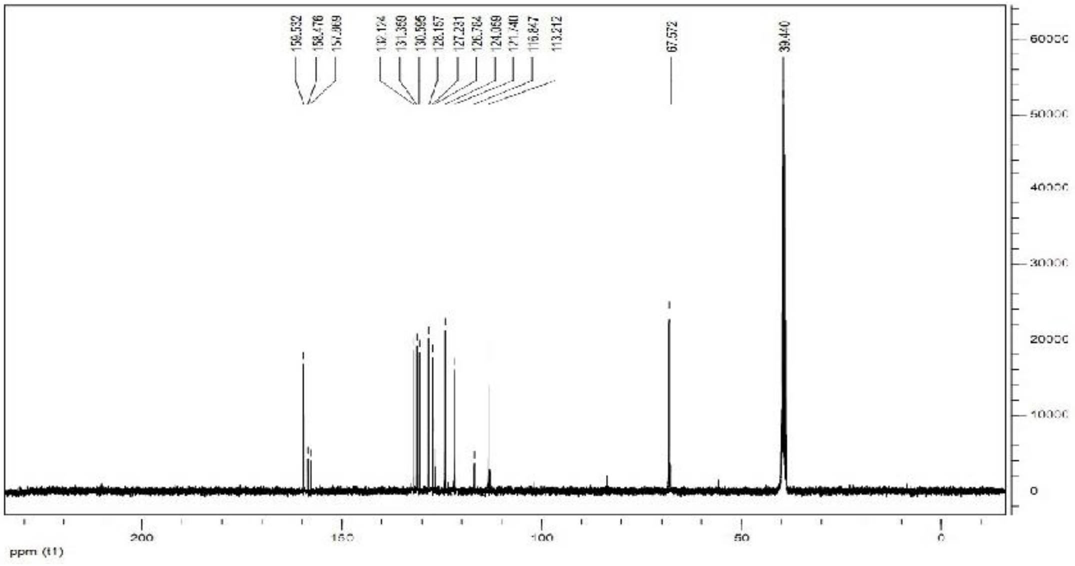
A new symmetrical Schiff base ligand, H_2L, was respectively synthesized by the condensation reaction of 2-[2-(2-formyl phenoxy)ethoxy]benzaldehyde with 2-aminobenzenethiol in a 1:2 molar ratio. After preparation of the above Schiff base ligand the complexes 1-4 in the presence of either Cd(II), Zn(II), Co(II) and Mn(II) were synthesized, respectively. These compounds are quite stable in air and can be stored in a desiccator for long periods of time without decomposition. The resulting compounds were characterized by IR and elemental analysis in all cases and ^{1}HNMR in the case of ligand and Cd(II) complex. Condensation of all the primary amino group is confirmed by the lack of N–H stretching bands in the IR reign (3150-3450 cm^{-1}) and the presence of strong C=N (Schiff base) stretching bands at 1585-1640 cm^{-1} [32]. For a number of complexes a broad intense band at ca. 1100 cm^{-1} due to ClO_4^- shows no splitting, indicating the absence of coordination of ClO_4^- for these compounds [33-34]. The NMR studies of Schiff base ligand (Figure 1) and complex 1 are completely consistent in their formulation. As can be seen in Figure 1, b, that shows the ^{1}HNMR spectra of ligand, H_2L, the aliphatic and aromatic protons completely confirmed with synthesized Schiff base. It is clear that the peak appeared at 8.44 ppm and is respectively related to imine (H=CN) group that shows fully condensed of primary amine and aldehyde. In addition, the ^{13}C NMR Figures 1 c, of this ligand as well as own^{1}HNMR confirmed with own formulation.


%T
100
80
60
40
20
0
4000
3700
3500
3300
3100
2900
2700
2500
2300
2100
1900
1700
1500
1300
1100
900
800
700
600
500
Wavenumber [cm-1]
3394.1 cm-1
3056.62 cm-1
2945.73 cm-1
2882.09 cm-1
1584.24 cm-1
1490.42 cm-1
1450.21 cm-1
1364.39 cm-1
1317.14 cm-1
1290.14 cm-1
1240.97 cm-1
1159.97 cm-1
1117.55 cm-1
934.342 cm-1
804.171 cm-1
751.139 cm-1
661.464 cm-1
625.780 cm-1
565.041 cm-1
524.543 cm-1
457.047 cm-1

(a)


8.445
8.027
8.006
7.967
7.765
7.745
7.632
7.610
7.593
7.470
7.428
7.364
7.331
7.311
7.214
7.196
7.161
7.138
4.831
4.278
3.358
2.507
20000
15000
10000
50000
0
1.00
1.81
2.23
1.36
1.83
0.86
10.0
5.0
ppm (t1)

(b)



(C)

Figure 1. IR (a), ^{1}H (b) and ^{13}CNMR (c) spectra of ligand H_2L

The NMR spectra of the cadmium complex confirm the formation of a fully condensed Schiff base complex. The chemical shifts in the spectra shows that the ligand have been coordinated to the Cd(II) metal ion. Solution conductivity measurements were performed to establish the electrolyte type of the complexes. The molar conductivities at 10^{-3} M concentration for the complexes in acetonitrile are in the range expected for their formulation as 1:2 electrolytes [32] as shown in Table 1.

Table 1. Molar conductivity data of H_2L complexes

Compound	**$[CdH_2L](ClO_4)_2$**	**$[ZnH_2L](ClO_4)_2$**	**$[CoH_2L](ClO_4)_2$**	**$[MnH_2L](ClO_4)_2$**
molar conductivity $cm^2\Omega^{-1}mol^{-1}$	256	249	277	268

Conclusion

The synthesis and characterization of a new Schiff base ligand, H_2L have been reported. The Cd(II), Zn(II), Co(II) and Mn(II) complexes of above ligand was prepared. After preparation of above ligand and complexes the IR and NMR spectroscopy of these compounds were studied.

Acknowledgments

We are grateful to the Payame Noor University for the financial support.

References

[1] S. Brooker, *Coord. Chem. Rev.*, **2001**, *222*, 33-56.

[2] W. Huang, H.B. Zhu, S.H. Goiu, *Coord. Chem. Rev.*, **2006**, *250*,414-423.

[3] A.L. Gavrilova, B. Bonish, *Chem. Rev.*, **2004**, *104*, 349-384.

[4] D. Brooker, J.Eur, *Inorg. Chem.*, **2002**, *12*, 2535-2542.

[5] P.A. Gale, *Coord. Chem. Rev.*, **2003**, *240*,191-221.

[6] P.D. Beer, E.J. Hayes, *Coord. Chem. Rev.*, **2003**, *240*, 167-189.

[7] V. McKee, J. Nelson, R.M. Town, *Chem. Soc. Rev.*, **2003**, *32*, 309-314.

[8] C. Suksai, T. Tuntulani, *Chem. Soc. Rev.*, **2003**, *32*, 192-198.

[9] R. Ziessel, *Coord. Chem. Rev.*, **2001**, *216/217*, 195-223.

[10] C.L. Wang, T. Zhang, H. Sun, *Coord Chem. Rev.*, **2004**, *248*, 147-236.

[11] P. Molenveld, J.F.J. Engbersen, D.N. Reinhoudt, *Chem. Soc. Rev.*, **2000**, *29*, 75-83.

[12] V. Alexander, *Chem. Rev.*, **1995**, *95*, 273-287.

[13] H. Okawa, H. Furutacki, D.E. Fenton, *Coord. Chem. Rev.*, **1998**, *174*, 51-75.

[14] A. Martell, J. Penitka, D. Kong, *Coord. Chem Rev.*, **2001**, *216*, 55-63.

[15] J. Nelson,V. McKee, G. Morganin: The K.D. Karlin (Ed.).,*Progress in Inorganic Chemistry*, **1998**, *47*, 167-186.

[16] S.R. Collinson, D.E. Fenton, *Coord. Chem. Rev.*, **1996**, *148*, 19-40.

[17] W. Radecka-Paryzek, V. Patroniak, J. Lisowski, *Coord. Chem. Rev.*, **2005**, *249*, 2156-2157.

[18] (a) P.A. Vigato, S. Tamburini, *Coord. Chem. Rev.*, **2004**, *248*, 1717-2128; (b) P. Guerriero, S. Tamburini, P.A. Vigato, *Coord.Chem Rev.*, **1995**, *139*, 17-243.

[19] P.A. Vigato, S. Tamburini, L. Bertolo, *Coord. Chem. Rev.*, **2007**, *251*, 1311-1492.

[20] J.D. Donald,G. Cesar, G.Ortiz, R. Damon, *Inorg. Chem. Acta.*, **2004**, *357*, 2143-2149.

[21] M. Dieng, O. Diouf, M. Gaye, A.S. Sall, P. Pérez-Lourido, L. Valencia, A. Caneschi, L. Sorace, *Inorg. Chem.Acta.*, **2013**, *394*, 741-746.

[22] Y. Fan, W. You, W. Huang, J. Liu, Y. Wang, *Polyhedron*, **2010**, *29*, 1149-1155.

[23] A.M. Guidote, K. Ando, K. Erada, Y. Kurusu, H. Nagao, Y. Masuyama, *Inorg. Chim. Acta.*, **2001**, *324*, 203-211.

[24] P.J. Toscano, K.A. Belsky, T.C. Hsieh, T. Nicholson,J. Zubieta, *Polyhedron*, **1991**, *10*, 977-991.

[25] R. Golbedaghi, S. Salehzadeh, H. Keypour, A.G. Blackman, *Polyhedron*, **2010**, *29*, 850-856.

[26] S. Salehzadeh, R.Golbedaghi, *Chem.*

Res., **2007**, *2*, 86-88.

[27] R. Golbedaghi, S. Salehzadeh, H.R. Khavasi, A.G. Blackman, *Polyhedron*, **2014**, *68*, 151-156.

[28] H. Keypour, M. Shayesteh, R. Golbedaghi, A. Chehregani, A.G. Blackman, *J. Coord. Chem*., **2012**, *65*, 1004-1016.

[29] I. Yilmaz, H. Temeland, H. Alp, *Polyhedron*, **2008**, *27*, 152-132.

[30] A.A. Ashraf, *Tetrahedron*, **2004**, *60*, 1541-1548.

[31] W. Zoubi, F. Kandil, M.K. Chebani, *Spectrochim. Acta*, **2011**, *69*, 1909-1914.

[32] N.S. Gill, R.H. Nutall, D.E. Scaife, *J. Inorg. Nucl. Chem*., **1961**, *18*, 79–87.

[33] A.J. Hataway, D.E. Underhill, *J. Chem. Soc*., **1961**, *11*, 3091–3096.

[34] M.F. Rosenthal, *J. Chem. Educ*., **1973**, *50*, 331–335.