

Synthesis of Iron (III), Cobalt (II), Nickel (II), Copper (II) and Zinc (II) complexes with new quadridentate N,O⁻ donor ligands

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(Received: September 09, 2008; Accepted: November 14, 2008)

ABSTRACT

The reaction between phenylalanine and oxalylchloride/malonylchloride results in new quadridentate ligands. bis-[1-phenyl-2-carboxy-2-ethyl]-oxamide [PCEOA], bis(1-phenyl-2-carboxy-2-ethyl) malonamide [PCEMA]. These ligands form 1:1 complexes of general formula $[M(L)(H_2O)_2]Cl$, $[M(L)]H_2O$, $M(L)$, $[M(L)]2H_2O$, $L=PCEOA$ and $PCEMA$. $M=Fe^{III}$, Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} . The organic compounds containing amide group play an important role in biology, as it constitutes the repeating unit of the polypeptide macro molecules. Further they have allocated the attention of co-ordination chemists as they serve as model for metal-peptide interactions and to metalloenzymes¹. In the present paper, the preparation and characterization of two new ligands bis-[1-phenyl-2-carboxyl-2-ethyl] oxamide [PCEOA] and bis-[1-phenyl-2-carboxyl-2-ethyl] malonamide [PCEMA] and their complexes with Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} are described.

Key words : Metal complexes, Iron, Cobalt, Nickel, Copper, Zinc

INTRODUCTION

All the chemicals used were of the Analar grade solid phenylalanine was used and the solvents were purified by distillation before use. The C, H and N were analyzed on the Perkin-Elmer 2400 instrument. ¹HNMR spectra were recorded as a Bruker WP80SY instrument at Institut für Anorganische and Analytische chemie, Technische Universität Berlin, Berlin, Germany. Conductance was recorded on a Digisun DI-909 conductometer. Infrared and electronic spectra were recorded on Perkin-Elmer 283 and Shimadzu UV-VIS 160 spectrophotometers respectively. ESR spectra were recorded at room temperature and liquid nitrogen temperature on JEOL-JES-PE-3X and varian ESR spectrometers respectively, at RSIC., IIT., Chennai. Thermograms were recorded on the Mettler-TA-2000C instrument.

Preparation of ligands

To phenylalanine (10g) suspended in dry benzene (50ml) was added oxalylchloride (2.6ml), malonylchloride (2.5ml) drop-wise very slowly with constant mechanical stirring. They were stirred for 4 to 5 hours at 60°C. Yellow coloured solids were formed, which were filtered and washed with dry benzene and acetone, dried in air and crystallized from methanol in presence of activated charcoal to yield the products: PCEOA (6.8g, 70%) m.p 195°C (Found: C, 62.13; H, 4.87; N, 7.06, $C_{20}H_{20}N_2O_6$ calcd. for: C, 62-50; H, 5-20; N, 7.29%); ν_{max} KBr 3400, 3030 (N-H) 2980, 2907, 2610 (COOH), 1675, 1630 (C=O) 1600 (amide-II), (DMSO-*d*₆) 12.28 (2H, s, COOH) 7.8 (2H, r, NH), 7.25-7.35 (10H, m, ArH). 4.00, 3.32_d (2H, d, CH₂-C) PCEMA (7.1g, 70%) m.p 190°C (Found: C, 62.98; H, 5.38; N, 6.84 $C_{21}H_{22}N_2O_6$ calcd for C, 63.31; H, 5.52; N, 7.03%) ν_{max} (KBr) 3450, 3030 (NH), 2980, 2907, 2610 (COOH) 1675,

1630 (C=O) 1600 (amide-II), δ (DMSO- d_6), 12.20 (2H, S, COOH) 7.8 (2H, br, NH), 7.25-7.35 (10H, m, ArH) 4.00, 3.32 (2H, CH₂-C) 2.63 (2H, s, OCCH₂OC).

Preparation of complexes

To PCEOA (1.6 m mol) or PCEMA (1.6 m mol) dissolved in methanol (30 ml) was added the hydrate metal salt FeCl₃, Co(OAc)₂, Ni(OAc)₂ and Zn(OAc)₂ (1.6 m mol) in methanol (20ml) slowly with stirring. The mixture was refluxed on a hot water bath for 3-5h. The resulting solid complexes were washed with cold methanol and dried over fused CaCl₂ (Yields 55.5-78%).

RESULTS AND DISCUSSIONS

The Fe^{III}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes with [PCEOA] and [PCEMA] are stable and non-hygroscopic. The molar conductance values of all the complexes in DMF except those of Fe^{III} complexes at a concentrations of 10⁻³ M are very low (5-11 Ohm⁻¹cm²mol⁻¹) indicating their non-ionic nature². The conductance values of the Fe^{III} complexes of [PCEOA] and [PCEMA] (26.5-25.6 Ohm⁻¹cm²mol⁻¹ respectively) in DMF suggest that the complexes are 1:1 electrolytes. The analytical and molar conductance studies suggest that the general formulae of complexes as [M(L)(H₂O)₂]Cl, [M(L)]H₂O, M[(L)], [M(L)]2H₂O, L=PCEOA and PCEMA. M= Fe^{III}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}.

The thermograms of Fe^{III} and Zn^{II} complexes of PCEOA and PCEMA exhibit endothermic peaks in the DSC curves in the temperature range 140-200°C and 70-110°C respectively and the percentage mass loss was found to correspond to two water molecules. The expulsion water molecules in the high temperature range in the Fe^{III} complexes confirms that they are coordinated³. The loss of two water molecules in the low temperature region in the Zn^{II} complexes indicates that they are lattice held³. The thermograms of the Fe^{III} complexes show second stage mass loss curves at 460-560°C with the corresponding exothermic peak in DSC⁵. The percentage loss was found to be slightly more than that required for the ligands indicating the loss of Cl⁻ ion also. The percentage of residue left 15.98 (15.92 calcd) and 15.487 (15.20 calcd) confirm to the oxide, Fe₂O₃ in both the cases.

Thermograms of the Co^{II}, Cu^{II} complexes exhibit endothermic peaks in the DSC curves in the temperature range 80-145°C and 60-100°C respectively and the percentage mass loss was found to corresponding two water molecules. The expulsion water molecules in the low temperature region indicates that they are lattice held⁶.

The exothermic peak at 340-550°C confirms the loss of ligand moieties. The percentage mass loss and the residue left account respectively for the ligand and the metal oxide Co₃O₄⁷, NiO⁸ and CuO⁹. The data confirm that formulae for the complexes are [M(PCEOA)] AND [M(PCEMA)] where M= Co^{II}, Ni^{II}, Cu^{II}. The Zn^{II} complexes exhibit exothermic peak in the temperature range 410-590°C and the corresponding mass-loss curve in the thermograms accounting to the loss of ligand. The residue left after the decomposition of organic moiety accounts to that of zero¹⁰.

The characteristic IR absorptions of the ligands PCEOA and PCEMA and their assignments are given in the experimental sections. The ν_{N-H} ligand bands shift to low frequency side by 50-130cm⁻¹ indicating the coordination of amide NH group¹¹ to the metal ions. The disappearance of ν_{COOH} absorptions confirms that the deprotonation takes place on coordination. This is further confirmed by the appearance of new absorptions around 1500 and 1390 cm⁻¹ characteristics of coordinated carboxylate anion group i.e. ν_{asym}(COO⁻) and ν_{sym}(COO⁻) respectively¹². In case of the Fe^{III} and Zn^{II} complexes, the broad absorption at 3350-2700cm⁻¹ are attributed to water molecules. An absorptions at 830cm⁻¹ in the case of the Fe^{III} complexes confirms that the water molecules are coordinated¹³. The Zn^{II} complexes show no absorption in this region indicating that the water molecules are not coordinated. The ν(C=O) band of amide group shifted to high frequency side by 10-25cm⁻¹ confirming that the amide carbonyl oxygen is not coordinated to the metal ion⁴. These changes in the IR spectra of the complexes indicating that ligands PCEOA and PCEMA act as quadridentate ligands coordinating through two amide nitrogen atoms and two carboxylate oxygen atoms. The amide II absorption is shifted to low frequency side by 30-50 cm⁻¹ in the spectra of the complexes, confirming the co-ordination of amide

nitrogen atom⁴. In addition all the complexes exhibit ν M-O absorptions at 400-425 cm^{-1} and ν M-N absorptions at 360-380 cm^{-1} in the far-IR region¹⁴.

The magnetic moments of all the complexes obtained from the corrected magnetic susceptibilities¹⁵ are presented in Table-1. The magnetic moments of the Fe^{III} are indicating them to be low spin complexes¹⁶ with significant orbital contribution¹⁷. The low values of the Co^{II} complexes also indicate them to be low-spin complexes. The Ni^{II} complexes are found to be diamagnetic. The magnetic moment value of the Cu^{II} complexes are close to the single electron moments of several Cu^{II} complexes. The magnetic property studies indicate that the ligands PCEOA and PCEMA are strong field producing ligands as evident forms similar N, O⁻ donor ligands¹⁸. The Zn^{II}(d^{10}) complexes exhibit very low magnetic susceptibilities and hence are diamagnetic.

The low-spin Fe^{III} complexes exhibit absorption at 25640, 29900 cm^{-1} (PCEOA) and 28570, 24690 cm^{-1} (PCEMA). The low spin Fe^{III} complexes are reported¹⁹ to absorb radiation corresponding to ${}^2E_g \leftarrow {}^2T_{2g}$, ${}^2A_{2g}$, ${}^2T_{1g} \leftarrow {}^2T_{2g}$, ${}^4T_{2g} \leftarrow {}^2T_{2g}$ and ${}^4T_{2g} \leftarrow {}^2T_{2g}$ transitions. However, all these four transitions are not intense and may not be observed generally. Hence, the absorptions are assignable to the above transitions.

The low-spin Co^{II} complexes of PCEOA and PCEMA exhibit three to five absorptions in the

electronic spectral region. Urbach *et al.*,²⁰ calculated single electron d-orbital energies for N_2O_2 -Co^{II} square planar chelates and proposed that a total of nine transitions are possible. Thus, the transitions observed in the regions 15875-28710 cm^{-1} . Indicate that the Co^{II} complexes of PCEOA and PCEMA have square planar geometry the electronic spectra of the diamagnetic Ni^{II}, d^8 complexes exhibit absorptions at 15625, 21370, 23780 cm^{-1} [Ni(PCEOA)] assignable to ${}^1A_2 \leftarrow {}^1A_1$ (ν_1) ${}^1B_2 \leftarrow {}^1A_1$ (ν_2), ${}^1E \leftarrow {}^1A_1$ (ν_3) transitions of Ni^{II} in square planar environment, D_{2d} point group.

The analytical and thermal studies indicate that the Cu(II) ion is coordinated to quadridentate ligands. The Cu(II) d^9 system with only one unpaired electron forms four coordinated (i) tetrahedral complexes ($\mu_{\text{eff}}=2.2\text{B.M}$) and (ii) square-planar complexes ($\mu_{\text{eff}}=1.8\text{B.M}$). The lower magnetic moment values (Table-1) and the electronic spectral absorption in the higher energy region at 15385 cm^{-1} [Cu(PCEOA)] and 15750 cm^{-1} [Cu(PCEMA)] as against the low energy (<10000 cm^{-1}) absorptions for tetrahedral complexes²¹ confirm that the Cu^{II} complexes of PCEOA and PCEMA have square planar geometry.

The ${}^1\text{H}$ NMR spectra (DMSO- d_6) of diamagnetic Ni^{II} and Zn^{II} complexes have been recorded in DMSO- d_6 . The conspicuous feature of these spectra as compared to those of the ligands is the absence of the signal at the downfield (11-5 ppm) of the COOH group. This confirms the

Table 1: Analytical and Physical data of complexes

Compd	Decomp Temp $^{\circ}\text{C}$	Metal % Found/cal	μ_{eff} (B.M)
[Fe(PCEOA)(H ₂ O) ₂]Cl	485	10.64 (10.96)	2.16
[Fe(PCEMA)(H ₂ O) ₂]Cl	400	9.97 (10.46)	2.18
[Co(PCEOA)]H ₂ O	350	12.57 (12.85)	2.20
[Co(PCEMA)]H ₂ O	375	12.83 (12.47)	2.20
[Ni(PCEOA)]	380	12.58 (12.31)	dia
[Ni(PCEMA)]	410	11.57 (11.72)	dia
[Cu(PCEOA)]2H ₂ O	340	12.88 (13.19)	1.84
[Cu(PCEMA)]2H ₂ O	400	12.83 (13.03)	1.83
[Zn(PCEOA)]2H ₂ O	410	13.28 (13.52)	dia
[Zn(PCEMA)]2H ₂ O	435	13.24 (13.35)	dia

deprotonation. The broad signal of NH proton shifted to low field side (from 8.2 to 9.5 ppm) in the spectra of the complexes indicating the coordination of amide nitrogen. The other proton signals bonded to carbon atoms (aromatic and aliphatic) did not show any shift. The spectra of the Zn^{II} complexes exhibit a new signal at 3.70 ppm characteristic of the protons of water molecules. In the Ni^{II} complexes, no signal was observed in this region confirming the absence of water molecules.

The ESR spectra of the Cu^{II} complexes recorded at room temperature and liquid nitrogen temperature were found to be anisotropic with only two peaks. From the spectra of the respective

complexes the parameters like g_{\parallel} (2.20), g_{\perp} (2.05), g_{av} (2.09) and G (4.00) have been obtained. Because of the poor resolution of the spectra even at the liquid nitrogen temperature, the A_{\parallel} and A_{\perp} values could not be obtained. The spin-orbit coupling constant (λ) values have been evaluated using the equations, $g_{\parallel} = 2.0023 - 8\lambda/\Delta E$ and were found to be 349 and 375 respectively, for [Cu(PCEOA)] and [Cu(PCEMA)]. The lower values of λ as compared to the free-ion value indicate that there is a considerable mixing of ground and excited state terms. The higher magnetic moment values (1.85 B.M) evaluated from the ESR spectra and the experimentally determined values confirm the same.

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