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NOVEL METAL (II) OXINATES: SYNTHESIS AND ANTIMICROBIAL STUDIES

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Abstract

By Mannich condensation reaction of 5-(4-chlorophenyl)-3H-[1,3,4]-oxadiazole-2-thione with formaldehyde and 5-aminoquinolin-8-ol hydrochloride, a novel ligand: 5-(4-chlorophenyl)-3-(((8-hydroxyquinolin-5-yl)amino)methyl)-3H-[1,3,4]-oxadiazole-2-thione was synthesized. Using transition metal (II) salts, some metal (II) oxinates of novel ligand were prepared. All newly synthesized compounds were analyzed by spectroscopic techniques and elemental analysis. Moreover, all compounds were screened for in vitro antimicrobial activity against representative panel of two Gram-positive and two Gram-negative bacterial strains and two strains of fungi taking ciprofloxacin as a reference standard. Novel compounds showed moderate to good antibacterial and antifungal activity.

Keywords 5-(4-chlorophenyl)-3H-[1,3,4]-oxadiazole-2-thione, oxine, Mannich condensation reaction, metal (II) oxinates, antibacterial and antifungal activity

Introduction

There is always requirement of novel antimicrobial agents having new structural characteristic and broad-spectrum of antimicrobial activity against resistant pathogens due to multidrug resistance of bacteria[I] and worldwide spread of drug- resistant pathogens[II]. Clubbed molecules possessing assorted pharmacophores may furnish good biological properties[III].

8-Hydroxyquinoline is nitrogen containing heterocyclic compound and known as oxine also. It is a chelating agent[IV] and has been used for the quantitative determination and separation of metal ions[V]. The complex formed between oxine and a metal ion is known as oxinate. Owing to diverse pharmacological and biological activities, the role of 8-hydroxyquinoline derivatives (8HQs) is noteworthy. Various biological properties like antiallergic, antiamoebic, anticancer, antimalarial, antineoplastic, antileishmanial and antifungal efficiency[V-XIII] have been reported. Antimicrobial properties like antibacterial[XIV-XVI], antimalarial[XVII-XIX], antiviral[XX], antitubercular[XXI] and antidental plaque activities[XXII-XXIII] of 8HQ and its derivatives have also been reported. 8-Hydroxyquinoline, at concentrations of 10-50 µg/mL, rapidly and selectively inhibits RNA synthesis in fission yeast. The effects of

8-hydroxyquinoline are remarkably similar to those of the antibiotic lomofungin[XXIV]. Iron bound to the lipophilic chelator (8HQ), results in substantial DNA-strand breakage of cultured human lung cells[XXV]. The Fe-8HQ complex acts as a cytostatic drug[XXVI]. Due to high lipophilicity, 8HQ can penetrate bacterial cell membrane and arrive at metal-binding site of bacterial enzymes. The metal-8HQ complex dissociates into a 1:1 ratio of 8HQ-metal charged complex and 8HQ free ligand[XXVII]. The charged 8HQ metal complex can bind and block the metal-binding sites on bacterial enzymes that offer the antimicrobial activity[XXVIII]. In addition, the dissociated free ligand of 8HQ possesses high chelating ability that could bind metallic prosthetic groups of microbial enzymes thereby leading to the inhibition of enzymatic activity[XXVII]. 8HQ-uracil metal complexes exhibited growth inhibition against many strains of Gram-positive and Gram-negative bacteria including resistant pathogens, such as *S. aureus*, *Enterococcus faecalis*, and *Candida albicans*[XXIX].

Oxadiazole moiety also is a fruitful source of bioactivity in the field of medicinal chemistry. It has wide-spectrum of biological and pharmacological activities. So many oxadiazole derivatives have shown therapeutic values like antimicrobial[XXX-XXXVII], antituberculosis[XXXVII-XXXIX], anticonvulsant[XL], CNS Stimulant[XLI], anticancer[XLII], anti-inflammatory[XLIII], antihypertensive[XLIV], hypnotic and sedative activities[XLV]. Quinoline-oxadiazole hybrid derivatives have shown potent antibacterial as well as antifungal activities[XLVI].

So, we were interested to club two different moieties-oxine and oxadiazole for enhancement of biological property. This research work presents the synthesis, characterization and antimicrobial study of a novel heterocyclic ligand, 5-(4-chlorophenyl)-3-(((8-hydroxyquinolin-5-yl)amino)methyl)-3H-[1,3,4]-oxadiazole-2-thione (CHHOT) and some transition metal oxinates of it.

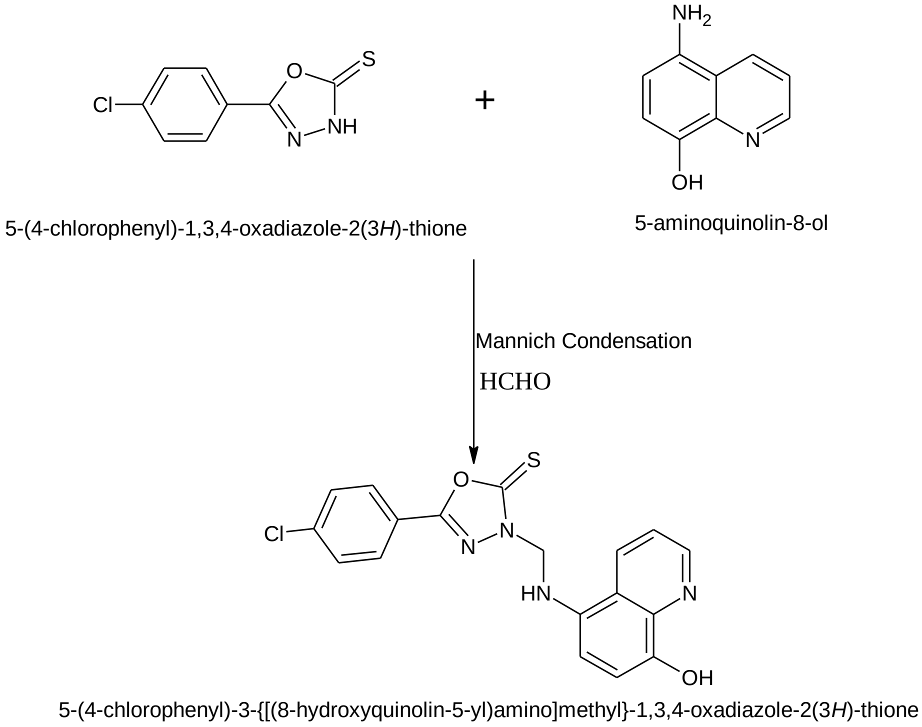
Methodology

Experimental

Melting points were determined by standard open capillary method and are uncorrected. Elemental analysis was performed with Perkins Elmer (USA) 2400-II CHN analyzer. The FT-IR spectra were recorded on Perkin Elmer Spectrum GX spectrophotometer using KBr pellets. The ^{1}H NMR spectra were recorded on Bruker 400 MHz instrument using DMSO-d6 as solvent and TMS as internal reference standard. Magnetic moments were determined by the Gouy method using mercury tetrathiocyanatocobaltate(II) $[HgCo(NCS)_4]$ as a calibrant and the diamagnetic corrections were made using Pascal's constant. The metal contents of the oxinates were determined using EDTA titration after decomposing the organic matter with $HClO_4$, H_2SO_4 and HNO_3 (1:1.5:2.5) mixture[XLVII].

Synthesis of a novel ligand (CHHOT)

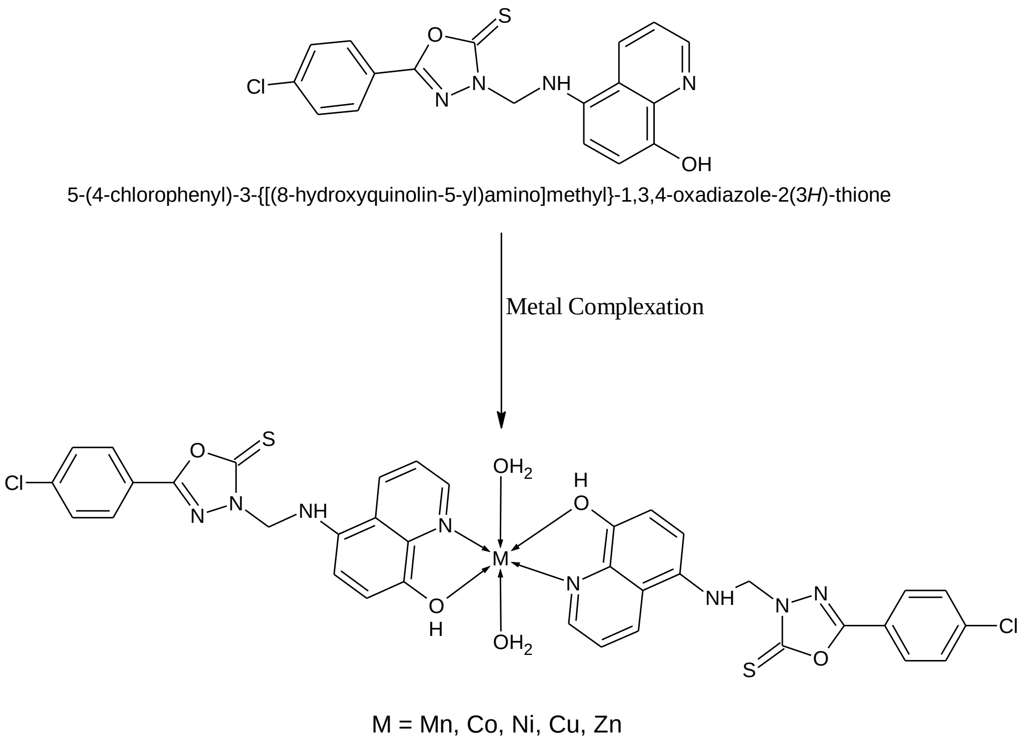
5-(4-chlorophenyl)-3H-[1,3,4]-oxadiazole-2-thione was prepared as per reported procedures[XLVIII-XLIX]. Then, by Mannich condensation reaction[XLVIII-L] of 5-(4-chlorophenyl)-3H-[1,3,4]oxadiazole-2-thione with formaldehyde and 5-aminoquinolin-8-ol hydrochloride, a novel ligand: 5-(4-chlorophenyl)-3-(((8-hydroxyquinolin-5-yl)amino)methyl)-3H-[1,3,4]-oxadiazole-2-thione (CHHOT) was prepared (Scheme 1). A mixture of 5-aminoquinolin-8-ol hydrochloride (0.01 mol), 5-(4-chlorophenyl)-3H-[1,3,4]-oxadiazole-2-thione (0.01 mol), formaldehyde (0.03 mol) and few drops of concentrated hydrochloric acid in isopropanol (50 mL) was stirred and warmed on the steam bath for about ten hours. End of reaction was monitored by TLC. Then, isopropanol was distilled out and water was added to extract product into aqueous layer. Methylene dichloride (50 mL) was charged to extract impurities and aqueous layer basified using 10% NaOH solution and extract product in methylene dichloride (2 X 50 mL). Finally organic layer dried over Na_2SO_4 and distilled out atmospherically and finally apply vacuum to get a product. The physicochemical parameters and characteristic FT-IR frequencies data are presented in Tables 1 and 2 respectively.



Scheme 1

General procedure for the synthesis of metal complexes

Metal (II) oxinates of novel ligand CHHOT were synthesized using reported procedure[LI]. A hot solution of transition metal (II) salt (2.5 mmol) in 50% aqueous formic acid (2.5 mL) was added drop by drop with continuous stirring to the hot 20% aqueous formic acid solution (20 mL) of CHHOT (5 mmol). Using 50% NH_4OH solution, pH was adjusted ~8.5 and resultant mixture was further digested for 4 hours in the water bath (Scheme 2). Thus obtained product was filtered, washed with hot water, and subsequently with small quantity of ethanol, acetonitrile and dried in a vacuum desiccator. The physicochemical parameters and characteristic FT-IR frequencies of metal (II) oxinates are presented in Tables 1 and 2 respectively.



Scheme 2

***In vitro* evaluation of antibacterial and antifungal activity**

All newly synthesized compounds were screened for in vitro antimicrobial activity against the representative panel of two Gram-positive and two Gram-negative bacterial strains and two strains of fungi[LII] taking ciprofloxacin as a reference standard drug. Agar cup plate method was used to evaluate antimicrobial activities. Antibacterial activities were evaluated against Gram-positive bacterial strains: *Staphylococcus aureus*, *Bacillus subtilis* and Gram-negative bacterial strains: Escherichia coli, *Pseudomonas aeruginosa* at 50 µg/mL concentration. Zone of inhibition was observed in mm. Antifungal activities were evaluated against fungal strains: *Aspergillus niger* and *Aspergillus flavus* at 1000 ppm concentration. Newly synthesized compounds exhibited moderate to good inhibitory action against test organisms.

Results and Discussion

Novel ligand, 5-(4-chlorophenyl)-3-(((8-hydroxyquinolin-5-yl)amino)methyl)-3H-[1,3,4]-oxadiazole-2-thione (CHHOT) and its octahedral metal (II) oxinates (1:2 metal to ligand ratio) were synthesized as per Scheme 1 and 2 respectively and characterized. In the IR spectrum of novel ligand CHHOT, absorption bands at 3294 cm^{-1} and 1408(s) cm^{-1} are due to O-H stretching vibration and O-H bending vibration respectively of 8HQ moiety. The inflections around 2920 cm^{-1} and 2850 cm^{-1} are attributed to asymmetric and symmetric stretching vibration respectively of $-CH_2$ group. The supporting band at 1450 cm^{-1} is also appeared due to CH_2 bending vibrations. The bands at 1593 cm^{-1} for C=N, at 1500 cm^{-1} for C=C and at 1478 cm^{-1} for C-C bond, assigned to the aromatic skeletal stretching vibrations of parent heterocyclic ring[LIII]. The N-H stretching vibration appeared at 3400(s) cm^{-1}, while N-H and C-N bending vibrations appeared at 1657 and 1263 cm^{-1} respectively. On comparing IR spectra of ligand and its metal (II) oxinates showed some significant characteristic differences[LIV]. One of the significant differences to be anticipated was the presence of more broadened band in the region of 2700-3400 cm^{-1} for the oxinates. Since the oxygen atom of the OH group of the ligand forms a coordination bond with the metal ions, the broadening of this band may be credited to the presence of coordinated water molecules[LV]. The band due to the C=N stretching vibration at around 1593 cm^{-1} was shifted to lower frequency, whereas, the band at 1408 cm^{-1} in the spectrum of CHHOT assigned to in-plane OH deformation was shifted towards higher frequency in the spectra of the oxinates owing to the formation of M-O bond[LV]. This has been further confirmed by the presence of weak band at 1092 cm^{-1} for C-O-M stretching vibration, while bands around ~763 cm^{-1} and ~520 cm^{-1} correspond to the N→M vibrations[LVI]. All these characteristics features of the FT-IR studies reveal the formation of novel ligand CHHOT and metal (II) oxinates of it. Structural analysis of the ligand was also carried out with the help of ^{1}H NMR using DMSO-d6 at room temperature. In case of ^{1}H NMR spectrum of CHHOT exhibited 3.80 (d, 2H, $-CH_2-$), 5.82 (t, 1H, NH), 9.00 (dd, 1H, H2 of quinoline), 9.71 (bs, 1H, OH). ^{1}H-NMR spectrum of $[Zn(CHHOT)_2]$ exhibited 3.91 (d, 4H, $-CH_2-$), 5.81 (t, 2H, NH), 8.90 (dd, 2H, H2 of quinoline). By comparing the ^{1}H-NMR data of the ligand and the metal oxinate of Zn(II), it was concluded that a broad singlet at δ 9.71 ppm due to the OH proton[LVII] will disappear in the spectrum of Zn(II) complex suggested that this proton has been lost due to coordination of oxygen atom to the metal ion[LVIII]. The H2 signal of the Zn(II) complex appeared at low magnetic field (δ 9.00) compared to that of ligand (δ 8.94), suggesting the involvement of N1 in the formation of complex. The absorptions of all quinoline protons are slightly downfield shifted; except H7 which is upfield shifted[LIX] which further indicate the coordination of oxygen atom to metal ion. The results of the magnetic moment values (Table 1) favour the octahedral geometry of all the metal (II) oxinates.

Novel ligand CHHOT and its metal (II) oxinates showed moderate to good antibacterial and antifungal activities. This might be owing to the additive biological effect-lipophilicity of parent molecules and/or due to the metal chelating properties. Of the studied oxinates, copper (II) oxinate exhibited better activity which was comparable to Ciprofloxacin, but was found less active than novel ligand CHHOT.

Table 1 Physicochemical parameters of ligand (CHHOT) and its metal (II) oxinates

Empirical formula of ligand / metal complexes	Mol. Wt.	% Yield	m.p. (°C)	Elemental Analysis calc. % (found %)						μ_{eff} B.M. (expected)
				C	H	N	S	Cl	metal	
CHHOT $C_{18}H_{13}N_4O_2SCl$	384.5	75	180	56.17 (56.10)	3.38 (3.30)	14.56 (14.50)	8.32 (8.30)	9.23 (9.20)	--	--
$[Mn(CHHOT)_2(H_2O)_2]$ $C_{36}H_{28}MnN_8O_6S_2Cl_2$	858	68	>300	50.34 (50.30)	3.26 (3.25)	13.05 (13.00)	7.46 (7.45)	8.27 (8.25)	6.41 (6.40)	5.63 (5.2-6.0)
$[Co(CHHOT)_2(H_2O)_2]$ $C_{36}H_{28}CoN_8O_6S_2Cl_2$	862	65	>300	50.11 (50.10)	3.24 (3.20)	12.99 (12.91)	7.42 (7.40)	8.23 (8.20)	6.84 (6.80)	4.70 (4.4-5.2)
$[Ni(CHHOT)_2(H_2O)_2]$ $C_{36}H_{28}NiN_8O_6S_2Cl_2$	862	64	>300	50.11 (50.09)	3.24 (3.21)	12.99 (12.90)	7.42 (7.39)	8.23 (8.20)	6.84 (6.81)	3.18 (2.9-3.4)
$[Cu(CHHOT)_2(H_2O)_2]$ $C_{36}H_{28}CuN_8O_6S_2Cl_2$	866.5	67	>300	49.85 (49.80)	3.23 (3.20)	12.92 (12.90)	7.38 (7.35)	8.19 (8.15)	7.32 (7.30)	1.89 (1.7-2.2)
$[Zn(CHHOT)_2(H_2O)_2]$ $C_{36}H_{28}ZnN_8O_6S_2Cl_2$	868	64	>300	49.76 (49.70)	3.22 (3.20)	12.90 (12.85)	7.37 (7.30)	8.17 (8.15)	7.48 (7.42)	diamagnetic

Table 2 FT-IR spectral frequencies of ligand (CHHOT) and its metal (II) oxinates (in cm^{-1})

Compound	ν(O–H)	ν(C=N)	ν(N→M)	ν(N→M)	ν(O→M)	ν(C-O-M)
$[Mn(CHHOT)_2(H_2O)_2]$	3365(br)	1564	522	766	1422	1090
$[Co(CHHOT)_2(H_2O)_2]$	3374(br)	1572	520	762	1423	1091
$[Ni(CHHOT)_2(H_2O)_2]$	3368(br)	1570	519	770	1420	1093
$[Cu(CHHOT)_2(H_2O)_2]$	3373(br)	1576	523	772	1425	1088
$[Zn(CHHOT)_2(H_2O)_2]$	3370(br)	1571	520	763	1421	1092
CHHOT	3294	1593	--	--	--	--

Table 3 Antimicrobial activities of ligand (CHHOT) and its metal (II) oxinates

Compound	Zone of inhibition (mm)[a]					
	Antibacterial activity				Antifungal activity	
	S.aureus	*B.subtillis*	*E.coli*	*P.aerugionsa*	*A.niger*	*A.flavus*
Oxine	24	22	26	22	21	19
CHHOT	32	33.5	30	29	37.5	34
$[Mn(CHHOT)_2(H_2O)_2]$	16	12	14	14	13	11
$[Co(CHHOT)_2(H_2O)_2]$	17	15.5	16	17.5	14	18
$[Ni(CHHOT)_2(H_2O)_2]$	19.5	16	14	19	16	15
$[Cu(CHHOT)_2(H_2O)_2]$	21	23.5	22	21	21.5	20
$[Zn(CHHOT)_2(H_2O)_2]$	14.5	16	11	12.5	12	15
Ciprofloxacin	28	42	26	35	44	38

[a] : results are taken in triplicate and average are shown.

Conclusion

Newly synthesized compounds displayed moderate to good antibacterial and antifungal activity. These results concluded that the novel ligand CHHOT and its metal (II) oxinates have the property to kill the microorganisms in some extent when compared with standard drug-ciprofloxacin; it gives a future scope to study the mechanism of action and would be worthy of further research.

References

I Li S, Wang Z, Wei Y, Wu C, Gao S, Jiang H, Zhao X, Yan H & Wang X, Biomaterials, 34, **2013**, 902.

II Sun X-Y, Wu R, Wen X, Guo L, Zhou C-P, Li J, Quan Z-S & Bao J, Eur J Med Chem, 60, **2013**, 451.

III Muregi FW, Ishih A, Drug Develop Res, 71, **2010**, 20.

IV Rubbo SD, Albert A, Gibson MI, Br J Exp Pathol, 31(3), 1950, 425–441.

V Albrecht M, Fiege M, Osetska O, Coord Chem Rev, 252(8–9), **2008**, 812–824.

VI Block JH, Wilson and Giswolid's Textbook of Organic Medicinal and Pharmaceutical Chemistry, 11th Ed, Lippincott Williams and Wilkins, Philadelphia, **2005**.

VII Short BR, Vargas MA, Thomas JC, O'Hanlon S, Enright MC, J Antimicrob Chemother, 57(1), **2006**, 104–109.

VIII Vanparia SF, Patel TS, Sojitra NA et al, Acta Chim Slov, 57(3), **2010**, 600–667.

IX Pierre JL, Baret P, Serratrice G, Curr Med Chem, 10, **2003**, 1077.

X Singh S, Bharti N, Mohapatra PP, Chem Rev, 109, **2009,** 1900.

XI Mekheimer R, Ahmed EK, Khattab AF, Bull Chem Soc Japan, 66, **1998,** 2936.

XII Yamato M, Ando J, Sakaki K et al, J Med Chem, 35, **1992**, 267.

XIII Tõugu V, Palumaa P, Coord Chem Rev, 256(19–20), **2012**, 2219–2224.

XIV Pavlov A, Takuchev N, Georgieva N, Biotechnol Biotechnol Equip, 26(1), **2011**, 164–169.

XV Jeon JH, Lee CH, Lee HS, J Korean Soc Appl Biol Chem, 52(2), **2009**, 202–205.

XVI Ahmed SM, Ismail DA, J Surf Deter, 11(3), **2008,** 231–235.

XVII Strobl JS, Seibert CW, Li Y et al, J Parasitol, 95(1), **2009**, 215–223.

XVIII Scheibel LW, Adler A, Mol Pharmacol, 22(1), **1982**, 140–144.

XIX Madrid PB, Sherrill J, Liou AP, Weisman JL, Derisi JL, Guy RK, Bioorg Med Chem Lett, 15(4), **2005**, 1015–1018.

XX Moret V, Dereudre-Bosquet N, Clayette P et al, Bioorg Med Chem Lett, 16(23), **2006**, 5988–5992.

XXI Darby CM, Nathan CF, J Antimicrob Chemother, 65(7), **2010**, 1424–1427.

XXII Warner VD, Musto JD, Sane JN, Kim KH, Grunewald GL, J Med Chem, 20(1), **1977**, 92–96.

XXIII Tanzer JM, Slee AM, Kamay B, Scheer E, Antimicrob Agents Chemother, 13(6), **1978**, 1044–1045.

XXIV Fraser RSS, Creanor J, Eur J Biochem, 46, **1974**, 67-73.

XXV Leanderson P, Tagesson C, Carcinogenesis, 17, **1996**, 545.

XXVI Hecht SM, Fed Proc, 45(12), **1986**, 2784–2791.

XXVII Anjaneyulu Y, Rao RP, Swamy RY, Eknath A, Rao KN, Proc Ind Acad Sci (Chem Sci), 91(2), **1982**, 157–163.

XXVIII Albert A, Gibson MI, Rubbo SD, Br J Exp Pathol, 34(2), **1953**, 119–130.

XXIX Srisung S, Suksrichavalit T, Prachayasittikul S, Ruchirawat S, Prachayasittikul V, Int J Pharmacol, 9(2), **2013**, 170–175.

XXX Moustafa AH, Saad HA, Shehab WS, El-Mobayed MM, Phosphorus, Sulfur, Silicon & the Related Elements, 183(1), **2008**, 115-135.

XXXI Kadi AA, El-Brollosy NR, Al-Deeb OA, Habib EE, Ibrahim TM, El- Emam AA, Eur J Med Chem, 429(2), **2007**, 235-242.

XXXII Lohray BB, Lohray VB, Srivastava BK, Kapadnis PB, Pandya P, Bioorg Med Chem, 12, **2004**, 4557-4564.

XXXIII Lohray BB, Lohray VB, Srivastava BK, Gupta S, Solanki M, Kapadnis PB, Takale V, Pandya P, Bioorg Med Chem Lett, 14, **2004**, 3139-3142.

XXXIV Weidner-Wells M, Werblood HM, GoldschmidtR, Bush K, Foleno BD, Hilliard JJ, Melton J, Wira E, Macielag MJ, Bioorg Med Chem Lett, 14, **2004**, 3060-3072.

XXXV Şahin G, Palaska E, Ekizoğlu M & Özalp M, Il Farmaco, 57, **2002**, 539.

XXXVI Chawla R, Arora A, Parameswaran MK, Sharma PC, Michael S & Ravi TK, Synthesis, 181, **2010**, 23.

XXXVII Patel RV, Patel PK, Kumari P, Rajani DP & Chikhalia KH, Eur J Med Chem, 53, **2012**, 41.

XXXVIII Küçükgüzel ŞG, Oruç EE, Rollas S, Şahin F & Özbek A, Eur J Med Chem, 37, **2002**, 197.

XXXIX Patel R, Kumari P & Chikhalia K, Medicinal Chemistry (Shariqah, United Arab Emirates), **2012**.

XL Ram VJ, Pandey HN, J Ind Chem Soc, 51, **1974**, 634–637.

XLI Dubey AK, Sangwan NK. Ind J Chem, 33B, **1994**, 1043–1047.

XLII Sun J, Zhu H, Yang Z-M & Zhu H-L, Eur J Med Chem, 60, **2013**, 23.

XLIII Ramalingam T, Deshmukh AA, Sattur PB, Naik SR, J Ind Chem Soc, 58, **1981**, 269–271.

XLIV Ponticello GS, Engelhardt EL, Baldwin JJ, J Heterocyclic Chem, 17, **1980**, 425–427.

XLV Adelstein GW, Yen CH, Dajani EZ, Bianchi RG, J Med Chem, 19, **1976**, 1221–1225.

XLVI Modh RP, Shah Dhruvin & Chikhalia KH, Ind J Chem, 52B(10), **2013**, 1318-1324.

XLVII Jeffery GH, Bassett J, Mentham J, Vogel's Text Book of Quantitative Inorganic Analysis, 6th Ed., Longman, Harlow, **1989**.

XLVIII Mamolo MG, Zampieri D, Vio L, Fermeglia M, Ferrone M, Pricl S, Scialino G,Banfi E, Bioorg Med Chem, 13, **2005**, 3797.

XLIX Aydogan F, Turgut Z, Olcay N, Erdem SS, Turk J Chem, 26, **2002**, 159.

L Sahoo PK, Sharma R, Pattanayak P, Med Chem Res, 19, **2010**, 127.

LI Bax R, Mullan N, Verhuef J, Int J Antimicrob Agent, 16, **2000,** 51-59.

LII Hawkey P, Lewis DA, Medical Bacteriology A Practical Approach (Oxford University Press, United Kingdom), **2004**.

LIII Silverstein RM, Webster FX, Spectrometric Identification of Organic Compounds, 6^{th} Ed, Wiley Interscience, New York, **2004**.

LIV Nakamoto K, Infrared Spectra of Inorganic and CoordinationCompounds, Part B, 5th Ed, Wiley Interscience, New York, **1997**.

LV Sadasivam V, Alaudeen M, Ind J Chem, 46A, **2007,** 1959.

LVI Charles RG, Frieser HF, Priedel R et al, Spectrochim Acta, 8, **1956,** 1.

LVII Satpathy KC, Pande AK, Mishra R et al, Synth React Inorg Met-Org Nano-Met Chem, 21, **1991,** 531.

LVIII Kidric J, Hadzi D, Kocjan D et al, Org Magn Reson, 15, **1981,** 280.

LIX Iggo JA, NMR Spectroscopy in Inorganic Chemistry, Oxford University Press, New York, **1999**

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