

"Synthesis and Characterization of Copper Complexes derived from Dimedone derivatives".

A. A. Kale^{1*}

1*.Post Graduate Dept. Of Chemistry

S.M.Joshi College, Dist-Pune, (Maharashtra)

*Corresponding author: E Mail- anandraoakale@gmail.com

Abstract: Reactive methylene group at C2 position in dimedone plays an important role in the synthesis of a variety of organic ligands. Condensed compounds 3, 5, 7 were synthesized by reaction with dimedone and different aromatic aldehydes. Synthesized condensed compounds 3, 5 and 7 were on reaction with hydroxyl amine hydrochloride to yield oximes ligands 8, 9 and 10 respectively. The synthesized oxime derivatives 8, 9, 10 were used further to synthesize metal complexes of copper 11, 12 and 13 respectively. All ligands were characterized by Mass, IR, ¹HNMR and CMR spectroscopic technique. The copper complexes obtained were characterized by using IR., TG-DTA, Magnetic susceptibility, and LC-MS techniques.

Key word: Metal complexes, Ligands, Antimicrobial activity, Magnetic susceptibility.

1.0 Introduction

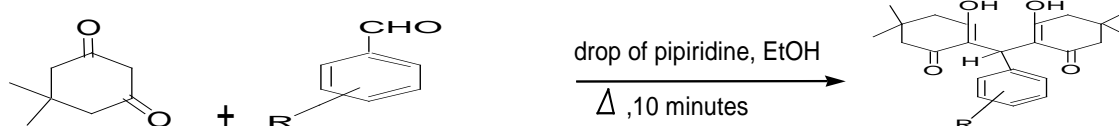
Co-ordination of a ligand to a metal is known to alter its chemical and biological activities. Influence of pi back – bonding on the reactivity of the nitrosyl group, nitrosation of activated methylene compounds via nitrosyl – ruthenium complexes was reported by (Bremard et al, 1979). Alkylation of dimedone with a tricarbonyl (diene) iron complexes was carried out by (Birch and Chamberlain, 1977). An intramolecular cyclization of enamines involving aryl palladium complexes and synthesis of carbazoles was explained by (Iida et al, 1980). The structural and spectroscopic study of ketoximato complexes was done by (Abraham et al, 1982). Studies on complexes of oxovanadium (II), manganese (II), Copper (II), Nickel (II), Zinc (II), iron (II), and uranyl with hydrazones β –diketone ligands was reported by (Abdel-Moez et al 1990). Synthesis and characterization of some transition metal complexes derived from dimedone bis (s- benzyldithiocarbamic acid) reported by (Abu El-Keash et al, 1991). Metal (III) complexes containing conjugated, nonaromatic anionic II – bound groups and addition polymerization catalysts from them was studied by (Wilson et al, 1996). Organic synthesis via Transition metal complexes of Chromium and Tungsten and their fragmentation to 2, 4 – Diene -5-one were reported by (Aumann et al, 1996). The stability of complexes of rare earth elements with dimedone and its 2- acetyl derivative by (Zhel'tvai, I.I, et.al, 1992). Hydrocarbon – bridged metal complexes addition of bis (ferrocenyl) -1,3 – diketones and metal diketonates to

coordinated, unsaturated hydrocarbons of cationic complexes was investigated by (Woissetschlager et al, 2000). Detection and spectrophotometric determination of copper with dimedone dioxime was done by (Belcher et al 1974). Xanthenes and acridine derivatives show biological activities. Oximes are used as analytical reagent, ketoxime of dimedone are reported to form metal complexes with Co (II) and Ru (III). Palladium –catalyzed intramolecular addition of amine to acetylenes was reported by (Fukuda et al, 1991). Synthesis using intramolecular Diels-Alder reactions of vinyl furans was done by (Cooper et al, 1988). Present work deals with synthesis and characterization of ligands and complexes. The Spectral and structural studies of the copper(II) complexes of 3,4-hexanedione Bis(3-ocyclothiosemicarbozones), was done by (Jasinski, et al, 2003)., The Synthesis and spectroscopic characterization of copper(II) complexes with some thiosemicarbazone derivatives, carried out by (El-Shazly et al, 2006). The Chelating activity of bis(diacetylmonoxime)thiocarbohydrazone towards VO₂⁺, Co(II), Ni(II), Cu(II) and Pt(IV) ions, by (El-Metwally and El-Asmy, 2006). Spectroscopic characterization and catalytic activity of Some Cu (II) thiosemicarbazide complexes, was done by Hamada, et, al.2006). Synthesis, characterization and oxygen affinity of Mn (II), Co (II) and Ni (II) complexes of diethylenetriamine Schiff bases was carried out by (Emara et al, 2008). Spectral and structural studies carried out for copper (II, III), nickel (II) and copper (II) complexes of dehydroacetic acid N4-dialkyl-and 3-azacyclothiosemicarbazones, by (Al-Saied et al, 2003). Synthesis and characterization of enolato-copper and -nickel complexes bearing Tp^{iPr}₂ ligand, [Tp^{iPr}₂M(XCHY)]_n [Tp^{iPr}₂=hydrators(3,5-diisopropylpyrazolyl)borato; n=1, 2], obtained from hydroxometal complexes, (μ-OH)₂(MTp^{iPr}₂)₂, and active methylene compounds, CH₂XY was carried out by Masato Kujime, Shiro Hikichi et.al. Copper (II) acetate promoted oxidative addition of 1, 3-dicarbonyl compounds to alkenes under aerobic conditions Javed Iqbal, *, Beena Bhatia and Naresh K. Nayyar.

2.0 Materials and Methods

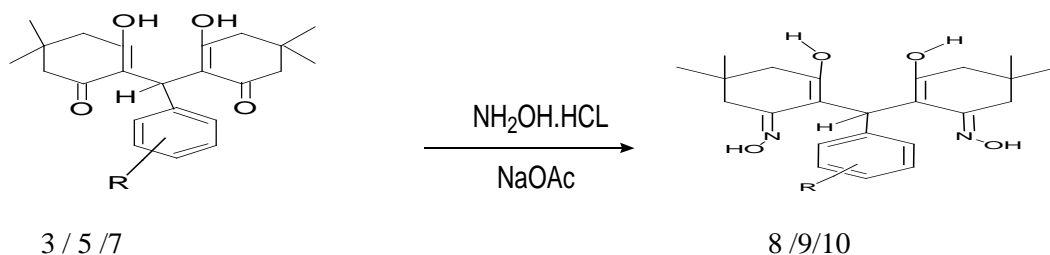
2.1 Synthesis of ligands: Using dimedone 1 and different aldehydes 2, 4, 6, condensed compounds 3, 5, 7 are synthesized respectively (Scheme-I). The oxime derivatives 8,9,10 synthesized from 3, 5, and 7 with hydroxyl amine hydrochloride and sodium acetate respectively as per Scheme-II. The following Scheme is used for synthesis.

Scheme-1



1	2/ 4 / 6	3 / 5 / 7
	(2, R=H),	(3, R=H)
	(4, R= meta-NO ₂)	(5, R= meta-NO ₂)
	(6, R= Ortho -Cl)	(7, R= Ortho -Cl)

Scheme-II

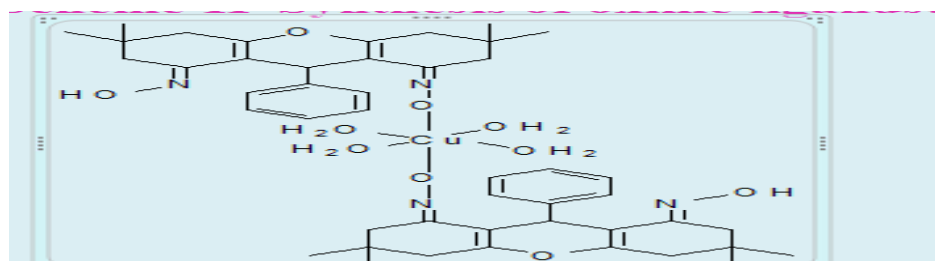


The compounds obtained in above reactions have been characterized by modern spectral techniques like IR, NMR, CMR, Mass spectrometry etc. The synthesized oxime derivatives 8, 9, 10 were used further to synthesize metal complexes of copper 11, 12 and 13 respectively. The complexes obtained are characterized by using IR., NMR, TG-DTA, Magnetic susceptibility, and LC-MS techniques.

2.2 Synthesis of Copper complexes

2.2.1 Synthesis of 2-[2'-Hydroxy -4,4'-dimethyl -6-oxo-cyclohex-1-enyl)-phenyl-methyl]-5,5-dimethyl -cyclohexane -1,3-dioxime Copper (II) tetrahydrate (11)

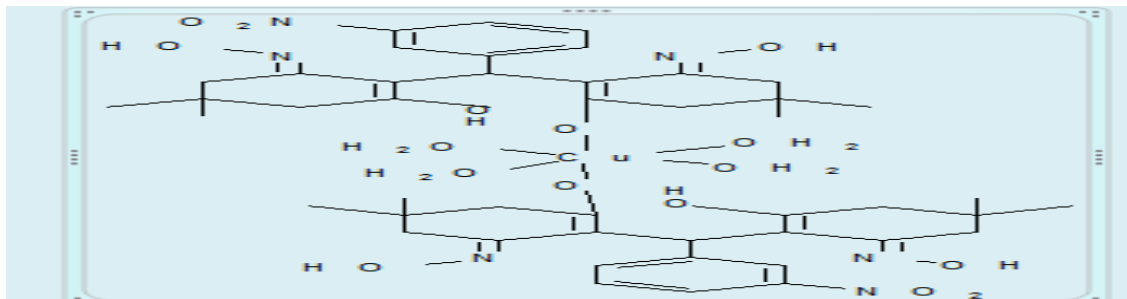
Copper acetate dihydrate (0.61mmoles, 0.1g) was taken in 25 ml of distilled methanol. To this a solution of (0.369 mmoles, 0.147g) of compound 8 in 25 ml distilled methanol was added. The reaction mixture was refluxed for 28 hours. The solvent was then removed under reduced pressure. The residue was triturated with chloroform. The chloroform solution was removed, triturating with petroleum ether, yielded a light brown product 11.



2.2.2 Synthesis of 2-[2'-Hydroxy -4, 4'-dimethyl -6-oxo-cyclohex-1-enyl)- 3 nitro phenyl-methyl]-5,5-dimethyl -cyclohexane -1,3-dioxime copper (II) tetrahydrate (12)

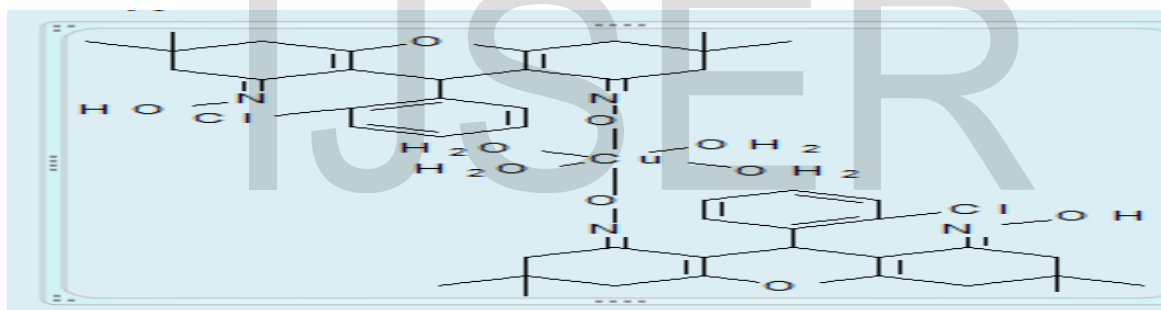
Copper acetate dihydrate (0.61 mmoles, 0.1g) was taken in 25 ml of distilled methanol. To this was added a solution of (0.165 g, 0.372 mmoles) of compound 9 in 25 ml distilled methanol. The reaction

mixture was refluxed for 30 hours. The remaining procedure was carried exactly same as described above (Part B -synthesis of complex 11) yielded a dark brown product 12.



2.2.3 The synthesis of 9-(2-Chloro-phenyl)-3, 3, 6, 6, 9-pentamethyl-3, 4, 5, 6, 7, 9-hexahydro-2H-xanthen-1, 8-dione dioxime copper (II) tetrahydrate (13)

Solution of copper acetate dihydrate (0.61mmoles, 0.1g) was taken in 25 ml of distilled methanol. To this was added a solution of (0.4 mmoles, 0.162g of compound 10 in 25 ml distilled methanol. The reaction mixture was refluxed for 22-24 hours. The remaining procedure was carried exactly same as described above (Part B -synthesis of complex 11) yielded a dry brown product 13



2.3 Results and discussion

2.3.1 Table-II: Characterization of copper complexes

The copper complex no. 11, 12, and 13 are dark brown powder and the % yields are 42.00, 52.00 and 53.00 respectively. The magnetic moment of complex no. 11, 12, and 13 are 4.92 B.M, 4.5 BM and 4.25 B.M. respectively.

Tests	Complex-11	Complex-12	Complex-13
Color	dark brown powder	dark brown powder	brown powder
Mol. formula	$C_{46}H_{70} Cu N_4O_{12}$	$C_{46}H_{64} CuN_6O_{16}$	$C_{46}H_{68} Cl_2Cu N_4O_{10}$
[M+1]	938 amu	1019amu	997 amu

Elemental analysis	C, 59.48.66; H, 7.54; Cu, 6.36; N, 6.25; O, 17.24	C, 54.27; H, 6.29; Cu, 5.92; N, 8.26; O, 25.17	C, 55.48; H, 6.33; Cal, 7.07; Cu, 5.88; N, 5.63; O, 15.95
M.P. °C	1190	186	180

2.3.2 Copper Complexes

Complexes 11

The IR spectrum of the ligand showed broad bands at 3474 and 3230 cm^{-1} due to enolic group. The band at 1709, 3230 cm^{-1} is due to C=N stretching, 1613 cm^{-1} , 3230 cm^{-1} due to C=C stretching, 1560, 3230 cm^{-1} and 1462 cm^{-1} due to aromatic stretching. The bands at 741 cm^{-1} and 698 cm^{-1} due to monosubstituted aromatic ring. The IR of the copper complex displayed new bands at 3784 and 3630 cm^{-1} (Table-III) which can be assigned to coordinated water molecule. The band at 1709 cm^{-1} is not seen distinctly as in the ligand however a broad band in the region 1700-1600 cm^{-1} are observed, probably due to merging of bands due to C=C and coordinated C=N. The spectrum shows two strong and fairly resolved peaks at 1541 cm^{-1} , 1525 cm^{-1} in addition to the peak at 1560 cm^{-1} which is seen in the spectrum of the ligand. The peaks of enolic -OH at 1262 and 1225 cm^{-1} in the ligands are not observed in the spectrum of the complex indicating the absence of enolic -OH. The ^1H NMR spectrum of the complex reveals the absence of the broad singlet at 10.8 δ (2H) which was assigned to the enolic -OH in the ligand. The aromatic protons appeared between 7.2 δ to 7.9 δ . The oxime -OH at 11.2 δ (4H) appears as a broad signal between 7.8 to 8.0 δ (2H). This indicates the effect of metal binding to -N-OH of the ligand. The methyne proton which is seen as a singlet at 4.98 δ (1H) is observed as broad weak signal in the complex (Table-IV). From the IR and NMR data it can be said that the oxime ligands binds to the metals through the oxime oxygen. The LCMS (Table-I) of the complex shows peaks at 1214 and 1127 amu due to adduct formation with acetonitrile used as the mobile phase. The next peak at $m/z = 928$ corresponds to the molecular formula $\text{ML}_2 \cdot 4\text{H}_2\text{O}$. The base peak at $m/z = 665$ corresponds to the adduct of ML with acetonitrile. The peak at 572 amu can be assigned to the species $\text{ML}(\text{H}_2\text{O})_2(\text{ACN})_2$. The thermo gravimetric analysis of the complex show a loss of 10% in temperature range 40-145 °C corresponding to four water molecules (expected weight loss about 8%) The dehydrated complex with formula ML_2 shows a further weight loss of 40 % up to 480 °C corresponding to the loss of one ligand. Metal analysis found is 7.03 % which in agreement with the expected of 6.36%. Magnetic moment was found to 4.92 B.M.

Complex 12

The IR spectrum of the oxime ligand shows well resolved strong band in the region 3290 -3000 cm^{-1} assignable to -OH of the oxime and enolic -OH. The sharp and weak intensity band at 1707 cm^{-1} due to tautomeric form of enolic hydroxyl group which is in conjugation with a double bond attached to the -N-

OH group weak intensity band at 1664 cm^{-1} has been assigned to -C=N of the oxime. The bands at 1250 cm^{-1} and 1163 cm^{-1} could be assigning to -C-O stretching.

The FTIR of the metal complex shows new band 3879 cm^{-1} and 3776 cm^{-1} which can be assigned coordinated water molecules. The well separated band 3292 cm^{-1} , 3215 cm^{-1} and 3078 cm^{-1} could be due to hydroxyl group. The presences of two well separated peaks are 1665 cm^{-1} , indicates the presence of uncoordinated oxime group. There is no change the C=N stretching frequency, the band appear 1668 cm^{-1} in the both ligands and the complex. The band at 1707 cm^{-1} in the ligand not visible in the complex. Similarly the band at 1250 cm^{-1} in the ligand due to C-O stretching shows a large shift in the complex and is observed at 1203 cm^{-1} . The band seen at 1163 cm^{-1} in the ligands also shows a shift to 1155 cm^{-1} . These observation confirm that at the coordination of the ligand to the metal is trough the hydroxyl oxygen. A medium intensity band also appears at 908 cm^{-1} in the complex. The ^1H NMR spectrum of enolic protons which are observed at 11.857δ in the ligand are absent in the complex. A multiplate of the methylene protons at C-4 and C-6 at 2.44δ in the ligand appear to the slightly deshielded and appear at 2.48δ in the complex. The aromatic cluster of C-2", C-5", C-6", and C-4" protons which appear at 7.253δ has been broadened from 7.9 to 7.23δ . This broadening can be attributed binding of the ligand to the paramagnetic metal centre. The signal due to C-9 methyne proton also shows a shift and appears at 4.82δ . There is no observable change in C3' and C5' methyl protons which experience in the sin shielding in the legend and appear at 1.086δ in the complex while in the legend they are observed at 1.061δ except for the broadening of the signal. These observations lend support to the conclusion drawn from the IR data. In the LCMS technique the spectra always show adducts of the solvents used as the mobile phase. In the present spectrum of the complex a peak at $m/z = 1063$ amu has appeared due to the adduct formation with the nitrile group of the mobile phase. Thus the molecular weight was confirmed to be 1017 amu which matches with the molecular formula $\text{ML}_2 \cdot 4\text{H}_2\text{O}$. The base peak at $m/z = 601$ can be attributed to the loss of one ligand molecule and one water molecule, leaving behind a fragment $\text{ML}_3 \cdot \text{H}_2\text{O}$ in which the metal would have coordination number equal to 4. These results are in well agreement with the data obtained from the thermogravimetric analysis. The magnetic moment was found to be 4.5 BM.

Complex- 13

The FTIR spectrum of the metal complex shows new well resolved strong band 3555 cm^{-1} indicating the presence of coordinated water molecules A remarkable feature of this IR is that the bands in the region 3300 to 3100 cm^{-1} are absent, The bands at 1269 cm^{-1} and 1230 cm^{-1} are also absent. The nature of the spectrum is distinctively different in the region 1700 to 1500 cm^{-1} from the ligand. The well resolved band which appeared at 1705 cm^{-1} in the ligand seems to have merged with the broad band at

1626 cm^{-1} Two bands are observed one at 1578 and another at 1560 cm^{-1} . This shift in band due to C=N stretching in IR of complex and absence of bands in the region 3300-3100 cm^{-1} indicates that the oxime group has participated in binding to the metal. Although the band at 1230 cm^{-1} is absent the band at 1193 cm^{-1} is present and there is new broad band 3381 cm^{-1} . On the basis of this data it can be concluded that the complex has M-L bonding through one of the oxime, -OH. The enolic OH is also absent indicating the probability of cyclization of the enolic -OH. The ^1H NMR spectrum of the complex shows an overall broadening effect. The enolic protons observed at 8.99 δ in the ligand are absent in the complex. The methylene protons at C-4, C-5 which appear between at 2.76 and 2.79 δ in the ligands appear as a broad multiplet between 2.152 and 2.783 δ and 3.21 δ . The aromatic cluster for C 3'', C4'', C5'' and C6'' protons seen in the ligands ^1H NMR between 6.97 to 7.35 δ appear to have broadened in the region 6.96 to 7.2044 δ . The signal due to methylene protons at C-7 also shows a shift from the 5.26 to 5.35 δ . The LCMS spectrum of the complex shows a peak at $m/z = 1197$ amu due to solvent adduct of the complex. The peak at $m/z = 995$ corresponds to the molecular formula $\text{ML}_2 \cdot 4\text{H}_2\text{O}$. The base peak 927 amu indicates the loss of four water molecules to give the residue containing a four coordinate metal. The metal analysis result indicates that the % of metal in the complex is 5.27%. This is in agreement with the proposed formula. The % weight loss observed in the TGA studies corresponded to the loss of 4 water molecules followed by the loss of one ligand. The magnetic moment was found to be 4.25 BM. The antibacterial and entomological activity study of all above ligands metal complexes is under process.

2.4 Conclusions:

Reaction of dimedone with benzaldehyde and substituted benzaldehyde leads to the condensation of reaction in the 2:1 mole ratio. Ligands synthesized 8, 9 and 10 used further for copper complexes synthesis 11, 12 and 13 respectively. The antibacterial and entomological activity study of all above ligands is under process. The metal complexes synthesized will be tested for 11, 12 and 13 antibacterial and entomological activity in future.

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