第 28 卷第 6 期 无 机 化 学 学 报 Vol.28 No.6
2012 年 6 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 1245-1250

VO(Ⅱ), Fe(Ⅱ), Co(Ⅱ), Ni(Ⅱ)和 Cu(Ⅱ)的 2,3-二(3,5-二甲基-1*H*-吡唑基)喹啉配合物的合成与表征

Sandhya Rani D[1,2] Anantha Lakshmi P V*[,1,3] Kamala Prasad V[2] Jayatyaga Raju V[1,4]
([1]*Department of Chemistry, University College of Science, Osmania University, Hyderabad*-500007, *Andhra Pradesh, India.*)
([2]*Denisco Chemicals Private Limited, Plot#D-24, Phase-I, IDA, JeedimetlaHyderabad*-500055, *Andhra Pradesh, India.*)
([3]*Department of Chemistry, University College for Women, Osmania University, Koti, Hyderabad*-500001, *Andhra Pradesh, India.*)
([4]*Departement of Chemistry, The University of Dodoma, P.O.box Number* 259, *Dodoma,Tanazania*)

摘要：合成了 VO(Ⅱ),Fe(Ⅱ),Co(Ⅱ),Ni(Ⅱ)和 Cu(Ⅱ)的 2,3-二(3,5-二甲基-1*H*-吡唑基)喹啉配合物(BDMPQ)并用元素分析、电导、热分析、光谱和顺磁共振等技术对其表征。结果表明所有配合物均为八面体构型。BDMPQ 起中性双二齿 NN 供体的作用并形成 多核配合物。

关键词：金属配合物；2,3-二(3,5-二甲基-1*H*-吡唑基)喹啉；NN 供体；多核配合物
中图分类号：O614.4 **文献标识码**：A **文章编号**：1001-4861(2012)06-1245-06

Synthesis and Characterization of VO(Ⅱ), Fe(Ⅱ), Co(Ⅱ), Ni(Ⅱ) and Cu(Ⅱ) Complexes of 2, 3-Bis(3, 5-dimethyl-1*H*-pyrazol-1-yl) Quinoxaline

Sandhya Rani D[1,2] Anantha Lakshmi P V*[,1,3] Kamala Prasad V[2] Jayatyaga Raju V[1,4]
([1]*Department of Chemistry, University College of Science, Osmania University, Hyderabad*-500007, *Andhra Pradesh, India.*)
([2]*Denisco Chemicals Private Limited, Plot#D-24, Phase-I, IDA, JeedimetlaHyderabad*-500055, *Andhra Pradesh, India.*)
([3]*Department of Chemistry, University College for Women, Osmania University, Koti, Hyderabad*-500001, *Andhra Pradesh, India.*)
([4]*Departement of Chemistry, The University of Dodoma, P.O.box Number* 259, *Dodoma, Tanazania*)

Abstract: VO(Ⅱ), Fe(Ⅱ), Co(Ⅱ), Ni(Ⅱ) and Cu(Ⅱ) complexes of 2, 3-bis (dimethyl -1H-pyrazol-1-yl)quinoxaline (BDMPQ) have been synthesized and characterized by elemental analysis, conductance, thermal, spectral and ESR techniques. Octahedral geometries have been proposed for all the complexes. BDMPQ acts as a neutral bis-bidentate NN donor and forms polynuclear complexes.

Key words: metal complexes; 2, 3-bis(dimethyl-1*H*-pyrazol-1-yl)quinoxaline, NN donor, polynuclear

Quinoxalines are an important class of nitrogen-containing heterocycles with a variety of biological activities, specifically as AMPA/GlyN receptor antagonists[1-3], angiotensin II receptor antagonists[4-5], anticancer agents[6], anti-infection agents[7] and immunomodulating agents[8]. Metal complexes of quinoxaline derivatives have received attention because of their potential metal binding properties and promising applicabilities[9-16].

Pyrazole and its synthetic analogues exhibit industrial, agricultural and biological applications.[17-21] Pyrazoles are an interesting group of compounds many of which possess broad spectrum pharmacological properties, such as analgesic, antipyretic, antidepressant and antirheumatic[22-23] and are also well known for their pronounced anti-inflammatory activity[24] as

收稿日期:2011-11-30。收修改稿日期:2012-01-29。
*通讯联系人。E-mail:ananthaprasad2003@yahoo.co.in

well they are used as potent antidiabetic agents [25]. Several studies have centered around synthesis and structural studies of metal complexes of pyrazole containing ligands due to the anticarcinogenic and antiviral activity [26-29] of these donor ligands and complexes obtained from them.

The metal complexes of ligands containing both the heterocyclic systems, quinoxaline and pyrazole, have received less attention in spite of their potential metal binding properties and promising applicabilities[30-31].

Thus the aim of the present work is to synthesize and characterize 2, 3-bis (dimethyl-1*H*-pyrazol-1-yl) quinoxaline (BDMPQ) and its VO(Ⅱ), Fe(Ⅱ), Co(Ⅱ), Ni(Ⅱ) and Cu(Ⅱ) complexes.

1 Experimental

1.1 General

All the chemicals used were either of AR or chemically pure grade. IR spectra were recorded using KBr discs in the 4 000~400 cm^{-1} region on Perkin-Elmer 1600 series FTIR and in Nujol media in the 1 000~200 cm^{-1} region on a Perkin-Elmer IR spectrometer model NO.17. Electronic spectra of solids were recorded on a Cary-2390 UV-Vis-NIR spectrophotometer. The elemental analysis was carried out using Heraus-CHN-rapid analyzer. The ^{1}H-NMR spectrum was recorded on XL-200 MHz spectrometer in DMSO-d_6 solvent. Metal contents were estimated using an AAS Perkin Elmer-2380. Magnetic susceptibilities of complexes were measured on a Faraday balance (CAHN-7550-03 USA) at room temperature using $Hg[Co(NCS)_4]$ as calibrant. Diamagnetic corrections using Pascals constants and temperature independent paramagnetic corrections were computed. [32] The electrical conductance measurements were recorded using 10^{-3} mol·L^{-1} solutions in DMSO with an Elico conductivity bridge (Model CM-180) and dip type cell calibrated with KCl solutions. Total chloride content was estimated by argentometry. EPR was recorded on Jeol SE-3X spectrometer at RT and liquid nitrogen temperature.

1.2 Synthesis of the ligand

BDMPQ was prepared by a four step process involving the synthesis of quinoxaline-2, 3-dione,[33] 2, 3-dichloro quinoxaline [34] and 2, 3-dihydrazino quinoxaline.[11] Acetyl acetone (10 mL) was added to a solution of 2, 3-dihydrazino quinoxaline (0.36 g) in DMF (50 mL). The mixture was refluxed for 3 h and then cooled. The orange colored needles obtained were filtered and washed with small amounts of DMF and Methanol. Then it was dried in vacuo (Fig.1).

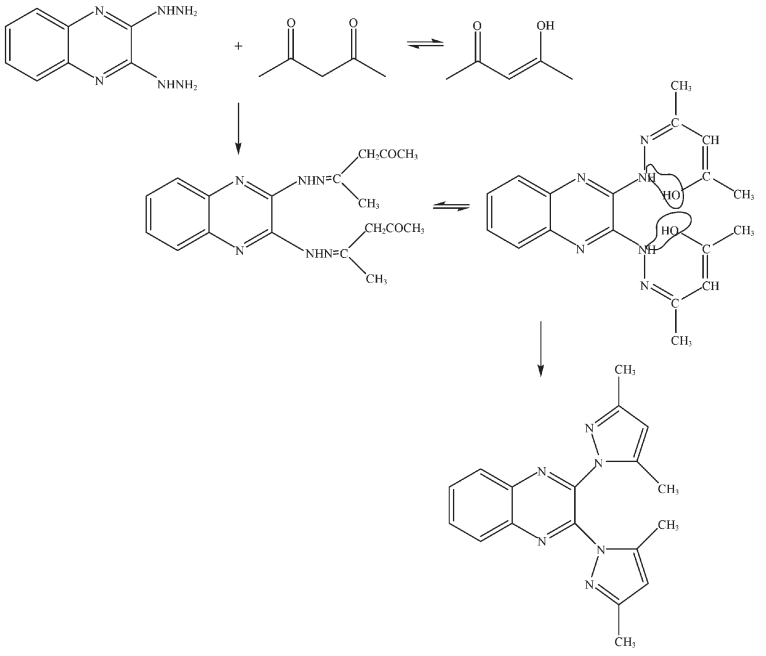


Fig.1 Proposed mechanism for the synthesis of BDMPQ

Yield: 55%, m.p. 280 ℃; UV-Vis (solid) λ_{max}: 291, 438 nm; ^{1}H NMR (DMSO-d6) δ: 2.2-2.8 (-CH_3) (12), 6.2 (=CH-) (2) and 7.3~7.8. (aromatic) (4); IR (KBr) ν: 1544($\nu_{C=N}$ quinoxaline ring), 1 504($\nu_{C=N}$ non-quinoxaline ring), 1 014 cm^{-1} (ν_{N-N}); [M+] *m/z* 318; Anal. calcd for $C_{18}H_{18}N_6$: C 67.92; H 5.66; N 26.42; found: C 67.85; H 5.60; N 26.92.

1.3 Synthesis of the complexes

The VO(Ⅱ) and Fe(Ⅲ) complexes were isolated from THF and other metal complexes were isolated from DMF. To the THF/DMF solution of divalent/trivalent metal chloride (0.001 mol) [Fe(Ⅲ) (0.163 g); Co(Ⅱ) (0.238 g); Ni(Ⅱ) (0.237 g) and Cu(Ⅱ) (0.170 g)], THF/DMF solution of BDMPQ (0.001 mol, 0.32 g) was added. The pH value of the reaction mixture was adjusted to ~7, using ammonia solution. The mixture was refluxed for 3 h. The complex precipitated was filtered in hot condition, washed with methanol, petroleum-ether and dried in vacuo. In case of VO(Ⅱ) complex vanadyl sulphate (0.162 g) was used and the same procedure was adopted. The purity of metal complexes was tested by TLC using different solvent mixtures. Yields: 50%~60%.

[(VO)(BDMPQ)SO_4]: >300 ℃; μ_{eff}: 1.9; UV-Vis (solid) λ_{max}: 445, 475, 510 nm; IR (KBr) ν: 1570, 1537, 1153, 1059, 930, 855, 648, 482 cm^{-1}. Anal. calcd for $VC_{18}H_{18}N_6O_5S$: V 10.60, C 44.91, H 3.74, N 17.46, S 6.65; found: V 10.62, C 44.84, H 3.72, N 17.41, S 6.60.

[Fe (BDMPQ)Cl_2]: >300 ℃; μ_{eff}: 4.07; UV-Vis (solid) λ_{max}: 800 nm; IR (KBr) ν:1561, 1527, 1046, 505, 453, 316 cm^{-1}. Anal. Calcd. for $FeC_{18}H_{18}N_6Cl_2$: Fe 12.58, C 48.53, H 4.04, N 18.87, Cl 15.95; found: Fe 12.50, C 48.44, H 4.01, N 18.79, Cl 15.91.

[Co (BDMPQ)Cl_2]: >300 ℃; μ_{eff}: 4.1; UV-Vis (solid) λ_{max}: 300, 354, 445~627 nm; IR (KBr) ν: 1577, 1531, 1046, 633, 514, 412, 298 cm^{-1}. Anal. Calcd. for $CoC_{18}H_{18}N_6Cl_2$: Co 13.63, C 48.21, H 4.01, N 18.75, Cl 15.84; found: Co 13.53, C 48.15, H 3.98, N 18.71, Cl 15.90.

[Ni (BDMPQ)Cl_2]: >300 ℃; μ_{eff}: 3.06; UV-Vis (solid) λ_{max}: 363, 530, 490, 636 nm; IR (KBr) ν: 1577, 1531, 1033, 625, 501, 432, 301 cm^{-1}. Anal. Calcd. for $NiC_{18}H_{18}N_6Cl_2$: Co 13.16, C 48.21, H 4.01, N 18.75, Cl 15.83; found: Co 13.08, C 48.17, H 4.03, N 18.70, Cl 15.80.

[Cu (BDMPQ)Cl_2]: >300 ℃; μ_{eff}: 2.01; UV-Vis (solid) λ_{max}: 314, 345, 530, 589, 951 nm; IR (KBr) ν: 1562, 1532, 1055, 591, 526, 465, 322 cm^{-1}. Anal. Calcd. for $CuC_{18}H_{18}N_6Cl_2$: Cu 14.03, C 47.73, H 3.95, N 18.56, Cl 15.69; found: Cu 14.57, C 47.63, H 3.95, N 18.51, Cl 15.65.

2 Results and discussion

All the metal complexes are coloured and stable to air and moisture. They decompose at high temperatures. They are soluble in DMF and DMSO and insoluble in all other common organic solvents like methanol, chloroform, acetone etc.

Elemental analysis shows that the metal to ligand ratio is 1:1 in all the complexes. The data suggest the presence of two chlorides per metal ion and also indicates the presence of one sulphate per metal ion in VO(Ⅱ) complex.

The conductance studies were carried out in 1×10^{-3} mol·L^{-1} DMF solution. The low molar conductance values of all the complexes indicate their non-electrolytic nature.

In the IR spectra of all the complexes there is an upward shift in $\nu_{C=N}$ (quinoxaline ring) and $\nu_{C=N}$ (non-quinoxaline ring) frequencies. This indicates metal binding through an NN sequence involving both the nitrogens. A shift of $\nu_{C=N}$ band to a higher frequency[35] may be attributed to ring electron delocalization in the direction which increases electron density between carbon and nitrogen, thus resulting in an increase in the bond order. This can be a direct consequence of the participation of more electronegative nitrogen atom of the azomethine function in coordination. The ν_{N-N} frequency shows an upward shift [12] in all the complexes, indicating the involvement of one of the nitrogens in bonding. In VO(Ⅱ) complex, the characteristic $\nu_{V=O}$ band is observed at 930 cm^{-1}. The non-ligand bands at 1 153, 1 059, 855 and 648 cm^{-1} found in the spectrum of this complex are consistent with mono dentate sulphate coordination.[36] The new

bands in the far-IR region of all the complexes are assigned to M-N, M-Cl vibrations.

The VO (Ⅱ) complex shows magnetic moment value of 1.9 B.M. which is well within the range expected for a d^1 configuration. The Fe(Ⅱ) complex has magnetic moment value of 4.07 B.M. which is consistent with the high-spin d^6 configuration. As trivalent iron chloride is used for the preparation of complex, the expected magnetic moment for iron (d^5 high spin state) complex is around 6.0 B.M. The observed low value accounts for four unpaired electrons suggesting reduction of the metal ion from +3 to +2 state. It may be recalled that the metal ion and the ligand were taken in 1∶2 molar ratio for the synthesis of complexes. Analytical data shows 1∶1 metal, ligand molar ratio in the complexes. This means that a part of the ligand is acting as a reducing agent while the remaining is involved in metal binding process.

The observed magnetic moments for Fe (Ⅱ) and Co (Ⅱ) with four and three unpaired electrons show certain sub-normalities, as compared to the expected values for high spin octahedral geometry. The magnetic moments can attain values up to 5.5 B.M. and 5.2 B.M. for Fe(Ⅱ) and Co(Ⅱ), respectively, due to the expected spin angular momentum and considerable orbital angular momentum in each case. The sub-normality is probably caused by the partial coupling of spins between the adjacent metal ions bonded to the quinoxaline ring nitrogens in mutually para position and with the possible extended conjugation. This phenomenon of metal-metal interaction is observed only in Fe (Ⅱ) and Co (Ⅱ) complexes and not in other complexes. The reason could be that the coupling of spins in the high spin octahedral complexes formed by BDMPQ is taking place only through the unpaired electrons present in t_{2g} orbitals of the metal ion. Fe(Ⅱ) and Co(Ⅱ) complexes have partially filled t_{2g} orbitals with the electronic configurations $(t_{2g})^4(e_g)^2$ and $(t_{2g})^5(e_g)^2$ respectively, while Ni(Ⅱ) and Cu(Ⅱ) complexes have completely filled t_{2g} orbitals, with $(t_{2g})^6$ $(e_g)^2$ and $(t_{2g})^6$ $(e_g)^3$ configurations, respectively.

The observed magnetic moment of Cu(Ⅱ) complex is 2.01 B.M., which is well within the range expected for a d^9 configuration.

The electronic spectrum of VO (Ⅱ) complex exhibits the bands at 445, 475, 510 nm which are attributed to $^2B_2 \rightarrow {}^2A_1$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$ transitions, respectively. These are consistent with octahedral geometry. The electronic spectrum of Fe(Ⅱ) complex exhibits a weak band at 800 nm which is reasonably assigned to $^5T_2 \rightarrow {}^5E$ transition and is in agreement with an octahedral geometry around Fe(Ⅱ) ion. The electronic spectrum of Co(Ⅱ) complex exhibits a multi structured band with two components in the region 445~627 nm, which are due to $^4T_1 \rightarrow {}^4T_1$ (P) and $^4T_1 \rightarrow {}^4T_1$ transitions, respectively. The absorptions at 300, 354 nm are assigned to charge transfer. The electronic spectrum of Ni(Ⅱ) complex exhibits bands at 363 and 530 nm which are attributed to spin allowed $^3A_2 \rightarrow {}^3T_1$(P) and $^3A_2 \rightarrow {}^3T_1$ transitions, respectively. The bands at 490 and 636 nm are assigned to two spin forbidden $^3A_2 \rightarrow {}^1T_2$ and $^3A_2 \rightarrow {}^1E$ transitions, respectively. The electronic spectrum of Cu (Ⅱ) complex exhibits bands at 314, 345, 530, 589, 951 nm. The first two bands are assigned to charge transfer transitions, the third, fourth and fifth bands are assigned to $^2B_1 \rightarrow {}^2E$, $^2B_1 \rightarrow {}^2B_2$ and $^2B_1 \rightarrow {}^2A_1$ transitions, respectively.

The ESR spectrum of VO (Ⅱ) complex (Fig.2) consists of well resolved hyperfine structure which is seen in the form of 8+8=16 line spectrum. The central intense 8 lines belong to g component and the low field and high field weak 8 lines belong to $g_{\parallel}$ component. Since some of the hyperfine lines

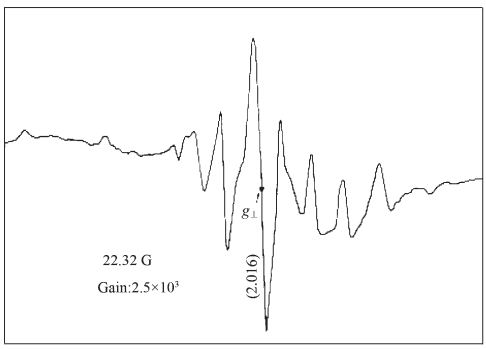


Fig.2 ESR spectrum of [(VO)(BDMPQ)SO_4]

belonging to parallel components overlap with those of perpendicular component only 13 lines can be seen clearly. It is possible to separate perpendicular components from parallel components by noting down hyperfine separation from the central intense line and also from the weak lines. Thus the g values and A values calculated are ($g_{//}$=2.048 5, $g_{\perp}$=2.016, $A_{//}$= 132.093 8 G, $A_{\perp}$=68.280 G). Both the g values are on the higher side with a special feature of $g_{//}$ being higher than $g_{\perp}$($g_{//}>g_{\perp}$) which suggests major distortion from octahedral geometry [37]. The A_{iso} value calculated from ($A_{//}+A_{\perp}$)/2 is 100.5 G. As $g_{//}>g_{\perp}$ the Δg value turns out to be -ve in this case.

The ESR spectrum of Cu(Ⅱ) complex (Fig.3) seems to be narrow with a better resolved hyperfine structure on the parallel component of g-tensor. The values evaluated for g tensor are $g_{//}$=2.398, $g_{\perp}$= 2.0825. The hyperfine coupling constant $A_{//}$ is 135 G which is higher.

The observed value of α^2 (0.85) of the complex is less than unity, which indicates that the complex has some covalent character in the ligand environment. The spin-orbit coupling constant, λ value (494 cm^{-1}) calculated using the relations, $g_{av}=1/3[g_{//}+2g_{\perp}]$ and $g_{av}=2[1-2\lambda/(10D_q)]$, is less than the free Cu(Ⅱ) ion (832 cm^{-1}) which also supports covalent character of ML bond in the complex. The sharper resolution in hyperfine signals indicates greater polarity of the bond.

These observations are characteristic of axially distorted octahedral symmetry for Cu(Ⅱ) complex in which the unpaired electron is present in the $d_{x^2-y^2}$ orbital [38]. The axial symmetry parameter G is 4.8 which suggests negligible exchange interactions.

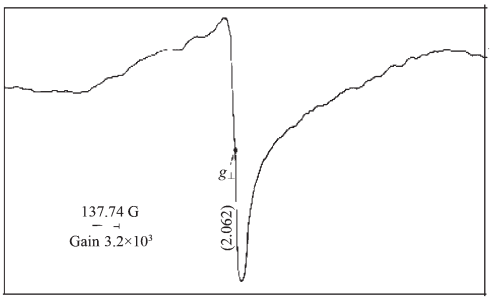


Fig.3 ESR spectrum of [(Cu)(BDMPQ)Cl_2]

3 Conclusions

Based on analytical, spectral and magnetic data, it is proposed that BDMPQ is behaving as neutral bis-bidentate NN donor and is forming polynuclear complexes.

The proposed structures are given in Fig.4 & 5.

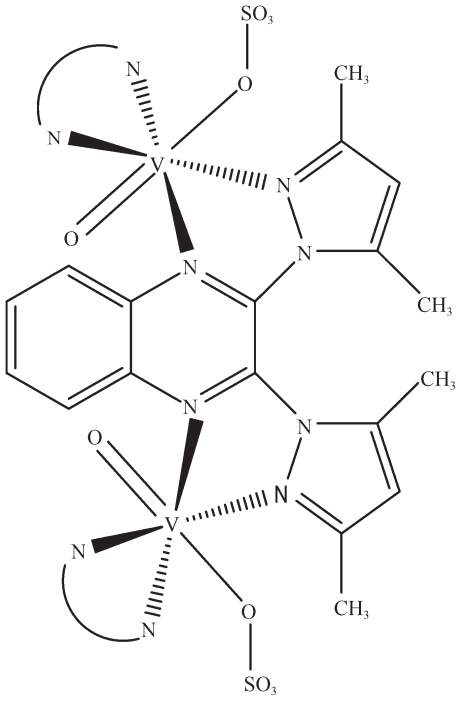
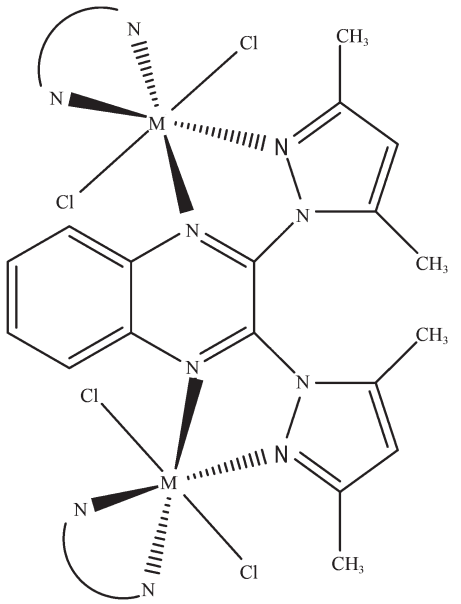


Fig.4 Proposed structure of [(VO)(BDMPQ)SO_4]



M=Fe(Ⅱ), Co(Ⅱ), Ni(Ⅱ), Cu(Ⅱ)

Fig.5 Proposed structure of [(M)(BDMPQ)Cl_2]

Acknowledgements: The authors are grateful to RSIC, IIT Madras for UV-Vis-NIR spectral facilities.

References:

[1]Nikam S S, Cordon J J, Rafferty M F J, et al. *J. Med. Chem.*, **1999**,**42**:2266-2271

[2]Auberson Y P, Bischoff V, Veenstra S J, et al. *Bioorg. Med. Chem. Lett.*, **1998**,**8**:65-70

[3]Auberson Y P, Acklin P, Veenstra S J, et al. *Bioorg. Med. Chem. Lett.*, **1998**,**8**:71-74

[4]Kim K S, Qian L G, Moreland S, et al. *Bioorg. Med. Chem. Lett.*, **1993**,**3**:2667-2670

[5]Kim K S, Qian L G, Miller A V, et al. *J. Med. Chem.*, **1993**, **36**:2335-2342

[6]Perez-Melero C, Maya A B S, Medarde M, et al. *Bioorg. Med. Chem. Lett.*, **2004**,**14**:3771-3774

[7]Hui X, Desrivot J, Figadere B, et al. *Bioorg. Med. Chem. Lett.*, **2006**,**16**:815-820

[8]Li J, Chen J, Zhang V V, et al. *Bioorg. Med. Chem.*, **2006**,**14**: 5527-5534

[9]Dianzhong F, Wang M, Wang B. *Polyhedron,* **1992**,**11**:1109-1112

[10]Dianzhong F, Yukin Z, Wang V. *Polyhedron*, **1992**,**11**:1113-1116

[11]Rani D S, Lakshmi P V A, Jayatyagaraju V. *Trans. Met. Chem.*, **1994**,**19**:75-77

[12]Ananthalakshmi P V, Sandhyarani D, Jayatyagaraju V. *Asian J. Chem.*, **1995**,**7**:296-306

[13]Sandhyarani D, Jayatyagaraju V, Ananthalakshmi P V. *Indian J. Chem.*, **1999**,**38**A:385-387

[14]Lakshmi P V A, Reddy P S, Raju V. *J. Bull. Chem. Soc. Ethiop*. **2008**,**22**(3):385-390

[15]Lakshmi P V A, Shyamala B S, Raju V J. *Polish J. Chem*. **2009**,**83**:1555-1563

[16]Lakshmi P V A, Reddy P S, Raju V J. *Spectrochim. Acta A*: *Mol. Biomol. Spectrosc*. **2009**,**74**:52-57

[17]El-Kashef H S, El-Emary T I, Gasquet M, et al. *Pharmazie*, **2000**,**55**(8):572-576

[18]Taha M L, Moukha-Chafiq O, Lazrok H B, et al. *Nucleosides Nucleotides & Nucleic Acid*, **2001**,**20**:955-958

[19]Vicentini C, Forlani G, Manfrini M, et al. *J. Agric. Food Chem.*, **2002**,**50**:4839-4845.

[20]Brozozonski Z, Saczawski F. *Eur. J. Med. Chem.* **2002**,**37** (9):709-720

[21]Hough L B, Nalwalk J W, Stadel R, et al. *J. Pharmacol. Ex. Ther.*, **2002**,**303**(1):314-322

[22]Jung J C, Watkins E B, Avery M A. *Heterocycles*, **2005**,**65** (1):77-94

[23]Palaska E, Aytemir M, Uzbay T, et al. *Eur. J. Med. Chem.*, **2001**,**36**(6):539-543

[24]Bansal E, Srivastava V K, Kumar A. *Eur. J. Med. Chem.*, **2001**,**36**(1):81-92

[25]Ahn J H, Kim H M, Jung S H, et al. *Bioorg. Med. Chem. Lett.*, **2004**,**14**(17):4461-4465

[26]Berta H, Vukadin M L, Petra B, et al. *Australian J. Chem.*, **2010**,**63**(11):1557-1564

[27]Seubert C K, Sun Y, Lan Y, et al. *Eur. J. Inorg. Chem.*, **2011**,**2011**(11):1768-1775

[28]Türkoglu G, He inemann F W, Burzlaff N. *Dalton Trans.*, **2011**,**40**(17):4678-4686

[29]Nagababu P, Naveena L L J, Satyanarayanaa S, et al. *J. Iran. Chem. Soc.*, **2009**,**6**(1):145-152

[30]Sandhyarani D, Jayatyagaraju V, Ananthalakshmi P V. *Indian J. Chem.*, **1999**,38A: 843-846

[31]Srinivasa B, Naveen V K, Gurunath S K, et al. *Eur. J. Med. Chem.*, **2010**,**45**(2):455-462

[32]Figgis B N, Lewis J. *Modern Coordination Chemistry*. New York: Interscience Inc, **1960**.

[33]Philips M A. *J. Chem. Soc.*, **1928**:2393-2399

[34]Cheeseman G W H, Rafiq M. *J. Chem. Soc* (C)., **1971**:452-454

[35]Arali V K H, Revankar V K, Mahale V B, et al. *Tran. Met. Chem.*, **1994**,**19**:57-60

[36]Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. 3rd *Ed.*, New York: Wiley, **1997**.

[37]Dash D C, Mahapatra A, Mahapatra R K, et al. *Indian J. Chem.*, **2008**,47A:1009-1013

[38]Raman N, Johnson R S. *J. Serb. Chem. Soc.*, **2007**,**72**(10): 983-992