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Research Article

CYCLOHEXANE OXIDATION: SYNTHESIS AND CHARACTERIZATION OF AMINO ACID METAL COMPLEXES AND THEIR CATALYTIC ACTIVITY EVALUATION

[*]Merajuddin S. Ahmed, Ahmed Mubarak T., Mujahid Alam M., & Halima Abdullah Al-Ahmari A.
Department of Chemistry, Faculty of Science, King Khalid University, P. O. Box 9004, Abha 61413, Saudi Arabia
[*]Author for Correspondence

ABSTRACT
The complexes of Mn (II), Co (II), Ni (II) and Zn (II) with amino acids, L-alanine (Ala) and L-phenylalanine (Phe.ala) were synthesized and characterized by elemental analysis, UV-visible, IR, photoluminance, NMR, SEM and X-ray diffractogram data. In these complexes, the amino acids coordinated in 1:2 ratio with metals and they exhibited different geometries as distorted octahedral, octahedral, tetrahedral and square planar. The catalytic activities of the complexes was studied for the oxidation of cyclohexane, using aerial oxygen, and different oxidants, H_2O_2, Na_2O_2, KIO_4 and TBHP in acetonitrile as solvent, without solvent system and in autoclave at different temperatures.

Key Words: *Amino Acids, Metal Complexes, L-alanine, L-phenylalanine, Cyclohexane Oxidation*

INTRODUCTION

Saturated hydrocarbons are abundant in nature, they are interesting compounds as are main constituents of natural oil and natural gas and consequently they are important feedstocks for chemical production. Alkane's C-H bond (s) can be converted to C-OH or C=O functionalities leading to the production of more valuable products used for fine chemicals. However, activation of the former bonds in such stable compounds is difficult, which still prevents their generalized use in the direct synthesis of value added chemical products (Weissermel *et al.,* 1993; Ullmann 2002; Sheldon *et al.,* 2007).

The catalytic reaction of organic compounds especially the fictionalization of hydrocarbons via the oxidation reactions using hydrogen peroxide as oxidant is the very useful reaction and has been studied comprehensively over the past few years. Research on the fictionalization of cyclohexane by the oxidation reactions assumes special attention due to immense industrial importance (Shilov *et al.,* 2000) of its functionalized products. For example, cyclohexanol is used in the manufacture of adipic acid, which is again a raw material of nylon 6, 6' (Tian, 2004), soaps, detergents, rubber materials, pesticides, and etc., whereas cyclohexanone is utilised as an industrial solvent and activator in oxidation reactions (Schuchardt *et al.,* 2001; Ammoumraoui *et al.,* 2011; Retcher *et al.,* 2008). Some reports have been found for the oxidation reaction of cyclohexane under aerobic, room temperature condition and the microwave condition using different transition metal complexes as catalysts (Ceyhan *et al.,* 2012; Jin *et al.,* 2006; Yuan *et al.,* 2007; Fetizon *et al.,* 1993; Simandi *et al.,* 1992; Parshell *et al.,* 1992; Sawyer *et al.,* 1991). Recently, numerous attempts have been made to prepare new heterogeneous catalysts for the oxidation of cyclohexane, because of their reusability compared to homogeneous catalysts (Antony *et al.,* 2013).

The finding of efficient catalysts for the selective insertion of one oxygen atom from oxygen donors, like dioxygen, hydrogen peroxide, alkylhydroperoxide, sodium periodate into various organic molecules, under mild conditions, remains a difficult task in the fields of chemical and biological catalysis (Barton *et al.,* 1993).

In continuation to our effort in developing novel transition metal complexes with amino acids for oxidation of cyclohexane, herein we report the synthesis, characterization and catalytic activity evaluation of these amino acid metal complexes under various oxidants such as aqueous H_2O_2, Na_2O_2, KIO_4 and TBHP in presence of acetonitrile as solvent, solvent free conditions and in autoclave system.

MATERIALS AND METHODS

The $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, L-alanine, L-phenylalanine, acetone, diethyl ether and petroleum ether were purchased from Sigma Aldrich and used as received without further purification. Ethanol, chloroform, acetonitrile, cyclohexane, cyclohexanol, cyclohexanone were obtained from Fluka chemicals. H_2O_2, Na_2O_2, KIO_4, TBHP were purchased from Merck Co. $NiCl_2 \cdot 6H_2O$ and $ZnCl_2$ were purchased from Loba Chemie. All chemicals and reagents used in the present study were of analytical grade. The FTIR spectra were recorded on a Shimadzu JASCO FTIR-460 plus spectrometer using KBr pellets or neat. The UV-visible spectra of the compounds were recorded on Shimadzu UV-2100 spectrophotometer. Gas chromatographic analysis was performed with a Shimadzu 2014 GC system equipped with a packed chromosorb column fused and FID detector. Scanning electron microscopy (SEM) results were performed on gold coated samples using a JEOL-JSM-6390 LV. ^1H NMR spectra of ligands and complexes were measured on a Brucker 500-DRX Avance spectrometer at 500 MHz using TMS as internal standard. The elemental analysis of the complexes were recorded by using Perkin-Elmer CHN-2400 analyzer their results were found to be good agreement with the calculated values. Photoluminance spectra of the complexes and ligands were recorded on LUMINA fluorescence spectrometer of Thermo Scientific Co. USA. The XRD measurements were performed on Schimadzu DX-6000 using Cu for Kα-particle source.

Synthesis of Metal Complexes

General Procedure for the Preparation of the Amino Acid Metal Complexes

In separate experiments, the Mn (II), Co (II), Ni (II) and Zn (II) were complexed with L-alanine (Ala) and L-phenylalanine (Phe.ala) in (1:2) (metal: ligand) molar ratios. To a 50 mL ethanol solution of MnCl2·4H2O (1.97 gm), $CoCl_2 \cdot 6H_2O$ (2.37 gm), $NiCl_2 \cdot 6H_2O$ (2.37 gm) and $ZnCl_2$ (1.36 gm) respectively. Later, 0.01 M Na_2CO_3 solution was added to adjust P^H. The ligands solution of L-alanine (1.8 gm), and L-Phenylalanine (3.3 gm) in ethanol was added to obtain 1:2 ratios. The resulting mixture was stirred under reflux at 80 ^{0}C for 3 hrs. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixtures were cooled to room temperature; the solid products were separated by filtration and then recrystallized by using a mixture of acetone and diethyl ether in the ratio 1:2 under heating with stirring. After, the resultant mixture was cooled, the solids was separated and collected by filtration, and then dried under vacuum.

Complex of Mn-Ala: IR (KBr, ν cm^{-1}): 3089 (ν_{NH2}), 1592 ($\nu_{C=O}$), 485 (ν_{Mn-N}), 1016 (ν_{Mn-O}). Elemental analysis: C: 12.59 %, H: 4.89 %, N: 4.89 %, Cl: 24.80%.

Complex of Co-Ala: IR (KBr, ν cm-1): 3084 (ν_{NH2}), 1620 ($\nu_{C=O}$), 1014 (ν_{Co-O}), 485 (ν_{Co-N}). Elemental analysis: C: 11.04 %, H: 5.52 %, N: 4.29 %, Cl: 21.75 %.

Complex of Ni-Ala: IR (KBr, ν cm-1): 3085 (ν_{NH2}), 1622 ($\nu_{C=O}$), 1014 (ν_{Ni-O}), 539 (ν_{Ni-N}). Elemental analysis: C: 17.40 %, H: 5.80 %, N: 6.76 %, Cl: 17.14 %.

Complex of Zn-Ala: IR (KBr, ν cm-1): 3083 (ν_{NH2}), 1587 ($\nu_{C=O}$), 1014 (ν_{Zn-O}), 540 (ν_{Zn-N}). Elemental analysis: C: 23.05 %, H: 3.84 %, N: 8.96 %, Cl: 22.69 %.

Complex of Mn-Phe.ala: IR (KBr, ν cm-1): 3351 (ν_{NH2}), 1583($\nu_{C=O}$), 1033(ν_{Mn-O}), 541 (ν_{Mn-N}). Elemental analysis: C: 29.84%, H: 4.97%, N: 3.86%, Cl: 19.59%.

Complex of Co-Phe.ala: IR (KBr, ν cm-1): 3328 (ν_{NH2}), 1617 ($\nu_{C=O}$), 1078 (ν_{Co-O}), 525 (ν_{Co-N}). Elemental analysis: C: 26.87 %, H: 5.47 %, N: 3.48 %, Cl: 17.64 %.

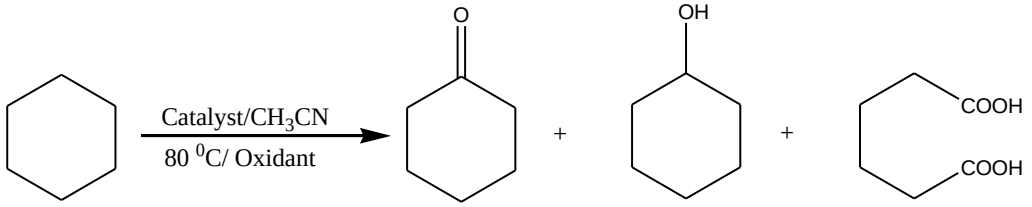
Complex of Ni-Phe.ala: IR (KBr, ν cm-1):3355 (ν_{NH2}), 1557 ($\nu_{C=O}$), 1074 (ν_{Ni-O}), 469 (ν_{Ni-N}). Elemental analysis: C: 38.19 %, H: 5.65 %, N: 4.95 %, Cl: 12.53 %.

Complex of Zn-Phe.ala: IR (KBr, ν cm-1): 3333 (ν_{NH2}), 1560 ($\nu_{C=O}$), 1074 (ν_{Zn-O}), 525 (ν_{Zn-N}). Elemental analysis: C: 46.52 %, H: 4.30 %, N 6.03 %, Cl: 15.27 %.

Cyclohexane Oxidation Reactions

All the catalytic reactions were performed in 50 mL glass flask and autoclave sealed with Teflon faced silicon septa. Reactions were performed under magnetic stirring, at 80 ^{0}C, for 2 hr and 4 hr. Cyclohexane oxidation was carried out using various oxidants H_2O_2, Na_2O_2, KIO_4 and TBHP as oxygen donor in presence of acetonitrile as solvent and solvent free condition. The reaction mixtures were directly

analyzed by packed chromosorb column gas chromatography, and the retention times of the products were confirmed by comparison with that of authentic product samples. Control reactions were conducted in the absence of the catalyst under the same conditions no product formation was observed (Scheme 1).

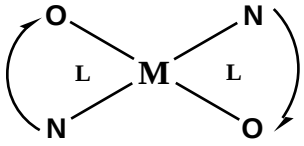


Scheme 1

RESULTS AND DISCUSSION

Characterization of Complexes

Amino acids; Alanine and Phenylalanine were successfully complexed with Mn, Co, Ni and Zn as described in the experimental section that the synthesis of complexes were performed using metal chloride salt (M) and amino acids (L) in 1:1 and 1:2 (M: L) ratio, but we found that in both cases the complex formation was not controllable. Therefore, we can generalize that metal ion can bind to two amino acids to form a complex. Different analytical techniques were applied to elucidate the structure of these complexes.



FT-IR Spectra

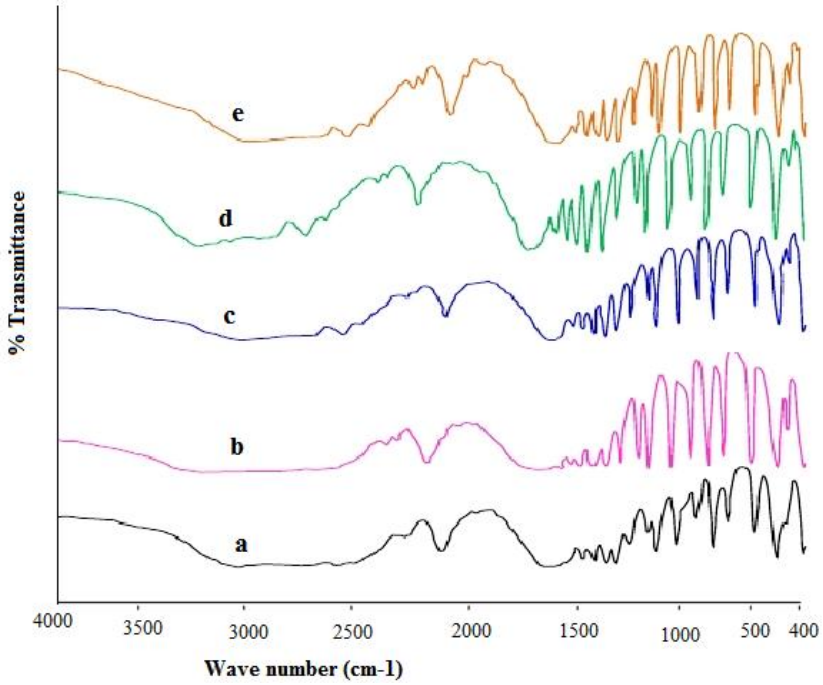


Figure 1: FT-IR spectra of (a) pure Alanine, (b) Mn-Alanine, (c) Co-Alanine, (d) Ni-Alanine, (e) Zn-Alanine

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It is known that metal ions act as Lewis acid and coordinates to the potential proton-binding sites of the ligands. The coordination results and effects in the bond strength of the ligand can in turn changes the vibrational energy of the ligand. The infrared spectral comparison of free ligand and metal complexes are shown in (Figure 1). The vibrational for alanine modes due to carboxylate and amino groups was found to exist at 1680-1540 cm^{-1} (COO^{-}), 3150–3000 cm^{-1} ($–NH_2$). Further to this 1410 cm^{-1} (weak) for symmetric stretching of COO^{-} and 660 cm^{-1} for COO^{-} (deformation). Moreover, 1660–1610 cm^{-1} and 1550–1480 cm^{-1} were also assigned for ($–NH_2$) vibrations for bending. Changes were observed in the IR bands of ($–NH_2$) and (COO^{-}). New bands were exhibited in the range of 400–660 cm^{-1}, which are tentatively assigned for the M–N coordination and M–O coordination was also observed in the range of 940–1210 cm^{-1}. It is concluded that, in metal complexes shifts in M–C=O and M–NH_2 bands as well as the widening of the bands were clearly reveals the formation of metal complexes with a bidentate mode.
The IR spectral analysis for the Phenylalanine metal complexes have shown in Figure 2. The widening of bands between 3360–3040 and 1660–1540 cm^{-1}, as compared to the free amino acid clearly indicates that the complexations with the metal have occurred. Further, evidence to these findings was in agreement with the related work appeared very recently.

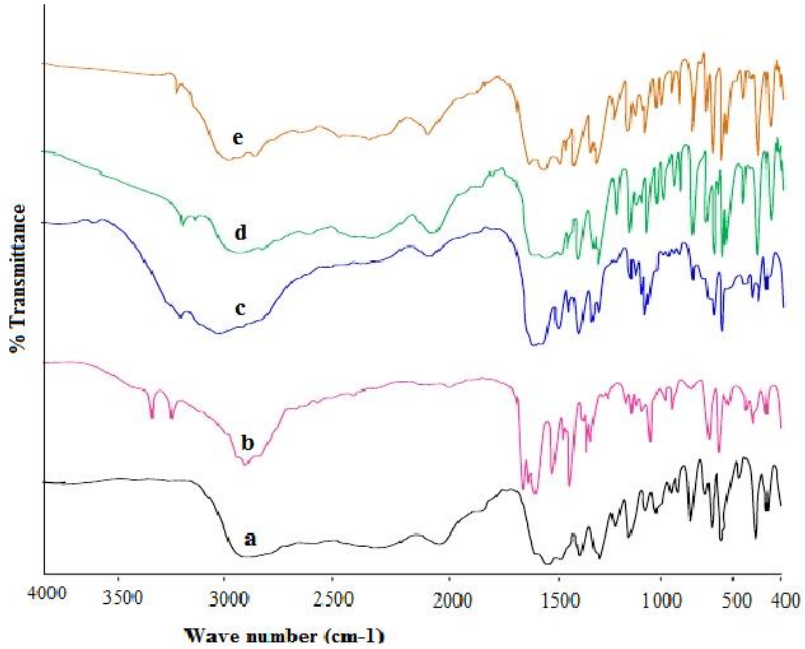

Figure 2: FT-spectra of (a) pure Phenylalanine, (b) Mn-Phenylalanine (c) Co-Phenylalanine, (d) Ni-Phenylalanine, (e) Zn-Phenylalanine

Scanning Electron Microscopy (SEM)

The final evidence of the complexes composition was deduced from their SEM analysis. The SEM-micrographs for the M-Alanine (Metal) and M-Phenylalanine were given in the Figure 3 and 4. The morphology, texture and shape of the synthesized complexes with varying thickness in the range of 2 µm to 8 µm are shown. The Mn-Ala complex has shown the structure possessing layered crystallite. The Co-Ala complex was showing the structure possessing rods with gonal geometry. The flakes and the tubular structures were also seen in Ni-Ala and Zn-Ala complexes. Whereas Mn-Phe.Ala, Co-Phe.Ala, Ni-Phe.Ala and Zn-Phe.Ala complexes have shown coarse, crinkly and tubular structures in their morphology. High magnification samples were used to observe the detailed surface structures of the complexes, which may explain the behavior of these complexes and their catalysts for the oxidation of cyclohexane.

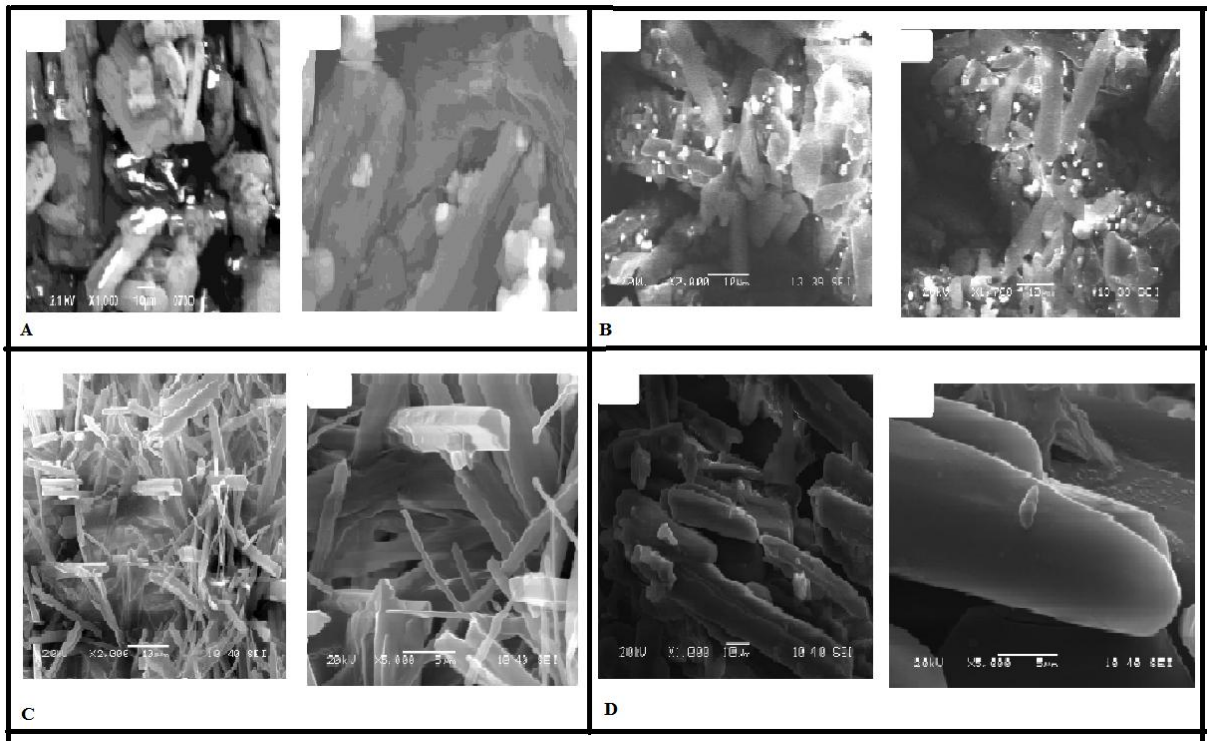

Figure 3: SEM micrographs of A). Mn-Ala complex, B). Co-Ala complex, C). Ni-Ala complex and D). Zn-Ala complex

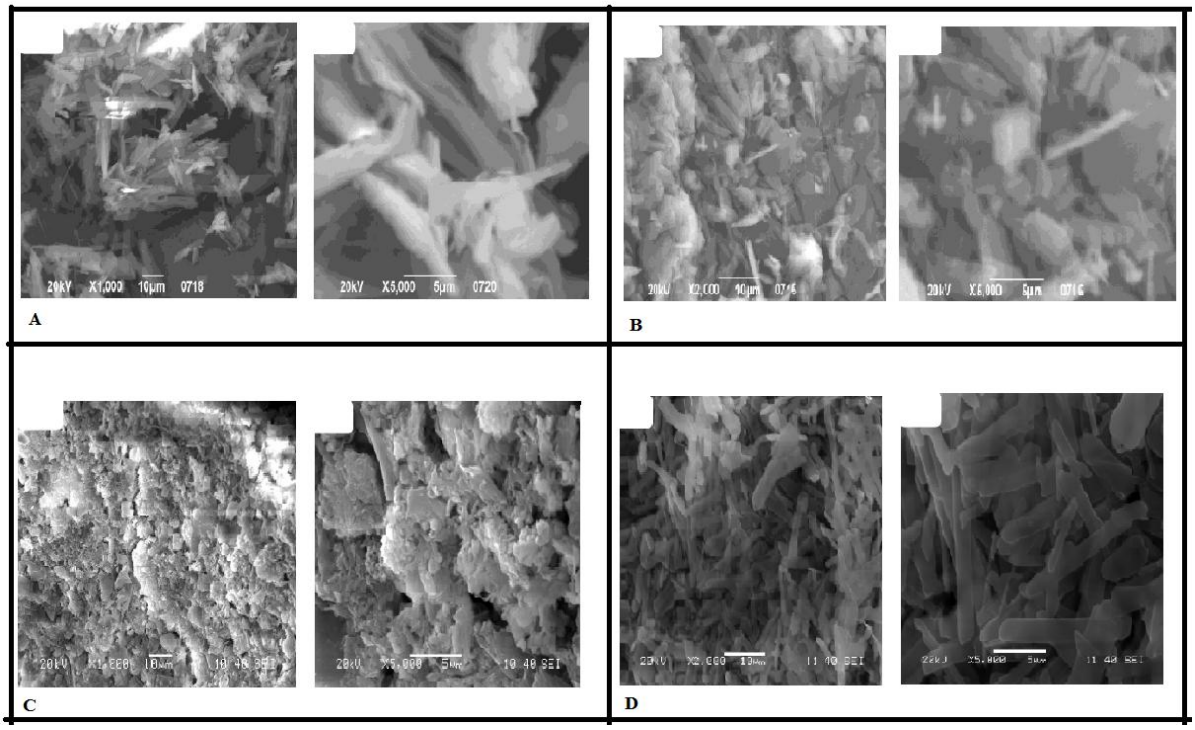

Figure 4: SEM micrographs of A). Mn-Phe.Ala complex, B). Co-Phe.Ala complex, C). Ni-Phe.Ala complex and D). Zn-Phe.Ala complex

Nuclear Magnetic Resonance (NMR)

More evidence to complexes formation was revealed from the NMR analysis of the ligand and complexes. The NMR for the M–Alanine complexes recorded in DMSO-d_6 showed that of the complexes were not soluble. The solubility could have been achieved if a mixture of "DCI" and D_2O was used along with DMSO-d_6. The non availability of the "DCI" restricted us to be confined to the soluble complexes spectral analysis only. Almost all the complexes of M-Alanine were not soluble in DMSO-d_6 except Co–Alanine, showed the solubility.

The ^1H NMR spectra as compared to the free ligand was very noticeable, the chemical shifts were appeared at δ 2.5 (s, 1H) and 3.4 (dd, 2H, -NH_2) and no change was found for –CH_3 protons. The NMR spectra for M-Phe.Ala complexes were recorded. The complexes of Co-Phe.Ala were found paramagnetic. This was again a confirmation for the complexes formed as Co (II) has the electron density such that they behave paramagnetically. This is in agreement with another study found in the literature too. The ^1H NMR of Mn–Phe.Ala analysis exhibited three peaks at δ 2.4 (br, s, 1H), 3.3 (d, 2H, -CH_2), 4.1 (br, 2H, NH_2) along with the phenyl protons at 6.7-7.1 as (m, 5H, Aromatic). The other complexes were defiance to solubility.

X-RAY Diffraction (XRD)

Further evidence to suggest this justification was revealed by the powder XRD analysis of the complexes. The results are shown in Figure 5 and 6. The database for the pure alanine as given by (JCPDS; card No. 11-0993) showed the orthorhombic phase structure. X-ray powder diffraction pattern for M-Alanine complexes is given in Figure 5. It clearly provides the evidence for the formation of complexes. The consistency in the complexes was materialized when new peaks at 30-40 θ, indicating the existence of crystalline particles of the complexes.

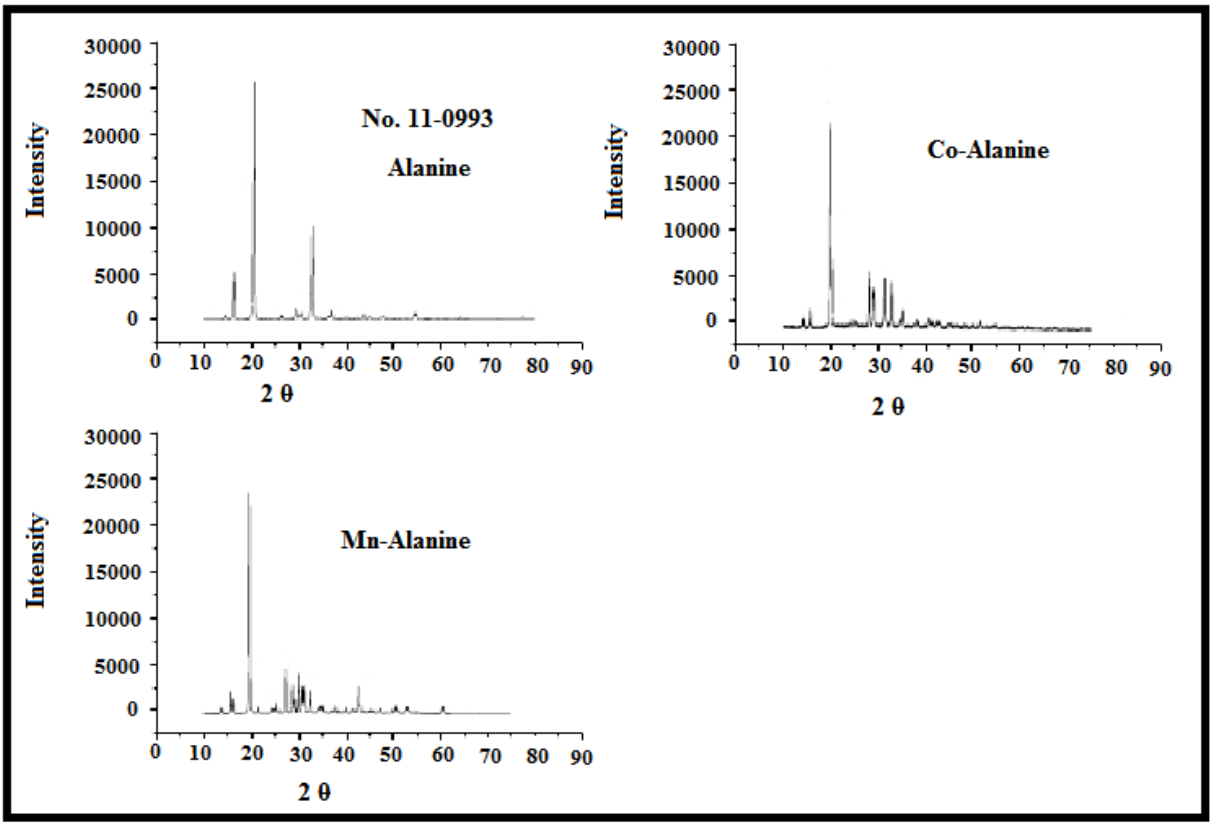

Figure 5: XRD – Diffractogram for the pure Alanine, Mn-Alanine and Co-Alanine complexes

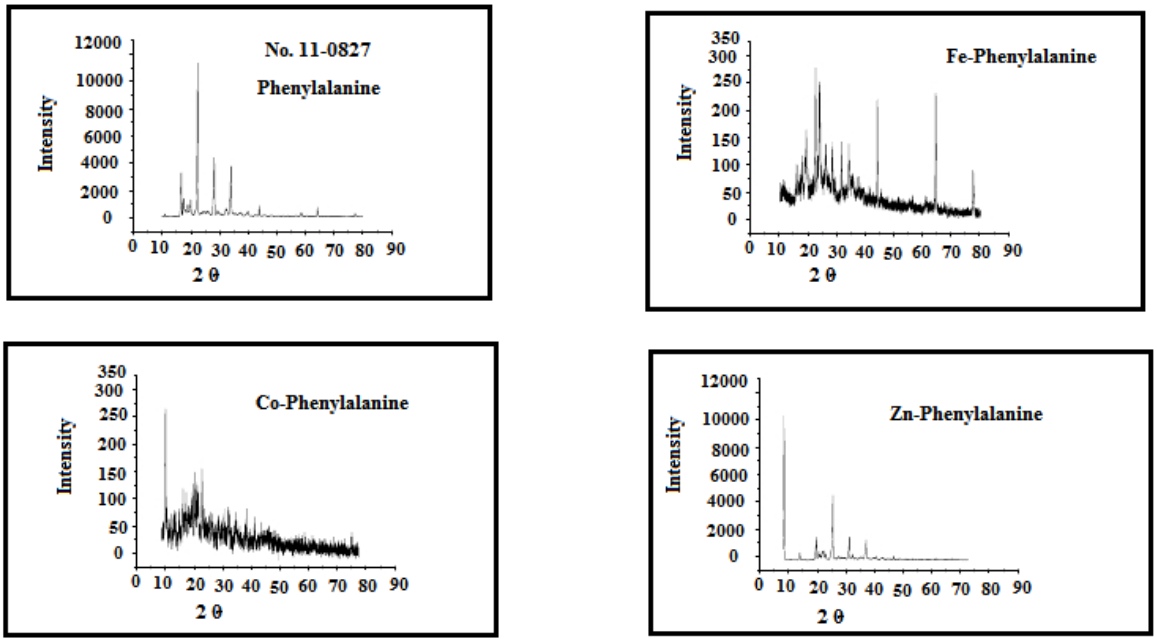

Figure 6: XRD –Diffractogram for the pure Phenylalanine, Fe-Phenylalanine, Co-Phenylalanine and Zn-Phenylalanine complexes

Photoluminescence of the Metal Complexes

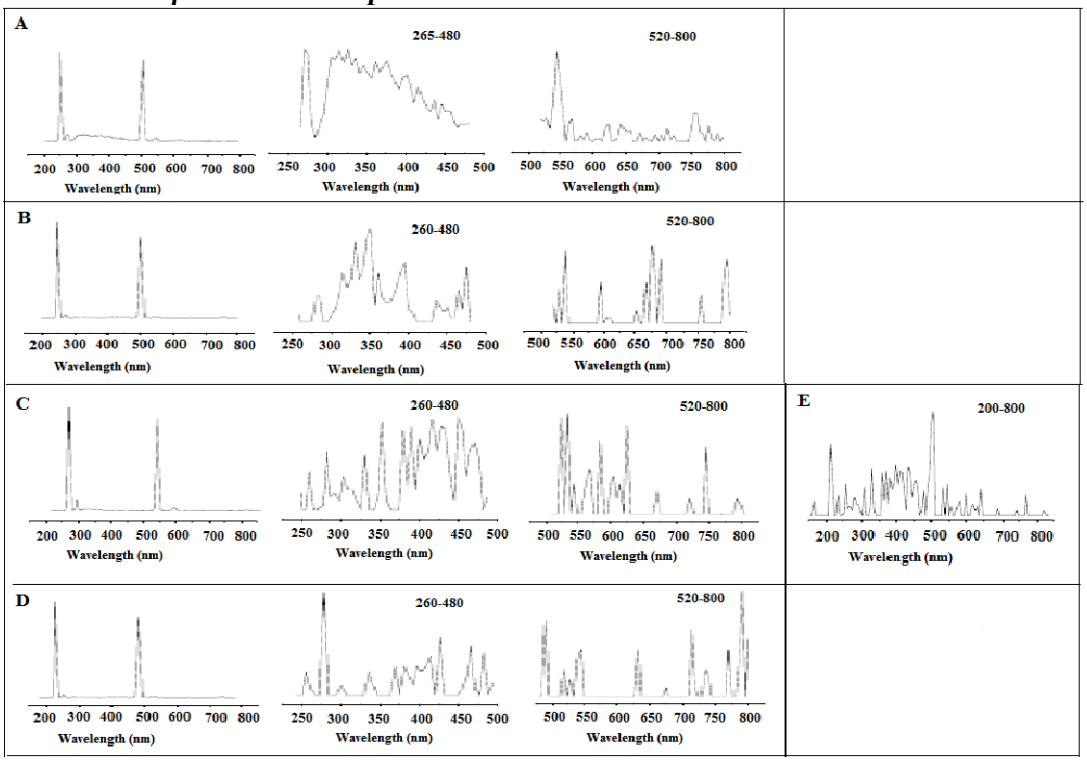

Figure 7: Photoluminance spectra of A). pure Alanine, B). Mn-Ala complex, C). Ni-Ala complex, D). Zn-Ala complex and E). Co-Ala complex

The UV and photoluminescence spectroscopy have provided a consistence evidence of complexation. The UV spectra for the plain amino acid ligand complexes were recorded. New absorption peaks were seen for the complexes of M-Alanine and M-Phenylalanine at λ_{max} 265, 276 & 324 nm. Further, photoluminescence in solution were recorded using at λ_{max} 200-800 nm, where excitation and emission spectra were recorded. The results are shown in Figure 7 and 8. As mentioned earlier, the majority of these complexes were not soluble in DMSO or Ethanol. The photoluminescence was recorded only for the soluble complexes. The recorded emission spectra showed an interesting evidence for the complex formation. The emissions at λ_{max} 556-566 and 660-730 nm gave an evidence that the metal atoms are transferring energy to the ligand (Alanine) and to the benzene ring (Phenylalanine) and hence, promoting the photoluminescence to the organic ligand.

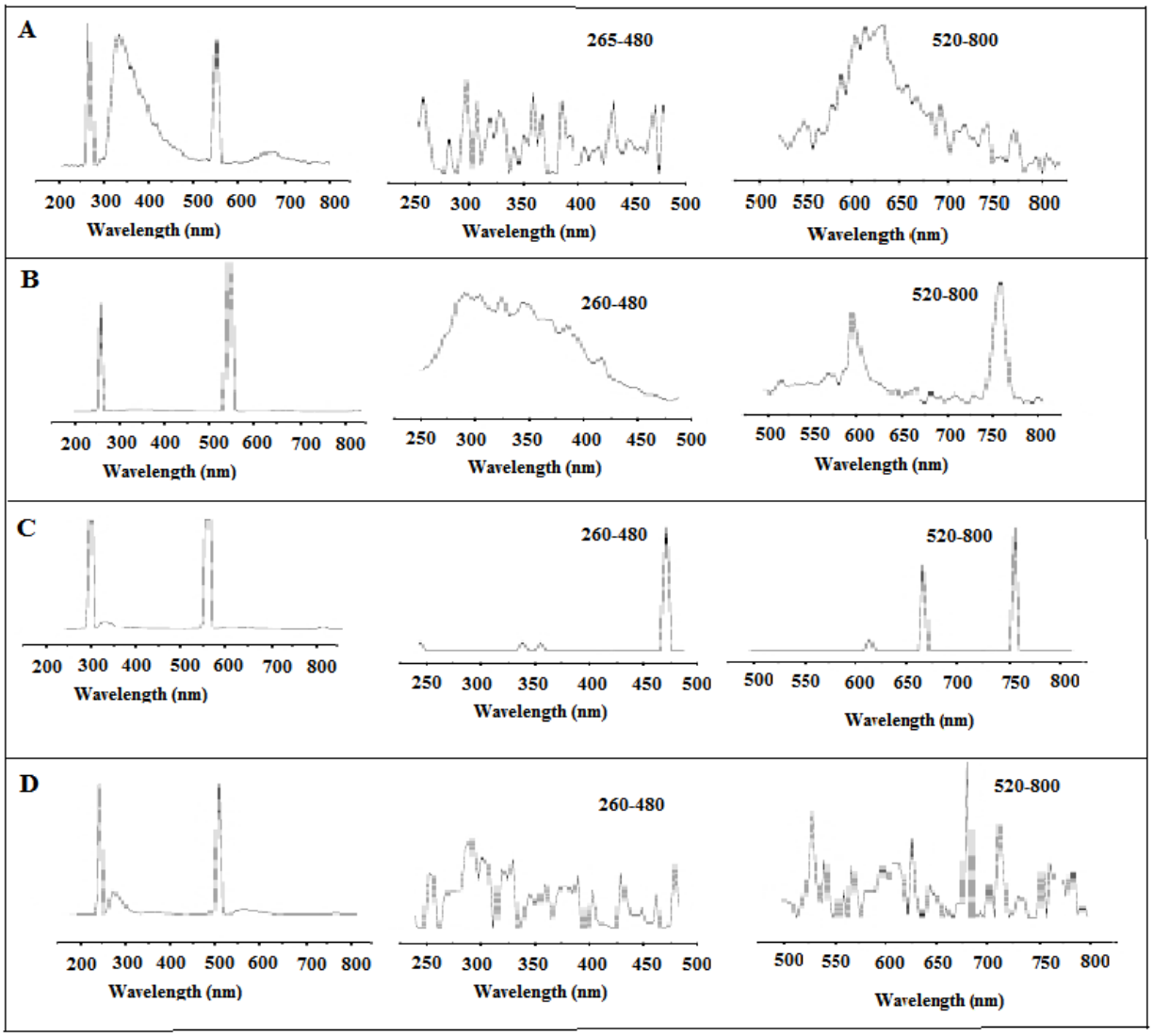

Figure 8: Photoluminance spectra of A). pure Phenylalanine, B). Mn-Phe.Ala complex, C). Ni-Phe.Ala complex and D). Zn-Phe.Ala complex

The photoluminence emission spectra showed an interesting evidence for the complex formation. The emission λ_{max} 556-566 and 660-730 nm provide evidence that the metal atoms are transferring energy to

the ligand (alanine) and to the benzene ring (Phe.ala) and hence promoting the photoluminescence to the organic ligand.

After successfully characterizing these synthesized complexes were applied for cyclohexane oxidation reactions in presence of acetonitrile and solvent free conditions using different oxidants at 80 ^{0}C. The similar reactions were conducted in autoclave too.

Oxidation of Cyclohexane using Metal Complexes with Different Oxidants in Solvent System

In a general procedure, the oxidation of cyclohexane was performed by using acetonitrile as a solvent and H_2O_2, Na_2O_2, KIO_4 and TBHP as oxidants. In a typical method the oxidants were subjected in acetonitrile (30 mL) in the molar ratio of 2:10, 5:10 (1:5, 1:2) with respect to cyclohexane (10 mL).

The oxidants and complexes were taken in a two necked septa sealed flask fixed with reflux condenser in (30 mL) acetonitrile as a solvent system. Cyclohexane was added drop wise to the contents in flask using syringe and needle.

Temperature was maintained at 80^{o}C and the reactants were kept under stirring for 2 hrs and 4 hrs. At each time intervals, the samples were collected, dressed and analyzed by GC. The results are summarized in Table 1.

Table 1: Oxidation of Cyclohexane using Metal Complexes with Different Oxidants in Acetonitrile Solvent System at 80 °C

Metal complex (II)	**Oxidant with product *i. e.*, cyclohexanone formation**							
	H_2O_2		**Na_2O_2**		**KIO_4**		**TBHP**	
	2 hr	**4 hr**	**2 hr**	**4 hr**	**2 hr**	**4 hr**	**2 hr**	**4 hr**
Ala	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Mn-Ala	2-3%	2-3%	Traces	Traces	2-3%	2-3%	2-3%	4-6%
Co-Ala	Traces	Traces	Traces	Traces	Nil	Nil	Traces	3-5%
Ni-Ala	Nil	Nil	Nil	Nil	Traces	Traces	Traces	Traces
Zn-Ala	Traces	Traces	Traces	Traces	Nil	Nil	Traces	Traces
Phe. Ala	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Mn- Phe.Ala	Traces	3-5%	Nil	Nil	Traces	Traces	2-3%	3-5%
Co- Phe.Ala	Traces	Traces	Traces	Traces	Nil	Nil	1-2%	1-2%
Zn- Phe.Ala	Traces	Traces	Nil	Nil	Nil	Nil	Traces	Traces

Note: *Traces means less than 1%, Nil means no product formation was observed*

Oxidation of Cyclohexane using Metal Complexes with Different Oxidants under Solvent Free System

In a modified method the oxidants H_2O_2, Na_2O_2, KIO_4 and TBHP and the complexes were taken together with cyclohexane itself and kept stirred at 80°C for 2 hrs and 4 hrs.

The samples were collected time to time at regular intervals and analyzed by GC. The results are presented in Table 2.

Table 2: ***Oxidation of Cyclohexane using Metal Complexes with Different Oxidants under solvent free system at 80 °C***

Metal complex (II)	Oxidant with product *i. e.*, cyclohexanone formation							
	H_2O_2		Na_2O_2		KIO_4		TBHP	
	2 hr	4 hr	2 hr	4 hr	2 hr	4 hr	2 hr	4 hr
Mn-Ala	Traces	Traces	Nil	Nil	2-3%	2-3%	5-7%	5-7%
Co-Ala	Traces	Traces	Nil	Nil	2-3%	2-3%	2-3%	2-3%
Ni-Ala	Nil	Nil	Nil	Nil	Traces	Traces	1-2%	1-2%
Zn-Ala	Traces	Traces	Traces	Traces	1-2%	1-2%	3-5%	3-5%
Mn- Phe.Ala	Traces	Traces	Nil	Nil	3-5%	3-5%	6-8%	6-8%
Co- Phe.Ala	Traces	Traces	Nil	Nil	3-5%	3-5%	5-6%	5-6%
Zn- Phe.Ala	Traces	Traces	Nil	Nil	2-3%	2-3%	7-8%	7-8%

Oxidation of Cyclohexane using Different Oxidants with Metal Complexes in Autoclaves without Solvent System

In a more precise way, the complexes were subjected for oxidation processes using different oxidants *i.e.*, H_2O_2, Na_2O_2, KIO_4 and TBHP with cyclohexane in autoclave.

In different experiments the contents cyclohexane (20 mL) metal complex (100 mg and 200 mg) and oxidants (1 mole and 2 moles) were taken and kept stirred at 80 ^oC and 100 ^oC for 2 hrs and 4 hrs. The pressure in the autoclave was 1 bar and 2 bar, kept under well stirred. The autogenous pressure developed in the autoclave during the reaction was 1 bar and 2 bar. The samples were collected at regular time intervals and analyzed by GC and IR. The results are summarized in Table 3.

Table 3: Oxidation of Cyclohexane using Metal Complexes with Different Oxidants in autoclave under solvent free system

Metal complex (II)	Oxidant with product *i. e.*, cyclohexanone formation							
	H_2O_2		Na_2O_2		KIO_4		TBHP	
	2 hr	4 hr	2 hr	4 hr	2 hr	4 hr	2 hr	4 hr
Mn-Ala	3-5%	3-5%	Traces	Traces	3-5%	3-5%	4-6%	4-6%
Co-Ala	Traces	Traces	Nil	Nil	Traces	Traces	Traces	3-5%
Ni-Ala	Nil	Nil	Nil	Nil	Traces	Traces	2-3%	2-3%
Zn-Ala	2-3%	2-3%	Nil	Nil	Traces	Traces	3-5%	3-5%
Mn- Phe.Ala	Traces	Traces	Nil	Nil	Traces	Traces	2-3%	3-5%
Co- Phe.Ala	Traces	Traces	Nil	Nil	Traces	Traces	2-3%	3-4%
Zn- Phe.Ala	Traces	Traces	Nil	Nil	Traces	Traces	3-5%	3-5%

When similar reactions were carried out under same reaction conditions using ligands (Alanine and Phenylalanine) no product formation was observed, this shows that amino acids itself can't initiate the oxidation reaction. From the above studies, Ni (II) complex was found less active while Co (II) and Zn (II) complexes have shown active moderately, whereas Mn (II) complex was found good interms of cyclohexanone yield. When the reactions carried out with H_2O_2 and TBHP as oxidants yielded better

results than those with Na_2O_2 and KIO_4. The activity of the metal complexes varies as, Mn (II) complex > Co (II) complex > Zn (II) complex > Ni (II) complex.

Conclusion

In summary, we synthesized different amino acid complexes with Mn (II), Co (II), Ni (II), Zn (II) metals and characterized by FT-IR, ^{1}H NMR, XRD, SEM and UV-Visible photoluminance. These complexes have been effectively used as catalysts for the oxidation of cyclohexane in the presence of different oxidants under solvent and solvent free conditions. The oxidized products of cyclohexane are cyclohexanol and cyclohexanone. It was found out that the order of catalytic activity of the complexes in the reaction of cyclohexane oxidation was as follows: Mn > Co > Zn > Ni. Future work to investigate the potential of a one-step cyclohexane oxidation is planned to evaluate a better process to enhance the desired product formation.

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