Copper(II) complexes are widely studied by inorganic chemistry researchers because of their user friendliness.\textsuperscript{1-5} These are air- and moisture-stable, have informative and easy-to-obtain UV-Visible and EPR spectroscopic signatures and often undergo reactions in solution effectively within mixing. The d\textsuperscript{9} copper(II) ions is usually found in tetragonal coordination, with four equatorial bonds and another one or two longer axial bonds, although some four coordinated tetrahedral and planar complexes are also known. Most of the copper(II) complexes are blue or green in colour because of d-d absorptions in 600-900 nm region. Copper complexes are known to have a broad spectrum of biological action.

The first report of the metal complexation of a polymeric amine in the literature described the binding of Cu\textsuperscript{2+} and Ni\textsuperscript{2+} by branched polyethyleneimine.\textsuperscript{6} These water soluble complexes in principle, can be investigated by conventional solution chemistry methods.\textsuperscript{7-9} however, relatively few investigations of the interaction of metal ions with such polymeric ligands have been carried out, despite the fact that binding of a metal ion by a polymer has some very interesting aspects and even high potential for applications. There are many reports in which some kind of interaction between polymeric amines and metal ions was observed yet rarely was this interaction investigated by methods generally used in coordination chemistry.\textsuperscript{10-13}
Even a recent report on the chelating properties of linear and branched polyethyleneimine gives only cursory information about this interaction.\textsuperscript{14-16}

This chapter describes the synthesis and characterization of some new as well as known water soluble branched polyethyleneimine-copper(II) complexes with different amounts of copper(II) complex moieties bound to the polymer chain.

3.1. Experimental section

3.1.1. Materials

The following chemicals were used as received: Copper(II) chloride dihydrate, 1,10-phenanthroline and 2,2'-bipyridine were obtained from Merck, India. Copper(II) perchlorate and branched polyethyleneimine (BPEI) (Mw ca. 25,000) were obtained from Sigma-Aldrich. L-valine, L-tyrosine and L-arginine were obtained from Loba Chemie, India.

3.1.2. Instrumentation

The carbon, hydrogen and nitrogen contents of the samples were determined at Sophisticated Analytical Instruments Facility (SAIF), Lucknow, India. Absorption spectra and thermal denaturation studies were recorded on a UV-Vis-NIR Cary 300 Spectrophotometer using cuvettes of 1 cm path length. FT-IR spectra were recorded on a FT-IR JASCO 460 PLUS spectrophotometer with samples prepared as KBr pellets. EPR spectra were recorded on JEOL-FA200 EPR spectrometer.
3.2. Synthesis of ordinary precursor copper(II) complexes

The following precursor complexes which are known in the literature were prepared using the methods as reported.

3.2.1. \([\text{Cu}(\text{L-val})(\text{phen})(\text{H}_2\text{O})]\text{Cl·H}_2\text{O}\)\(^6\)

To a solution containing copper(II) chloride dihydrate (2.558 g, 15 mmol) and 1,10-phenanthroline monohydrate (2.973 g, 15 mmol) in 50 ml (v/v) of ethanol water, 15 ml of aqueous solution of L-valine (1.758 g, 15 mmol) and NaOH (0.6 g, 15 mmol) were added with stirring. The mixture was then refluxed for 30 min, filtered and the resulting filtrate was left to evaporate at room temperature. Blue crystals were formed after a month. The crystals were filtered off and dried in vacuum.

3.2.2. \([\text{Cu}(\text{L-tyr})(\text{phen})(\text{H}_2\text{O})]\text{ClO}_4\cdot\text{H}_2\text{O}\)\(^7\)

To a mixture of L-tyrosine (2.172 g, 12 mmol) and KOH (0.672 g, 12 mmol) in aqueous solution, a hot solution of Cu(OAc)$_2$·H$_2$O (2.388 g, 12 mmol) was added under stirring. The resulting solution was treated with a methanolic solution of (10 ml) of 1,10-phenanthroline monohydrate (2.376 g, 12 mmol) under stirring for 3h at 60 ºC. After cooling the solution to room temperature an aqueous solution of NaClO$_4$·H$_2$O (2.172 g, 12 mmol) was added and stirred for another 20 min. The product precipitated out from the reaction mixture and it was filtered off, washed with ethanol followed by ether. The solid was dried in vacuum.
3.2.3. [Cu(L-arg)(phen)(H₂O)]Cl₈

An aqueous solution of CuCl₂·2H₂O (1.7 g, 10 mmol) was reacted with an aqueous solution of L-arginine (2.3 g 11 mmol) treated with NaOH (0.4 g, 10 mmol) followed by slow addition of 1,10-phenanthroline monohydrate (1.8 g, 10 mmol) in methanol with stirring at 60 °C for 3h after that the solution was filtered. Slow evaporation of the filtrate yielded a solid product which was filtered off and the solid was washed with cold methanol and dried.

3.2.4. [Cu(phen)₂Cl]Cl⁹

Twelve millimoles (2.05 g) of CuCl₂·2H₂O was dissolved in 10 ml of distilled water. To that 4.33 g (24 mmol) of 1,10-phenanthroline dissolved in 10 ml of methanol was added. The green coloured solution was stirred about 1 h, then the solution was boiled for 5-10 min and filtered. The filtrate was kept at room temperature for slow evaporation. The complex separated out as green coloured crystals which were filtered off and dried in vacuum.

3.2.5. [Cu(bpy)₂Cl]Cl¹⁰

Fifteen milimoles (2.56 g) of CuCl₂·2H₂O was dissolved in 5 ml of warm distilled water. To that 4.69 g (30 mmol) of 2,2'-bipyridine dissolved in 10 ml of methanol was added and the mixture was refluxed with constant stirring for about 15 min. Then it was kept at room temperature. Blue coloured crystals were formed on cooling which were filtered off and kept in desiccator.
3.3. Synthesis of new polymer-copper(II) complexes

3.3.1. [Cu(L-val)(phen)(BPEI)]Cl·H₂O (1)

To a solution of [Cu(L-val)(phen)(H₂O)]Cl·H₂O (1.7 g, 3.94 mmol) in water, branched polyethyleneimine (BPEI) (0.15 g, 3.4 mmol) dissolved in ethanol (15 ml), was added slowly with stirring. The mixture was heated between 50-60 °C for 12 h in a water bath with constant stirring. The resulting dark blue solution was filtered and the filtrate was dialyzed approximately at 15 °C against distilled water for 4-5 days. The solvent was then evaporated by a rotary evaporator under reduced pressure at room temperature. The dark bluish filmy polymer-copper(II) complex obtained was pulverized and dried. Yield, 0.27 g. The degree of coordination was obtained from carbon content. (Anal. Calc.: C, 46.90, H, 5.57, N, 14.55, O, 5.83, Cu 46.80%. Found: H, 5.48, N, 15.15, O, 5.67, Cu 46.78% (x = 0.541 obtained from carbon content); IR (KBr, cm⁻¹): 3442, 2925, 1630, 1387, 852, 835, 730, 689; UV (λ_max, nm): 265, 292, 640; EPR (77 K, methanol at liquid nitrogen temperature): g_iso = 2.051, at room temperature g_iso = 2.079.

Another two samples of the same polymer-copper(II) complex with different degrees of coordination (i.e., various amount of copper(II) complex units bound to the polymer chain) were synthesized by changing the concentration of reactants in the reaction solution, duration of the reaction time and reaction temperature. The degree of coordination, x, values were calculated from copper analysis and are 0.433 and 0.238.
3.3.2. [Cu(L-tyr)(phen)(BPEI)]ClO₄ (2)

To a solution of branched polyethyleneimine (BPEI) (0.15 g, 3.4 mmol) dissolved in water/ethanol mixture (15 ml), [Cu(phen)(L-tyr)(H₂O)]ClO₄ (0.8 g, 1.4 mmol) in water was added slowly with stirring. The mixture was heated between 50-60 °C for 15 h in a water bath with constant stirring. The resulting dark blue solution was filtered and the filtrate was dialyzed approximately at 15 °C against distilled water for 4-5 days. The solvent was then evaporated by a rotary evaporator under reduced pressure at room temperature. The dark bluish filmy substance obtained was pulverized and dried. Yield, 0.23 g. (Anal. Calc.: C, 33.77, H, 4.40, N, 14.50, O, 5.81, Cu 18.35%. Found: H, 5.02, N, 14.25, O, 5.77, Cu 18.37% (x = 0.182 obtained from carbon content). IR (KBr, cm⁻¹): 3446, 2924, 1630, 1390, 1099, 852, 838, 730, 693; UV (λmax, nm): 272, 294, 645. EPR (77 K, methanol at liquid nitrogen temperature): g∥ 2.211 and g┴ 2.017 at room temperature giso = 2.0753.

The same polymer-copper(II) complex samples with two different degree of coordination, x, values were synthesized by changing the amount of precursor complex in the reaction solution, duration of the reaction time and reaction temperature. The x values were obtained through copper analysis and are 0.182 and 0.149.

3.3.3. [Cu(L-arg)(phen)(BPEI)]Cl (3)

To a solution of BPEI (0.15 g, 3.4 mmol) dissolved in ethanol (15 ml), [Cu(phen)(L-arg)(Cl)]Cl (1.9 g, 3.56 mmol) in water/ethanol was added slowly with stirring. The mixture was heated between 50-60 °C for 16 h in a water bath with occasional stirring. After being warmed enough, the dark blue solution was filtered
and the filtrate was dialyzed approximately at 15 ºC against distilled water for 4-5 days. Afterwards the solvent was evaporated by a rotary evaporator under reduced pressure at room temperature. A dark bluish filmy substance was obtained. It was pulverized and dried. Yield, 0.24 g. (Anal. Calc.: C, 40.77, H, 3.38, N, 17.7, O, 4.12, Cu 25.45%. Found: H, 3.40, N, 17.5, O, 4.13, Cu 25.41% (x = 0.586 found from carbon content). IR (KBr, cm\(^{-1}\)): 3433, 2925, 2928, 1581, 1412, 1317, 835, 679; UV (\(\lambda_{\text{max}}\), nm): 273, 294, 642. EPR (77 K, Methanol at liquid nitrogen temperature): g\(^\parallel\) 2.35 and g\(^\perp\) 2.04 at room temperature g\(_{\text{iso}}\) = 2.09.

The above polymer-copper(II) complex samples with two different degree of coordination (x) were synthesized by varying the amount of [Cu(phen)(L-arg)(H\(_2\)O)]·Cl in the reaction mixture (between 0.6 and 1.0 g) and changing the reaction time but keeping the range of temperature same. The x values obtained for these samples through copper analysis are 0.262 and 0.055.

3.4. Synthesis of known polymer-copper(II) complexes

The following complexes were synthesized as described earlier with slight modifications in the procedures.

3.4.1. [Cu(phen)\(_2\)BPEI]\(\text{Cl}_2\cdot4\text{H}_2\text{O}\) (4)

To a solution of BPEI (0.15 g, 3.40 mmol of monomer unit) in ethanol, [Cu(phen)\(_2\)Cl]Cl (1.8 g, 3.24 mmol) in water was added slowly with stirring. The mixture was heated between 50 and 60 ºC for 15 h in a water bath. After being warmed enough, the coloured mixture was filtered and the filtrate was dialyzed...
against cold water for 4-5 days. The solvent was then evaporated in a rotary evaporator under reduced pressure at room temperature. A bluish filmy substance was obtained which was kept in vacuum. The same polymer complex samples with two different degrees of coordination were synthesized by changing the amount of precursor complex in the reaction solution, duration of the reaction time and reaction temperature.

The complexes were characterized through their known UV-Visible, IR spectra\textsuperscript{11} and copper analysis. The degree of coordination (x) obtained for these complexes are x = 0.156, 0.307 and 0.326.

3.4.2. [Cu(bpy)_2BPEI]Cl_2·4H_2O (5)\textsuperscript{12}

To a solution of BPEI (0.15 g, 3.4 mmol) dissolved in ethanol (15 ml), [Cu(bpy)_2Cl]Cl_2 (2.0 g, 3.85 mmol) in water/ethanol was added slowly with stirring. The mixture was heated between 50-60 \degree C for 18 h in a water bath with constant stirring. After that the dark blue solution was dialyzed approximately at 15 \degree C against distilled water for 4-5 days. The solvent was then evaporated by a rotary evaporator under reduced pressure at room temperature. A dark bluish filmy substance was obtained. It was pulverized and dried. The same polymer-copper(II) complexes with two different degrees of coordination were synthesized by changing the amount of [Cu(bpy)_2Cl]Cl in the reaction solution, duration of the reaction time and reaction temperature. The complexes were characterized through their known UV-Visible, IR spectra\textsuperscript{11} and copper analysis. The degree of coordination (x) obtained for these complexes from copper analysis are x = 0.156, 0.307 and 0.326.
3.5. Copper analysis

Copper content in the copper(II) complexes was estimated by the following method. A known weight of the complex (0.02 g) was dissolved in 2 ml of concentrated nitric acid. The solution was gently warmed. After being cooled, the pH of the solution was adjusted to >5 with 6 M NaOH. The solution was transferred into 10 ml volumetric flask and made upto the mark with aqueous NH₃. The absorbance of this solution was measured against a reagent blank. From the absorbance, the concentration of the copper was calculated.

3.6. Results and discussion

3.6.1. Degree of coordination

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\text{(1)}
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\text{(2)}
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Fig. 3.1. Schematic diagram of [Cu(L-val)(phen)(BPEI)]Cl (1), [Cu(L-tyr)(phen)-
(BPEI)]ClO₄ (2), [Cu(L-arg)(phen)(BPEI)] Cl (3), [Cu(L-arg)(phen)₂(BPEI)] Cl₂ (4)
and [Cu(bpy)₂(BPEI)]Cl₂ (5)
The structure of the polymer-copper(II) complexes are shown in Fig. 3.1. In this figure ‘x’ represents degree of coordination. The degree of coordination (x), means the number of moles of copper(II) chelate per mole of the repeating unit (amine group) of polymeric ligand (if all the repeating units of the polymer are coordinated to copper(II) complexes the value of x = 1.).

3.6.2. Spectral characterization

For the polymer-copper(II) complexes (1-3), the bands obtained around 1466 and 1387 cm\(^{-1}\) in IR region can be attributed to the ring stretching frequencies viz., \(\nu(C-C)\) and \(\nu(C-N)\) respectively of 1,10-phenanthroline. The out of plane bending values, \(\nu(C-H)\) at 852 and 730 cm\(^{-1}\) for the 1,10-phenanthroline ligand were red shifted around 835 and 689 cm\(^{-1}\) respectively in the complexes (1-3). These shifts can be explained by the fact that each of the two nitrogen atoms of phenanthroline ligands donates a pair of electron to the central copper atom forming coordinate bond. The band around 2925 cm\(^{-1}\) can be assigned to C-C stretching vibration of aliphatic CH\(_2\) of BPEI whereas the broad band observed around 3442 cm\(^{-1}\) is assigned to the N-H stretching of BPEI. Absence of band in the region of 1750-1700 cm\(^{-1}\) indicates that COO\(^{-}\) coordinated to the complex and it is shifted around 1630 cm\(^{-1}\) shows the coordination of COO\(^{-}\) to copper centre.

In the UV-Visible region, the intense absorption bands appear from 200 to 350 nm is attributed to intra ligand transitions. The other absorption band which appears around 640-645 nm is assigned to d-d transition. The EPR spectra of the polymer-copper(II) complexes (1-3), were recorded in X-band frequencies in room temperature...
as well as frozen solution (77 K) and are shown in Fig. 3.2. The complexes (1-3) exhibit well defined single isotropic feature near $g_{iso} = 2.051$. Such isotropic lines are usually results of intermolecular spin exchange, which broadens the lines. This intermolecular type of spin exchange is caused by the strong spin coupling which occurs during a coupling of two paramagnetic species. Spectra obtained from frozen solution of the complexes (2-3) have well documented features of axial symmetry. The existence of $g_{\parallel} > g_{\perp} > 2.0023$ suggest that $d_{x^2-y^2}$ is the ground state with the $d^9$ ($Cu^{2+}$) configuration.\textsuperscript{6-8}
Fig. 3.2. EPR spectra of [Cu(L-tyr)(phen)(BPEI)]ClO₄·H₂O recorded at room temperature (top) and at 77 K (bottom)
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References

