| ISSN: 2582-7219 | www.ijmrset.com |

| Volume 1, Issue 1, November 2018 |

Synthetic and Biocidal Studies of Cu-Hydrazone Complexes

[1]Nitin Gupta, [2]S.M. Nafees & [3]Seema Agarwal

[1]Assistant Professor, Dept. of Chemistry, Government College, Kota, India

[2,3]Associate Professor, Dept. of Chemistry, Government College, Kota, India

ABSTRACT: The hydrazones of nonsteroidal anti-inflammatory drugs (NSAIDs) diclofenac and ibuprofen are synthesized with aldehydes of pyridine and imidazole and are characterized by ^{1}H, ^{13}C and mass spectroscopy. Cu(II) complexes of hydrazones constructed from these ligands possess square planar geometry for bidentate diclofenac-hydrazone and tridentate ibuprofen-hydrazone conjugates with $[Cu(L)_2]$ and [Cu(L)Cl] compositions, respectively. The observed irreversible Cu(II)/Cu(I) redox couple in the range of +0.20 to +0.61 V is due to the substantial distortion in the square-planar geometry. ESR studies indicate the appreciably covalent character within M–L bonding due to extensive delocalization of electron from $d_{x^2-y^2}$ orbital. The hydrazone–NSAID conjugates exhibit substantial cytotoxicity against A-549, HCT-116 and MDA-MB-231 cancer cell lines with ibuprofen-imidazole-hydrazone ligand possessing the lowest IC_{50} (2.26 μM) amongst the synthesized NSAID-conjugates. Interestingly, its Cu(II) complex also displays excellent anticancer activity against MDA-MB- 231 with IC_{50} value of 3.58 μM. Such a feature may be ascribed to the synergistic association of Cu(II)–NSAID–hydrazone linkage. Thus, conjugation of NSAID with hydrazone and its complexation with a bioactive metal ion may be regarded as a potential strategy for designing of non-platinum biocidal agents.

KEYWORDS: Cu-hydrazone, biocidal, synthetic, drugs, anticancer, conjugates, geometry, ligands

I. INTRODUCTION

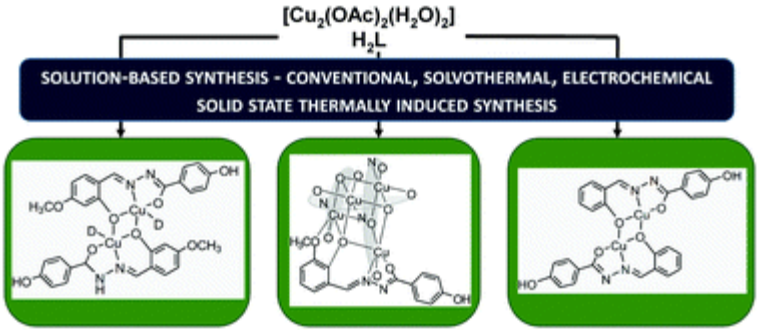
Potential bidentate hydrazone ligands, HL^1 (1) and HL^2 (2) prepared by the condensation of benzaldehyde or furfuraldehyde with benzhydrazide upon reaction with $[CuCl_2(PPh_3)_2]$ yielded corresponding mononuclear complexes of the compositions $[Cu(L^1)(PPh_3)_2]$ (3) and $[Cu(L^2)(PPh_3)_2]$ (4). The exact nature of coordination of the hydrazones to the metal ion and the structure of the complexes were confirmed by spectral and single crystal X-ray diffraction studies. Interestingly,[1,2] the reactions of 1 and 2 with $[CuCl_2(PPh_3)_2]$ resulted in the formation of the first structurally characterized copper(I) hydrazone complexes 3 and 4 along with the previously reported complex $[CuCl(PPh_3)_3]$ 5 as a minor product in both the reactions. The metal complexes 3 and 4 showed significant binding towards calf thymus DNA (CT-DNA) via groove binding mode with binding constants in the magnitude 10^4–10^5 M^{-1}. In addition, the antioxidant activities of the complexes were also investigated through scavenging effect on DPPH , $NO^{\cdot}$ and $OH^{\cdot}$ radicals. The density functional theory calculations of complex 4 also supported the structure and stability of the reduced complex.[3,4]

A series of copper(II) complexes with 4-hydroxybenzhydrazone-related ligands was synthesized by using various methods, including the conventional solution-based method, solvothermal route and electrochemical synthesis.[5,6] The complexes can be classified as mononuclear $[Cu(L^{3OMe})(py)]$ (2py), dinuclear $[Cu_2(L^H)_2(py)_2]$ (1py), $[Cu_2(L^H)_2]$ (1α and 1β), $[Cu_2(L^H)_2(py)_2]$ (1py), $[Cu_2(L^{4OMe})_2(py)_2]$ (3py), $[Cu_2(L^{4OMe})_2]$ (3), $[Cu_2(L^{4OMe})_2(MeOH)_2]$ (3MeOH), $[Cu_2(L^{4OMe})_2(EtOH)_2]$ (3EtOH), cubane tetranuclear $[Cu_4(L^{3OMe})_4]\cdot x$solv (*x*solv = $10H_2O\cdot CH_3OH$ and $2.8EtOH\cdot 0.2H_2O$ for 2MeOH and 2EtOH, respectively), or polynuclear $[Cu(L^H)(py)]_n$ (1py*), where L^H = 2-oxybenzaldehyde 4-hydroxybenzhydrazonato, L^{3OMe} = 3-methoxy-2-oxybenzaldehyde 4-hydroxybenzhydrazonato, and L^{4OMe} = 4-methoxy-2-oxybenzaldehyde 4-hydroxybenzhydrazonato ligands. The presented study indicates that complexes having different nuclearities and geometries can be achieved by changing the synthetic conditions and methods.[7,8] Thermally induced structural transformations of the dinuclear complexes under solvent-free conditions were also investigated. Crystal and molecular structures of 1β, 1py*, 2MeOH, 2EtOH, 2py, 3 and 3MeOH were determined using the single crystal X-ray

| ISSN: 2582-7219 | www.ijmrset.com |

| Volume 1, Issue 1, November 2018 |

diffraction method. All complexes were characterized using microanalysis, [9,10] FT-IR and CW-EPR spectroscopy, thermogravimetric analysis and a powder X-ray diffraction method.



Two new copper(I) hydrazone complexes have been synthesised from bivalent copper precursor [CuCl2(PPh3)2] and ferrocene containing bidentate hydrazone ligands HL1 (1) or HL2 (2). Based on the elemental analyses and spectroscopic data, the complexes are best formulated as [CuL1(PPh3)2] (3) and [CuL2(PPh3)2] (4) of the monovalent copper ion. Solid state structures of ligand 2 and its corresponding complex 4 were also determined.[11,12] The DNA/albumin interactions of all the synthesised compounds were investigated using absorption, emission and synchronous fluorescence studies. Further, antioxidant properties of all the compounds have also been checked against ABTS, O2− and OH radicals. Additionally, the in vitro cytotoxic activity of compounds 1–4 was assessed using tumour (HeLa, A431) and non-tumour (NIH 3T3) cell lines. The chemical reactivity, molecular structure, and surface characteristics of Cu(I) camphor hydrazone compounds indicate that exist a structural pathway for conversion of coordination polymers into dimers and vice versa.[13,14] By X-ray diffraction analysis two polymorphic forms of the chain compound [{CuCl}2(Me2NNC10H14O)]n were identified that essentially differ in the structural arrangement and geometry of the non-linear copper atom. The characterization of the dimer complexes [{Cu(Me2NNC10H14O)}2(μ-X)2] (X = Cl or Br) was also achieved by X-ray diffraction analysis showing the unusual arrangement of the camphor hydrazone ligands that occupy the same side of the molecule.[15,16] Bond lengths and torsion angles show that one of the polymorphic forms is structurally close to the related dimer. The surface composition of the coordination polymers [{CuX}2(YNC10H14O)]n (X = Cl, Y = NMe2, NH2; X = Br, Y = NH2) and dimers [{Cu(Me2NNC10H14O)}2(μ-X)2] (X = Cl or Br) studied by X-ray Photoelectron Spectroscopy corroborate the molecular properties and the reactivity trend.[17,18]

Copper ions, either alone or in copper complexes, have been used to disinfect liquids, solids and human tissue for centuries. Today copper is used as a water purifier, algaecide, fungicide, nematocide, molluscicide as well as an anti-bacterial and anti-fouling agent. Copper also displays potent anti-viral activity. This article reviews (i) the biocidal properties of copper; (ii) the possible mechanisms by which copper is toxic to microorganisms; and (iii) the systems by which many microorganisms resist high concentrations of heavy metals, with an emphasis on copper.[19,20]

The increasing incidence of nosocomial infections caused by glycopeptide-resistant enterococci is a global concern. Enterococcal species are also difficult to eradicate with existing cleaning regimens; they can survive for long periods on surfaces, thus contributing to cases of reinfection and spread of antibiotic-resistant strains.[21,22] We have investigated the potential use of copper alloys as bactericidal surfaces. Clinical isolates of vancomycin-resistant *Enterococcus faecalis* and *Enterococcus faecium* were inoculated onto copper alloy and stainless steel surfaces. Samples were assessed for the presence of viable cells by conventional culture, detection of actively respiring cells, and assessment of cell membrane integrity. Both species survived for up to several weeks on stainless steel. [23,24] However, no viable cells were detected on any alloys following exposure for 1 h at an inoculum concentration of $\leq 10^4$ CFU/cm^2. Analysis of genomic and plasmid DNA from bacterial cells recovered from metal surfaces indicates substantial disintegration of the DNA following exposure to copper surfaces that is not evident in cells recovered from stainless steel. The DNA fragmentation is so extensive, and coupled with the rapid cell death which occurs on copper surfaces, that it suggests that mutation is less likely to occur. It is therefore highly unlikely that genetic information can be transferred to receptive organisms recontaminating the same area.[25,26] A combination of effective cleaning regimens and contact surfaces containing copper could be useful not only to prevent the spread of viable pathogenic enterococci but also to mitigate against the occurrence of potential resistance to copper, biocides, or antibiotics and the spread of genetic determinants of resistance to other species.[27,28]

| ISSN: 2582-7219 | www.ijmrset.com |

| Volume 1, Issue 1, November 2018 |

II. DISCUSSION

Copper inputs from antifouling paints into the local marine environment are evaluated and how these inputs contribute to the overall copper concentration and whether regulators should be concerned. The importance of copper speciation and how this influences the bioavailability and toxicity of copper to marine organisms is discussed. Overall, the risk of copper in the marine environment from an antifouling paint perspective is critically evaluated, looking at the current methods of measurement and prediction and whether these provide adequate protection for marine life.[29,30]

New copper(II) hydrazone complexes with (Z)-2-(phenyl(2-(pyridin-2-yl)hydrazono)methyl)pyridine (L) were synthesized and characterized using various physicochemical methods. The geometry of complexes can be classified as mononuclear and binuclear. The complex 1 [Cu(L)Cl_2] is mononuclear whereas solid-state structures of complex 2 contains a mixture of co-crystals of mono- and binuclear complexes 2a [Cu(L)(H_2O)(SO_4)] and 2b [(L)Cu-(SO_4)$_2$-Cu(L)]. The molecular structure of 2 contains two units of mononuclear complex 2a and two units of binuclear complex 2b. Copper contains in all mono- and binuclear complexes are in a distorted square pyramidal geometry.[31,32] The present study indicates that complexes having different nuclearities and geometries can be achieved by changing synthetic conditions and methods. Variable temperature magnetic susceptibility measurements of the complexes have shown a weak anti-ferromagnetic interaction. The presence of weak anti-ferromagnetic interactions is mediated by intermolecular hydrogen bonding in 1 and by symmetric sulfate bridge in 2, respectively. The Epr spectra in polycrystalline state of 1 and 2 exhibited a broad signal at 2.149 due to the spin-spin interactions between two copper(II) ions. The cyclic voltammograms of complexes 1 and 2 in DMSO gave two irreversible redox waves. Density functional theory (DFT) calculations were evaluated in the study involved the molecular specification for the use of B3LYP/LANL2DZ formalism for copper atom and B3LYP/6-31G for the remaining atoms. Both complexes catalyzed the dismutation of superoxide (0_2).[33,34] Furthermore, copper complexes and ligand were tested to explore the anticancer properties. Promising cytotoxicity of synthesized compounds was observed on the selected cancerous cell line of neuroblastoma, lung carcinoma, hepatocellular carcinoma and breast cancer.[35,36]

A new binuclear copper(II) complex [Cu_2L_2(μ-SO_4)(dmf)] with the 2-acetylpyridinebenzoylhydrazone (HL) ligand was synthesized and characterized by elemental analysis, Fourier transform infrared (FT-IR), ultraviolet–visible (UV–Vis), single-crystal X-ray diffraction, density functional theory (DFT), and molecular docking studies. The crystal structure revealed each copper(II) atom coordinated to the *NNO* chelating system of the anionic hydrazone ligand and a sulfate bridged. The copper ions are connected by a sulfate bridge, which keeps a distance of 3.292(3) Å between the two copper(II) centers. Additionally, only one of the copper(II) atoms is coordinated to the oxygen atom of the *N*,*N*-dimethylformamide (dmf) solvent molecule, resulting in two different geometry to each metal center. Cu···O interactions are observed for the secondary coordination sphere of Cu1 and Cu2 atoms with distances of 2.545(2) and 2.821(3) Å, respectively. Theoretical studies with DFT were performed to optimize the geometry of the complex and investigate its spectroscopic properties supporting the experimental results. Two different approaches were used in computational calculations, the plane wave using Perdew–Burke–Ernzerhof (PBE) functional and the localized basis set using the following functionals: B3LYP, B3PW91, CAM-B3LYP, LC-wPBE, M06-2X, ωB97-XD, PBE1PBE, and HSEH1PBE. The in vitro antibacterial potential of the new complex was evaluated against pathogenic bacteria and fungi and compared with the free ligand. The molecular docking was used to predict the inhibitory activity of the ligand and complex against one Gram-positive bacteria (*Enterococcus faecalis*), one Gram-negative bacteria (*Enterobacter aerogenes*), and one fungi (*Candida albicans*) species.[37,38]

Two novel heterocyclic compounds (E)-2-(1-(pyridin-3-yl)ethylidene)hydrazinecarbothioamide (3APTSC) and (E)-3-(1-(2-phenylhydrazono)ethyl)pyridine (3APPH) derived from 1-(pyridin-3-yl)ethanone were synthesized and characterized by various spectroscopic techniques. The corrosion inhibition efficacies of these compounds on copper in 0.1 M HNO_3 were screened by electrochemical corrosion monitoring techniques such as potentiodynamic polarization studies and impedance spectroscopy. Investigations clearly established that 3APPH displayed higher corrosion inhibition efficiency on Cu than 3APTSC at all concentrations. The mechanism of inhibition was verified with the help of adsorption isotherms. 3APTSC and 3APPH obeyed Langmuir adsorption isotherm on Cu surface. Thermodynamic parameters such as adsorption equilibrium constant () and free energy of adsorption () were also evaluated. Potentiodynamic polarization investigations confirmed that the 3APTSC and 3APPH act as mixed type inhibitors. Surface analysis of the metal specimens was performed by scanning electron microscopy. Energy of HOMO and LUMO, their difference, number of electrons transferred, electronegativity, chemical hardness, and so forth were evaluated by quantum chemical studies. Agreeable correlation was observed between the results of quantum chemical calculations and other corrosion monitoring techniques.

| ISSN: 2582-7219 | www.ijmrset.com |

| Volume 1, Issue 1, November 2018 |

III. RESULTS

The only engineering metal that is relatively behaving as a noble metal is copper, which requires strong oxidizing agents for its corrosion or dissolution. But during certain industrial processes copper tarnishes or corrodes. Copper has an inevitable role in electronic industry. The chemical dissolution and electroplating of copper are the main processes used in the fabrication of electronic devices. The most widely used aggressive solution contains nitric acid and hence this medium has induced a great deal of research on copper corrosion . The most practical way to decrease the rate of corrosion in acidic medium is the use of corrosion inhibitors. Recently, researchers have shown that certain organic compounds create a barrier against the tarnishing of copper. Most of the excellent acid inhibitors are organic compounds containing nitrogen, oxygen, phosphorus, and sulphur. Organic compounds containing electron rich functional groups, π electrons in triple or conjugated double bonds, and heteroatoms such as nitrogen, sulfur, and oxygen are usually acting as good inhibitors since these compounds are easily adsorbed on metal surfaces . Structure and geometry of a molecule have a definite role in preventing the corrosion of metal in acid medium. Studies on the relation between adsorption and corrosion inhibition are of considerable importance. [39]

In recent years, the development of highly selective and sensitive chemosensors for transition metal ions has attracted significant interest due to their vital role in various biological and environmental processes. Among these metal ions, copper ions play a critical role in various biological processes and are also significant environmental pollutant in modern society. The over-accumulation of copper ions can cause a series of severe diseases such as Alzheimer's, Wilson's and Menke's diseases. Therefore, it is very important to detect rapidly Cu^{2+} in environmental and biological systems.

Up to now, many fluorescent probes have been reported. However, most of them usually require expensive instruments, involve complicated syntheses or are insoluble in aqueous solutions. For practical applications, it is necessary to develop Cu^{2+} sensors that are easily prepared and that can be easy detected rapidly without the help of instruments. In this respect, colorimetric chemosensors would appeared to be the most attractive and could be widely used owing to the low cost and lack of equipment required. Moreover, a colour change can easily be observed by the naked eye. However, so far, reported colorimetric Cu^{2+} probes are still relatively rare, and it is still a challenge to develop colorimetric chemosensing molecules to detect Cu^{2+} in aqueous solution.

Cancer treatment has traditionally been comprised of established treatments such as radiation, surgical excision, and chemotherapy, which can be used alone or in combination. Many therapeutic factors have been extracted from minerals, plants, and animals, the majority of them have been synthesized in the lab, making them a valuable source of innovation pharmacologically. Due to the in vitro cytotoxic effect of metal complexes, the interest in these compounds increases day by day in cancer treatment. The electronic nature of metals, modifications in ligands, and conformational changes in functional groups give rise to the discovery of drugs with different cytotoxic and pharmacokinetic properties. In recent decades, the number of persons receiving chemotherapy has increased considerably. Medicinal inorganic chemistry can take advantage of the unique properties of metal ions to generate new drugs. This has prompted chemists to use various approaches creating novel metal-based anticancer drugs with various mechanisms of action, which are significant in the pharmaceutical industry due to their potent anticancer properties. Schiff base ligands and transition metals are the most researched coordination chemicals. Their applications as anticancer medicines are becoming more significant. [40]

Hydrazones are a class of azomethine with a -C=NN- linkage, prepared by the reaction of hydrazide and aldehydes or ketones (1). In hydrazones, azomethine group gained much importance as compared to other organic compounds because carbon has both electrophilic and nucleophilic nature while both nitrogen atoms are in nucleophilic nature (2,3). All the hydrazone derivatives exist in ketoenol tautomerism via intermolecular proton transfer (4) and cis-trans form depends on azomethine bond, solvent, pH, and concentration. Hydrazone derivatives are considered as both proton donor and proton acceptor species and show intermolecular and intermolecular hydrogen bonding (5). This unique characteristic of hydrazone derivatives makes a them very important class of compounds. In the past few decades, hydrazone and their derivatives possessed many biological applications (6) (Figure 1,2) like antifungal ((E)-N'-[(5-Methyl-7- nitrobenzofuran-2-yl)methylene]-benzo-hydrazide, 1) (7), antibacterial (2,3,4 pentanetrione-3-[4-[[(5-nitro-2-furyl)methylene]-hydrazino]- carbonyl]phenyl]-hydrazone, 2) (8), intestinal antiseptic (4-hydroxybenzoic acid[(5-nitro-2-furyl)- methylene]-hydrazide, 3) (9), anticonvulsant (N'- (4-chloro-benzylidene)-nicotinohydrazide, 4) (10), analgesic (Decanoic acid (4-methoxy benzylidene)hydrazide, 5) (11), anti-cancer (1Hpyrazole-5-carbohydrazide hydrazone, 6) (12), antiinflammatory (Salicylaldehyde-2-(4-isobutylphenyl)-propionyl hydrazone, 7) (13), anti-platelet (Indole-3-carboxaldehyde 4-methoxyphenylhydrazone, 8) (14), anti-viral (N'-benzylidene-2- ((4,4-dimethyl-6-

| ISSN: 2582-7219 | www.ijmrset.com |

| Volume 1, Issue 1, November 2018 |

oxocyclohex-1-en-1-yl)- amino)acetohydrazide, 9) (15), anti-proliferative (2- (2-(2,4,6-trioxotetrahydro-pyrimidin-5(2H)-ylidene) hydrazinyl) benzoic acid, 10) (16), anti-malarial (4- ((2-(benzo[d]thiazol-2-yl)hydrazineylidene)-methyl)benzene-1,2-diol, 11) (17), and antituberculosis (N-isopropylisonicotino-hydrazide,12) (18), they were also used as organic, inorganic, and analytical reagents.[41]

IV. CONCLUSIONS

These hydrazone derivatives are widely used as spectrophotometric agents not only for detection of metals in sand, soil, water, pharmaceutical samples, alloys, wine, beer, bread, oil, fruits, and vegetables, but also for the detection of organic compounds like carbazoles, aldehydes, ketones, carboxylic acids, salicylic acid, aspirin, aromatic amines, heterocyclic bases, and many more in drugs, food, air, blood, and urine samples. These are also used as organic collectors in flotation for collecting different metals from water, where oleic acid is used as surfactant .Nowadays, they are used as dyes in DSSC due to their broad absorption band, as chemosensors, especially in tumor cells due to their florescence property, as indicators and as microbe detectors due to their pH sensoring properties. Hydrazone derivatives are also used as corrosion inhibitors for nickel, iron, steel, copper, etc. Hydrazone derivatives have many binding sites due to which they have ability to bind metals via coordinate covalent bond and anions via covalent bond. This property makes them a unique class of compounds among all organic compounds. These types of compounds are used in light emitting diodes and due to nonlinear optical properties, are also used in lasers, telecommunication devices, and optical switching. Hydrazone derivatives produce stable colors that can't fade after long washing and are used as dying reagents for the dying of nylon, cotton, polyester, and silk.

The heterocyclic hydrazones constitute an important class of biologically active drug molecules. The hydrazones have also been used as herbicides, insecticides, nematocides, redenticides, and plant growth regulators as well as plasticizers and stabilizers for polymers. The importance of the phenolic quinolyl hydrazones arises from incorporating the quinoline ring with the phenolic compound; 2,4-dihydroxybenzaldehyde. Quinoline ring has therapeutic and biological activities whereas, phenols have antiseptic and disinfectants activities and are used in the preparation of dyes, bakelite and drugs. The present study is planned to check the effect of the counter anions on the type and geometry of the isolated copper(II)- complexes as well as the ligational behavior of the phenolic hydrazone; 4-[(2-(4,8-dimethylquinolin-2-yl)hydra-zono)methyl]benzene-1,3-diol; (H2L). A phenolic quinolyl hydrazone (H2L) was allowed to react with various copper(II)- salts (Cl, Br, NO3, ClO4, AcO, SO42-). The reactions afforded dimeric complexes (ClO4, AcO), a binuclear complex (NO3) and mononuclear complexes (the others; Cl, Br, SO42-). The isolated copper(II)- complexes have octahedral, square pyramid and square planar geometries. Also, they reflect the strong coordinating ability of NO3, Cl, Br, AcO and SO42- anions. Depending on the type of the anion, the ligand showed three different modes of bonding viz. (NN)0 for the mononuclear complexes (3, 4, 6), (NO)- with O- bridging for the dimeric complexes (1, 5) and a mixed mode [(NN)0 + (NO)- with O- bridging] for the binuclear nitrato- complex . The ligational behavior of the phenolic hydrazone (H2L) is highly affected by the type of the anion. The isolated copper(II)-complexes reflect the strong coordinating power of the SO42-, AcO, Br, Cl and NO3 anions. Also, they reflect the structural diversity (octahedral, square pyramid and square planar) depending on the type of the counter anion.[42]

REFERENCES

1. (a) Cuzman, J., B.C. Gates, 2003. J. Chem. Soc. Dalton Trans., 3303, and references therein. (b) Ganesan, R., B. Viswanathan, 2004. J. Phys. Chem. B., 108: 7102.
2. Borja, M., P.K. Dutta, 1993. Nature., 362: 42.
3. Thomas, J.M., 1999. Angew. Chem. Int. Edit. Engl., 38: 3588.
4. Zsigmond, A., K. Bogar and F. Notheisz, 2003. J. Catal., 213: 103.
5. Ramamurthy, V., D.R. Sanderson and D.F. Eaton, 1993. J. Am. Chem. Soc., 115: 10438.
6. Ramamurthy, V., P. Lakshminarasimhan, C.P. Grey and L.J. Johnston, 1998. Chem. Commun., 2411, and refercnes therein.
7. Meinershagen, J.L., T. Bein, 1999. J. Am. Chem. Soc., 121: 448.
8. Sykora, M., K. Maruszewski, S.M. Treffert – Ziemelis and J.R. Kincaid, 1998. J. Am. Chem. Soc., 120: 3490.
9. Balkus Ir., K.J., A.G. Gabrielov and S. Bell, 1994. Inorg. Chem., 33: 67.
10. Bowers, C., P.K. Dutta, 1990. J. Catal., 122: 271.
11. Herron, N., 1986. Inorg. Chem., 25: 4714.
12. Balkus Jr., K.J., A.A. Welch and B.E. Gnade, 1990. Zeolites., 10: 722.
13. Kowalak, S., R.C. Weiss and K.J. Balkus Jr. 1991. J. Chem. Soc. Chem. Commun., 57.
14. Balkus Jr., K.I., A.G. Gabrielov, 1995. J. Inclus. Phenom. Molec. Recog. Chem., 21: 159.

| ISSN: 2582-7219 | www.ijmrset.com |

| Volume 1, Issue 1, November 2018 |

15. Bedioui, F., 1995. Coord. Chem. Rev., 144: 39.
16. Saha, P.K., S. Banerjee, S. Saha, A.K. Mukherjee, S. Sivasanker and S. Koner, 2004. Bull. Chem. Soc., Jpn., 77: 709.
17. Weckhuysen, B.M., A. Verberckmoes, I.P. Vannijvel, J.A. Pelgrims, P.L. Buskens, P.A. Jacobs and R.A. Schoonheydt, 1995. Angrew. Chem. Int. Edit. Engl., 34: 2652.
18. Koner, S., 1998. Chem. Commun., 593.
19. Tolman, C.A., J.D. Droliner, M.J. Nappa and N. Herron, 1989. Activation and Functionalisation of Alkanes, in: CL Hill (ED), Wiley, Chichester, pp: 303.
20. Chatterjee, D., H.C. Bajaj, A. Das and K. Bhatt, 1994. J. Mol. Catal., 92: 235.
21. Raja, R., P. Patnaswamy, 1997. J. Catal., 170: 244.
22. Vogel, A.I., 1989. A text Book of Quantitative Inorganic Analysis, Longman (5th ed.), London.
23. Szafran, Z., R.M. Pike and M.M. Singh, 1991. Microscale Inorganic Chemistry, John Wiley, New York.
24. Rakha, T.H., M.M. Bekheit and K.M. Ibrahim, 1992. Transition Met. Chem., 17: 517.
25. Ahmed, A.H., 2007. J. Mol. Stuct., 839: 18.
26. Salama, T.M., A.H. Ahmed and Z.M. El-Bahy, 2006. Micropor. Mesopor. Mater., 89: 251.
27. Ewing, W.G., 1975. Instrumental Methods of Chemical Analysis (4th ed.), McGraw – Hill Kogakusha, 1975, Vogel, A.I., 1975. A Text Book of Practical Organic Chem. (3rd ed.), Longman, pp: 704.
28. Lever, A.B.P., 1968. Inorganic Electronic Spectroscopy, Elsevier Publishing Company, Amsterdam.
29. Quayle, W.H., J.H. Lunsford, Inorg. Chem., 21: 2226.
30. Brunauer, S., L.S. Deming, W.S. Deming and E. Teller, 1940. J. Am. Chem. Soc., 62: 1723.
31. Kanttcheva, M., K. Hadjiivanov, A. Budneva and A. Davydov, 1992. Appl. Surf. Sci., 55: 49.
32. Busca, B., 1987. J. Mol. Catal., 43: 225.
33. Davydov, A., 1984. IR Spectroscopy Applied to Surface Chemistry of Oxides, Nauka, Novosibirsk.
34. Hadjiivanov, K., M. Kantcheva and D. Klissurski, 1996. J. Chem. Soc., Faraday Trans., 92: 4595.
35. Itho, Y., S. Nishiyama, S. Tsuruya and M.J. Masai, 1994. Phys. Chem., 98: 960.
36. Millar, G.J., C.H. Rochester and K.C. Waugh, 1992. J. Chem. Soc., Faraday Trans., 88: 1477.
37. Bijsterbosh, W.J., F. Kapteigin and A. Moulijn, 1992. J. Mol. Catal., 74: 193.
38. Busca, G., 1987. J. Mol. Catal., 43: 225.
39. Ghiotti, G., F. Bocuzzi and A. Chiorino, 1985. Stud. Surf. Sci. Catal., 21: 235.
40. Hadjiivanov, K., L. Dimitrov, 1999. Micropor. Mesopor. Mater., 27: 49.
41. Hadjiivanov, K., H. Kno¨zinger, 2000. J. Catal., 191: 480.
42. Marta, G., R. Ocule, L. marchese, G. Genti and S. Coluccia, 2002. Catal. Today., 73: 83.