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Synthesis and Thermal Degradation behavior of the Complexes of Monoethanolamine with Co (II), Ni (II), Zn (II) and Cd (II): A Comparative Study

Rafia Mushtaq, Mohd. Hanief Najar*, Kowsar Majid* and M. Abdullah Dar

Department of Chemistry, National Institute of Technology Srinagar, Hazratbal Srinagar-190006, J&K India.

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ABSTRACT

Complexes of monoethanolamine with Co, Ni, Zn and Cd are obtained according to the previously reported literature. Empirical formula assigned to the synthesized complexes from elemental analysis was found to be $[Co(MEA)(H2O)_2Cl_2]$, $[Ni(MEA)_2Cl_2]$, $[Zn(MEA)(H_2O)_2Cl_2]$ and $[Cd(MEA)_2SO_4]$. Thermogravimetry was done from ambient to 1000°C in order to check the thermal stability of complexes which was supported by FTIR spectra obtained at 150°C and 500°C. Initial decomposition temperature (T*i*) values of complexes from Thermogravimetry showed the following order of thermal stability: $[Cd(MEA)_2SO_4] > [Co(MEA)(H2O)_2Cl_2] > [Zn(MEA)(H_2O)_2Cl_2] > [Ni(MEA)_2Cl_2]$.

Introduction

After the preparation of Aminoalcohols or ethanolamine's by Wurtz in 1860, they have been used as ligands for the preparation of complexes with many transition metals. The bi-functional nature of ethanolamine's enables them to serve a variety of commercial applications such as inhibitors [1], surfactants, gas purification and herbicides [2] , Buffers [3] , catalysts [4], ion exchangers [5], additives in building material [6], electroplating [7]and dyes [8].

Ethanolamine's consists of Mono, Di and Tri ethanolamines. Among them Monoethanolamine is the strongest base. Monoethanolamine act both as monodentate and bidentate ligands [9]. Homo and hetero bimetallic ethanolamine derivatives of a number of metals have also been reported recently [10-13]. The coordination chemistry of aminoalcohols with metal ions deserves further study because they play important role in nature, for example, in hormones [14-15] and in amino sugars [16-17]. Very interesting but contradictory reports by various researchers from time to time make the investigation still interesting. For example, for the development and utilization of renewable energy sources, recently Fe(III)/Fe(II)-tea complex has found applications [18] which ensure that these complexes can show potential for various industrial and technological applications.

In the present work, the thermal degradation behavior of the complexes of monoethanolamine with Cobalt, Nickel, Zinc and Cadmium is studied. FTIR measurements are conducted at 150°C and 500°C to account for the degradation process.

Experimental

Materials and Physical measurements

Cobalt Chloride, Nickel Chloride, Zinc Chloride and Cadmium Sulfate were all provided by Loba Chemicals. Monoethanolamine was provided by Himedia. All the solutions were made in triply distilled water. Ethanol is used for washing. The reagents used were of Analytical grade. Fourier transform infrared (FTIR) spectra were recorded on Perkin Elmer RX-1 FTIR spectrophotometer. The spectra were taken in KBr disks. Thermogravimetry was done on SDT Q600 V8.3 built 101 Instrument in N_2 atmosphere under a constant heating rate of $10°Cmin^{-1}$. The temperature range was from ambient to 1000°C. An aluminum pan was used as reference.

Synthesis

Monoethanolamine complexes of metal ions are prepared under refluxing conditions. 1M solution (50 ml) of Monoethanolamine is mixed separately to the same volume of 1M solution of cobalt chloride, Nickel Chloride and Zinc Chloride. After mixing, mixtures are refluxed for 5-10 minutes pale violet, pale green and white precipitates are obtained in case Co, Ni and Zn respectively. Monoethanolamine complex of Cd is obtained by reflexing 0.1M solution of each monoethanolamine and Cadmium Sulfate (60ml) which results into the white colored precipitate. The precipitates are filtered off, washed several times with ethanol- water mixture and then dried in a desiccators. Obtained complexes are confirmed from various characterization techniques [19].

Results and Discussion

Elemental Analysis

The empirical formula assigned to the synthesized complexes was found to be $[Co(MEA)(H2O)_2Cl_2]$, $[Ni(MEA)_2Cl_2]$, $[Zn(MEA)(H_2O)_2Cl_2]$ and $[Cd(MEA)_2SO_4]$.

FTIR and Thermogravimetry

The Thermal analysis of the Co-complex is shown in the Fig. 1. The decomposition takes place in two stages. The first stage starts from 300 ºC and ends at 420 ºC with DTG maximum at 347 ºC, involves an observed weight loss of 16 % against calculated weight loss of 15.86 % because of the removal of two moles of water. The second stage starts from 530 ºC and ends at 800 ºC with DTG maximum at 740 ºC with observed weight loss of 26.2 % against the calculated weight loss of 26.89 % because of removal of 2 moles of CH_2, one mole of OH and one mole of NH_2. The residue left behind is $CoCl_2$ at 800 ºC.

The loss of different moieties at various decomposition steps was verified by recording the FTIR spectra of the complex by heating the complex to 150 ºC and to 500 ºC (Fig. 1 a, b). The FTIR spectrum of the complex at 150 ºC shows a very sharp peak at 3551 cm^{-1} because of νO-H of monoethanolamine

Tele:

E-mail addresses: haniefarf@gmail.com

confirming TG. Moreover the peaks because of δN-H, δO-H,τCH2.C-C at 1627 cm^{-1}, 1346 cm^{-1} and 723 cm^{-1} respectively are observed. The sample after being heated to 500 ºC has also been scanned for FTIR analysis as shown in Fig. 1b shows no such characteristic peaks confirming TG.

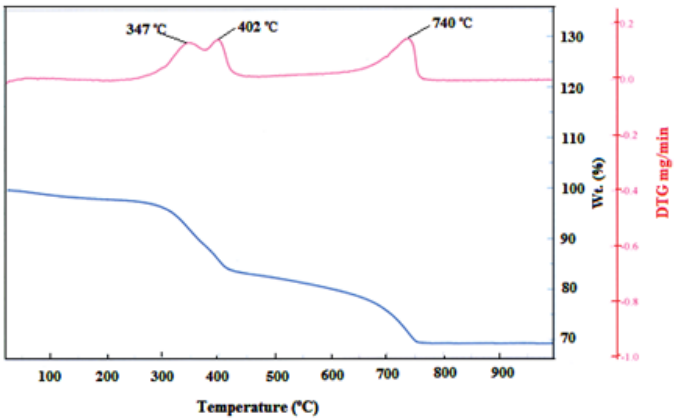

Fig 1. TG/DTG of Co-Monoethanolamine

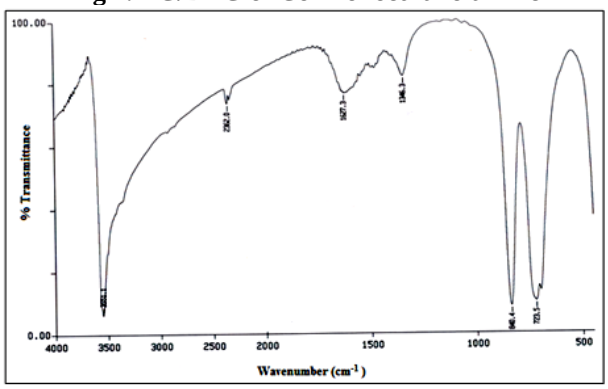

Fig 1a. FTIR of Co-Monoethanolamine at 150°C

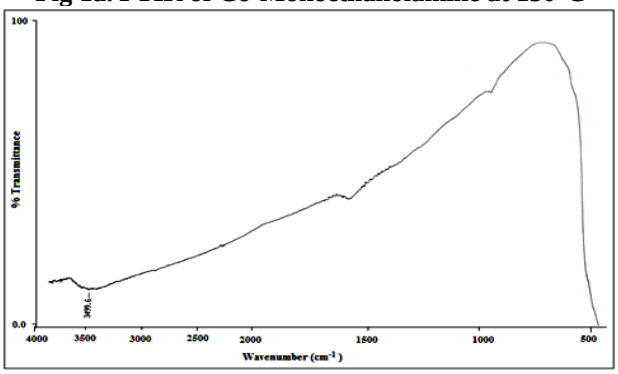

Fig 1b. FTIR of Co-Monoethanolamine at 500°C

In case of Nickel complex, decomposition takes place in three stages (Fig. 2).

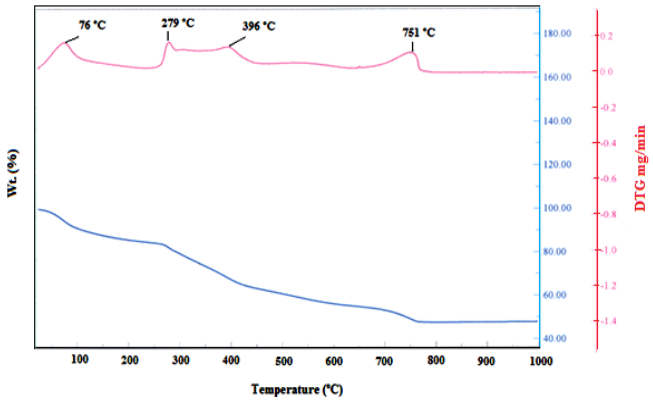

Fig 2. TG/DTG of Ni-monoethanolamine

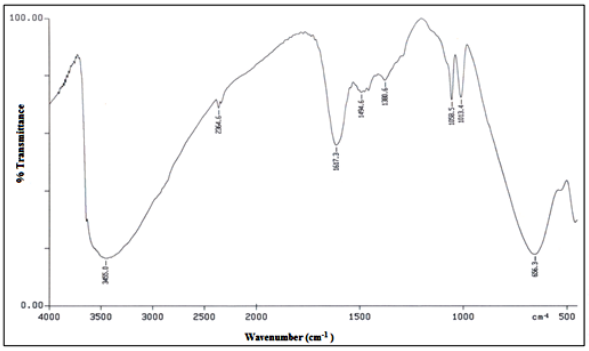

Fig 2a. FTIR of Ni-Monoethanolamine at 150°C

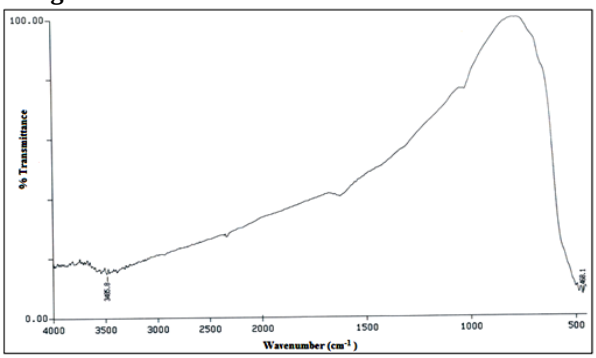

Fig 2b. FTIR of Ni-Monoethanolamine at 500°C

The first stage is from 20-120 ºC with DTG maximum at 76 ºC involving observed weight loss of 11.05 % against calculated weight loss of 11.1 % because of the removal of 2 moles of CH_2. The second stage starts from 140 ºC and ends at 450 ºC with DTG maximum at 279 ºC with observed weight loss of 24.61 % against the calculated weight loss of 24.62 % because of removal of 2 moles of CH_2, 2 moles of OH. The third stage starts from 450 ºC and ends at 900 ºC with DTG maximum at 751 ºC with observed weight loss of 12.34 % against the calculated weight loss of 12.34 % because of loss of 2 moles of NH_2. The residue left behind is $NiCl_2$ at 900 ºC with observed weight of 51.5 % against the calculated weight of 51.5 %.

At 150 ºC, the FTIR spectra of the complex shows a broad peak at 3455 cm^{-1} which can be because of ν O-H of monoethanolamine (Fig. 2a). The broadness of peak can be because of hydrogen bonding. Since there is no characteristic peak for water suggesting the synthesis of the complex without aqua ligand thereby supports elemental analysis. Moreover the peaks because of δN-H, δCH_2, δOH, νCO, γOHat 1617 cm^{-1}, 1494 cm^{-1},1058 cm^{-1}, 1380 cm^{-1}, 656 cm^{-1} are observed verifying the presence of monoethanolamine ligand in the complex. FTIR of the sample depict loss of all characteristic peaks at 500°C, confirming TG. The residue left is nearly 50%.

The thermogram of Zn complex is stable up to 100 ºC, where from decomposition takes place in two stages. The first stage starts from 100-240 ºC with DTG maximum at 168 ºC and involves an observed weight loss of 16.00 % against calculated weight loss of 15.40 % because of the removal of two moles of water. The thermogram of the complex is shown in the Fig. 3. The presence of water inside the coordination sphere is supported by thermal decomposition starting from 100ºC up to 240 ºC with DTG maximum at 168 ºC. Since there is no lattice water present, therefore TG shows the stability of the complex up to 100 ºC. The second stage starts from 460 ºC, ends at 900 ºC with DTG maximum at 512 ºC, with an observed weight loss of 25.34 % against the calculated weight loss of 26.18 % because of the removal of one mole of CH_2-CH_2-OH and one mole of NH_2. Therefore, thermogram shows two decomposition steps, the first one evolves coordinated water, while rest of the

moieties in the complex are removed in the second stage. The residue left behind is $ZnCl_2$ with an observed weight. of 57.97 % against calculated weight of 58.36 % at 900 ºC.

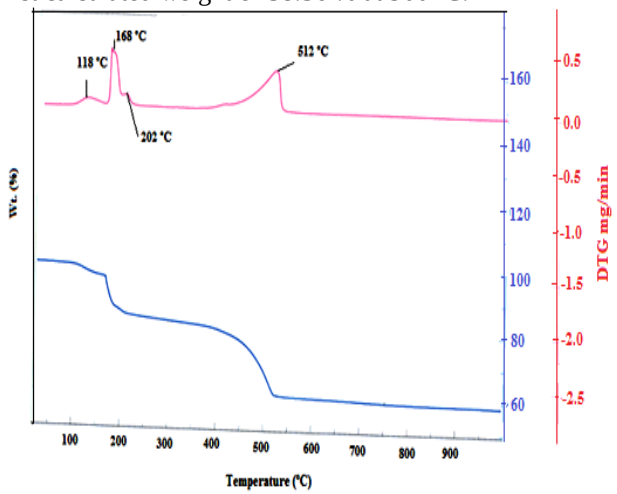

Fig 3. TG/DTG of Zn-Monoethanolamine

The thermal decomposition mechanism is further verified by recording FTIR spectra at 150 and 500 ºC. The two spectra are shown Fig. 3 a, b.

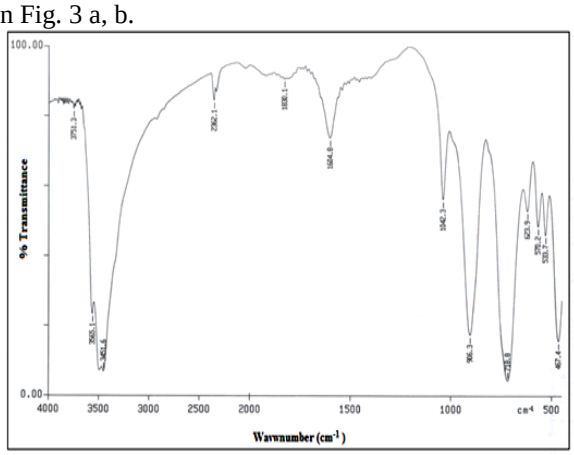

Fig 3a. FTIR of Zn-Monoethanolamine at 150°C

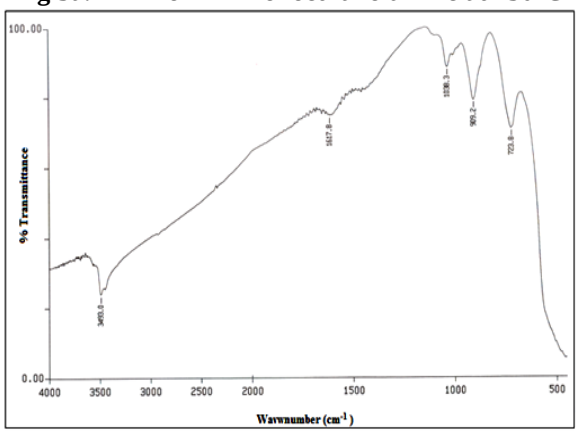

Fig 3b. FTIR of Zn-Monoethanolamine at 500°C

The FTIR spectra of the complex at 150 ºC shows a very sharp peak at 3565cm^{-1} because of νOH of monoethanolamine and other peak for νN-H. Moreover the peaks because of δNH, νCO, $^{\tau}$CH2.C-C, CH2.C-N, $^{\gamma}$OH and νM-N at 1607 cm^{-1}, 906 cm^{-1},718cm^{-1},1042cm^{-1}, 623 cm^{-1} and 467cm^{-1} respectively are observed.The sample after being heated to 500 ºC has also been scanned for FTIR analysis shows characteristic peaks at 3493cm^{-1}, 1617 cm^{-1}, 1038 cm^{-1} ,723 cm^{-1}. 684 cm^{-1} and 909 cm^{-1} for νOHor νN-H, δNH, $^{\rho}$CH2.C-N, $^{\tau}$CH2.C-C and for νCO respectively confirming TG observation of retention of amino alcohol moiety at 500 ºC.

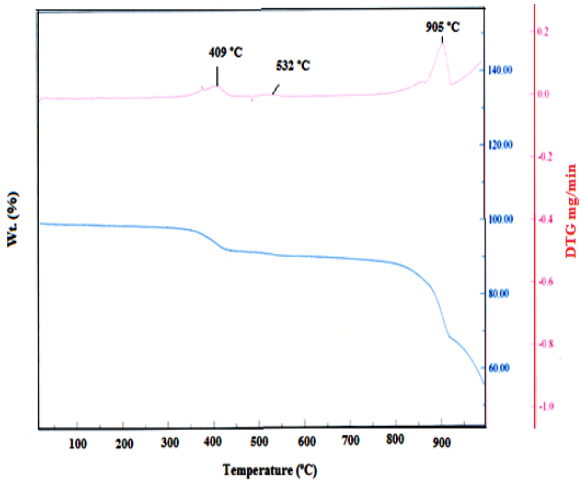

Fig 4. TG/DTG of Cd-monoethanolamine

The thermal decomposition of the Cd-complex is shown in Fig. 4. The thermogram shows no weight loss upto 400 ºC, which confirms the synthesis of the anhydrous complex and the stability of the complex up to 400 ºC. Then the curve shows two transitions, first starts from 400ºC -430 ºC with DTG maximum at 409 ºC with observed weight loss of 8.47 % against calculated weight loss of 8.48 % corresponding to the release of loss of two CH_2 molecules . The second stage starts from 830 ºC and ends at 960 ºC with DTG maximum at 905 ºC with an observed weight loss of 27.7 % against the calculated weight loss of 28.47 %. The weight loss is because of the removal of two moles of CH_2, two moles of OH and two moles of NH_2. The residue left behind is $CdSO_4$ with an observed weight of 63.02 % against the calculated weight of 63 % at 960 ºC. The second decomposition process is an incomplete one as the temperature range ends here.

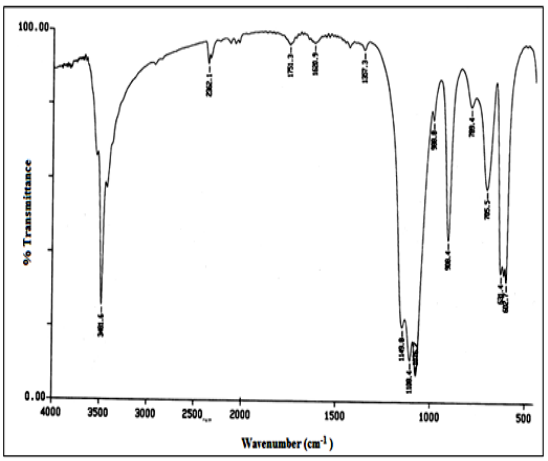

Fig 4a. FTIR of Cd-Monoethanolamine at 150°C

The loss of different moieties at various temperatures was further verified by carrying the FTIR analysis of the complex by heating the complex to 150 ºC and to 500 ºC. Since the thermogram shows stability up to 400 ºC, no weight loss is being observed, is confirmed by FTIR spectra of the complex at 150 ºC, (Fig. 4a). The spectra shows all the absorption peaks which are characteristic of the complex $[Cd(MEA)_2SO_4]$. The complex shows a very sharp peak at 3481 cm^{-1} because of νOH of monoethanolamine. Moreover the peaks because of δNH, νCO, $^{\tau}$CH2.C-C, $^{\rho}$CH2.C-N, $^{\gamma}$OH at1620 cm^{-1}, 1076 cm^{-1},705cm^{-1},1108 cm^{-1} and 631 cm^{-1} respectively are observed which are characteristic peaks of $[Cd(MEA)_2\ SO_4]$. There is no peak corresponding to that of lattice water or coordinated water which confirms the synthesis of the anhydrous complex. The sample after being heated to 500 ºC has also been scanned for FTIR analysis (Fig. 4b).

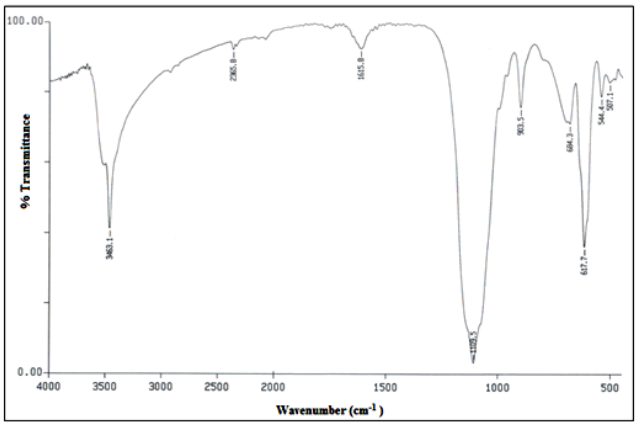

Fig 4b. FTIR of Cd-Monoethanolamine at 500°C

The FTIR shows peaks at 3463 cm^{-1}, 1615 cm^{-1}, 1109 cm^{-1} and at 684 cm^{-1} respectively for νOH, δNH, $^{\rho}CH2.C\text{-}N$ $_{and}{}^{\gamma}OH$ confirming the TG analysis. The thermogram at 500 ºC shows loss of only two moles of CH_2 and retention of rest of the moieties. Since TG and FTIR confirms that the complex is thermally stable up to 400 ºC, and hence can find applications in varied fields like lubrication, composite materials, additives, anti-corrosive agents etc.

From the above discussion it is evident that Monoethanolamine complex of the above mentioned metal ions follows the following stability order: $[Cd(MEA)_2SO_4]$ > $[Co(MEA)(H2O)_2Cl_2]$ > $[Zn(MEA)(H_2O)_2Cl_2]$ > $[Ni(MEA)_2Cl_2]$. This is because the initial decomposition temperature (T*i*) varies as Cd (400°C), Co (300°C), Zn (100°C) and Ni (25°C).

Conclusion

Monoethanolamine complexes of Co, Ni, Zn and Cd are obtained. Empirical formula assigned to the complexes from elemental analysis was found to be $[Co(MEA)(H2O)_2Cl_2]$, $[Ni(MEA)_2Cl_2]$, $[Zn(MEA)(H_2O)_2Cl_2]$ and $[Cd(MEA)_2SO_4]$. T*i* values of the complexes depict higher thermal stability of Cd complex than Co complex which intern showed higher thermal stability than Zn complex. Monoethanolamine complex of Ni showed the least stability. Thermo grams of different complexes obtained are well supported by FTIR at 150°C and 500°C.

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References

[1] Ross T K and Pearson C., Corrosion Sci., 1964; 4: 449.
[2] Esker T, Deboo A and Ishiwa Y., Ethanol amines CEH Repor., 1999.
[3] Aloisi M., Ann. Uni. Ferrera., 1949; 2: 101.
[4] Salem I A., Int. J. Chem. Kinet., 1994; 26: 341.
[5] Jakubovic A O., Polymer Sci., 1960; 117.
[6] Klement V S., Neft. Khoz., 1967; 45: 19.
[7] Tomiokudo K S and Asaoka N., Jpn. Kokai. Tokkoyo. Koho., 1992.
[8] Bechtold T, Burtgeher E, Amann A and Biobleter O., J. Chem. Soc. Faraday Trans., 1993; 89: 2451.
[9] Bombicz P, Madarasz J, Forisz and Fosh E L., Polyhedron., 1997; 16: 3601.
[10] Bradley D C, Mehrotra R C and Gour D P., Metal Alkoxides London Academic Press., 1978; 1-411.
[11] Kesseler V G, Hubert-Pfalzgraf L, Halut G S and Daran J C., J. Am. Soc. Chem. Commun. , 1994; 705.
[12] Mehrotra R C and Singh A., Prog. Inorg. Chem., 1997; 46.
[13] Sharma M, Singh A and Mehrotra R C., Polyherdon., 2000; 19: 77.
[14] Hawkins C j and Palmer J A., Aust. J. Chem., 1978; 3: 1689.
[15] Lindgren T, Sillanpaa R, Nortia T and Pilhaja K., Inorg. Chem. Acta., 1983; 73: 153.
[16] Muzarelli R A A, Chitin, Pergamon Oxford., 1977.
[17] Micera G, Deiana S, Dessi A, Decock P, Dubois B and Kozlow Ski H., Inorg. Chem. Acta., 1985; 107: 45.
[18] Wen Y H, Zhang H M, Qian P, Zhou H T, Zhao P, Yi B L and Yang Y S., Electrochemica Acta., 2006;51: 3769-3775.
[19] Nadia Z S, Alaa E A and Mamdouh S M., J. of Inorg. Biochem., 2003; 95: 141-148.