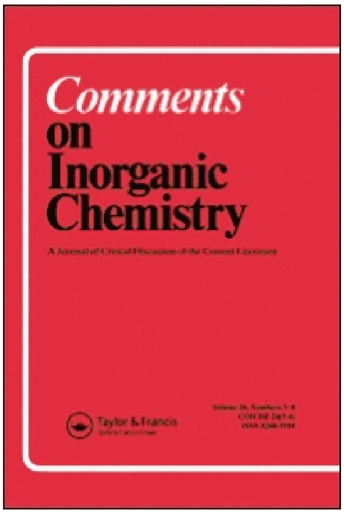

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Polymeric Amines as Ligands. Polyethyleneimines as Ligands in First and Second Coordination Sphere

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Polymeric Amines as Ligands. Polyethyleneimines as Ligands in First and Second Coordination Sphere

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Polymeric amines, containing the monomeric unit $-CH_2-CH_2-NH-$ (PEI or LPEI), are versatile ligands, forming complexes in aqueous solutions with many labile metal ions, even at relatively low pH, due to the strong chelate effect. The mean distances between the metal centers within a polymer chain is small in solutions with a low ratio N:M, even if the total metal concentration is low. This gives rise to metal–metal interactions, as, e.g., observed by ESR-spectroscopy. Non-labile metal ions, like Pt(II) or Ru(II), form complexes with these ligands too. It is also possible to bind both labile and non-labile metals in the same polymer chain. The polymeric ligand is, in its protonated form, a chelating hydrogen bridge donor, complexing anions as, e.g., cyano complexes strongly. The effects of first and second sphere complexation are discussed and some possible applications are mentioned.

Key Words: *polymers as ligands, second sphere complexes, anion complexation, magnetic interaction in polymers, ESR of polymer complexes*

Low molecular weight (two to six open chain amine groups) polyamines (pa) with chelating ligand building blocks analogous to ethylenediamine (en) have found extensive use in cordination

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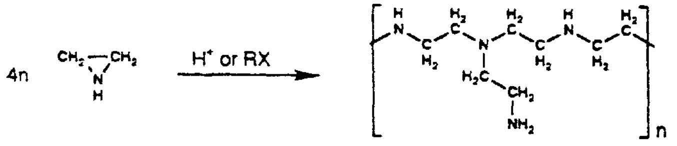
chemistry.[1] More recently, also cyclic polyamines (cpa) with three to twelve amine groups have been investigated.[2,3] Much knowledge has been accumulated on structures, thermodynamic stabilities, kinetic behavior, spectroscopic data, and on many other chemical and physical properties of complexes containing pa or cpa ligands.

It is therefore somewhat surprising that high moleclar weight polyamines (polymeric polyamines = ppa) have been investigated only scarcely[4] by coordination chemists, despite their availability as commercial products.[5] In this Comment we want to draw the attention of the coordination chemists to this interesting group of ligands which give rise to some phenomena not paralleled by the low molecular weight pa or cpa ligands. Research in this area is interdisciplinary, requiring the application of methods of coordination chemistry and of polymer chemistry. The present report focusses on the coordination chemistry aspects of the systems investigated.

THE LIGANDS

Polymeric polyamines (ppa) are available from various suppliers in different qualities.[5] Our investigations have been carried out either with branched polyethyleneimine (PEI) of Fluka Chemicals or with linear polyethyleneimine (LPEI) prepared according to the literature.[6] PEI is produced from aziridine by cationic polymerization, and it is therefore also designated as polyaziridine (e.g., in CA).



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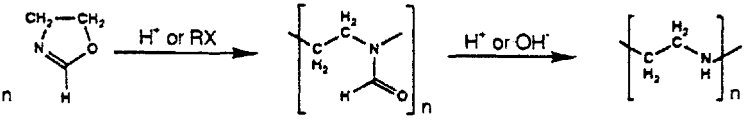

(2)

PEI contains primary:secondary:tertiary amine groups in a ratio of ca. 1:2:1.[7] PEI (Fluka, Polyimin P) is available as a 50% aqueous solution. At this concentration, which corresponds to a stoichiometry of $[-CH_2-CH_2-NH \cdot 2.6H_2O]_n$, the solution is a highly viscous syrup, which can be diluted in any proportion by water. At lower concentrations, the solution has a relatively low viscosity. The 50% solution can be nearly completely dehydrated either by heating to ca. 110°C during 24 hours under vacuum, or by freeze drying.

Strictly linear polyethyleneimine (LPEI) can be prepared by ring opening polymerization and subsequent hydrolysis of poly(N-formyl ethyleneimine).[6] It is obtained as a highly crystalline solid with the composition $(-CH_2-CH_2-NH \cdot 1.5H_2O)_n$ (reaction (2)) from aqueous solution.[8] It too can be dehydrated under the same conditions as PEI.

Concentrations of PEI and LPEI are given in the following by mol N per liter solution. This is the only well defined concentration unit in solutions of polymeric ligands, due to their molecular weight distribution. It is given by the mass of the solute and the volume of the solution. This definition of the concentration implies, however, that solutions of polymeric ligands are not homogeneous in the strict sense. There are regions within the polymeric coil with a high concentration of basic sites, whereas outside of the coils, there are no basic sites at all.

Which analytical methods are adapted to study the equilibria between polymeric ligands and metal ions in solution? In principle all potentiometric and spectroscopic methods developed by coordination chemists can be used. There should be caution, however, with potentiometric methods, because polyelectrolyte solutions deviate strongly from the thermodynamic ideal.[9] In addition, all the numerous methods used in biochemistry[10] to study interactions between enzymes and small molecules can be applied. In the following, we discuss potentiometric and spectroscopic titration methods and we focus the discussion especially on ESR and NMR. In these methods the shape of the signals depends on the rotational correlation time, which differs strongly between free and polymer bound species.

PEI AND LPEI AS POLYBASES

The polymeric amines are strong Bronsted polybases in aqueous solution. The conditional pK-values are quasi-continuous over a large region ($3 < pK_c < 9$).[11]

A titration curve (Fig. 1) shows two distinct "buffer" regions. The interpretation of the data by the concept of differential acidity constants[12] gives the proton affinity of PEI as a function of the degree of protonation. PEI exhibits a strong affinity for the first 25–30% of the protons ($pK_{Da} \approx 8.0$). By further protonation, the basic character decreases, as indicated by decreasing pK_{Da} values. This effect is much larger than in other polyelectrolytes[11] and it indicates a *chelate effect* on the proton, which can be accommo-

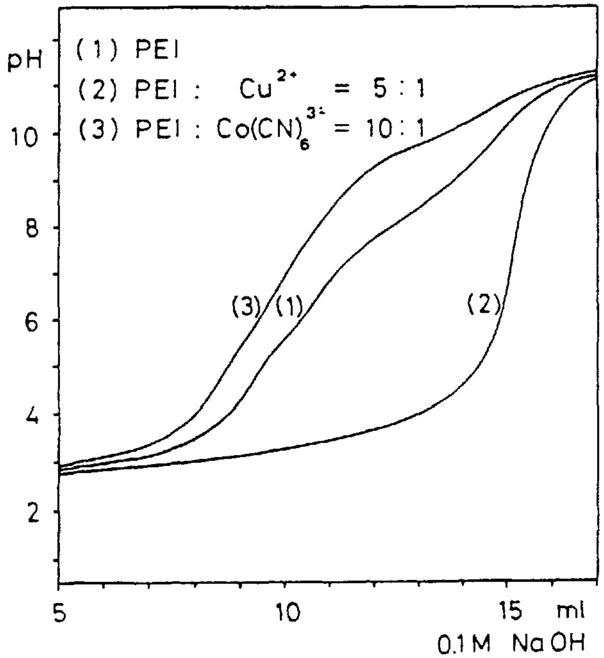

FIGURE 1 Titration curves of 50 ml PEI in H_2O with 0.1 M NaOH. (1) 5×10^{-3} mol N and 7.5×10^{-3} mol HNO_3; (2) 5×10^{-3} mol N, 7.5×10^{-3} mol HNO_3 and 1.0×10^{-3} mol $Cu(NO_3)_2$; (3) 5×10^{-3} mol N, 7.5×10^{-3} mol HNO_3 and 5×10^{-4} mol $K_3Co(CN)_6$.

dated through hydrogen bonding in the higher pH-region in pockets formed by several amine groups. A similar phenomenon has been observed for the cpa ligands.[3]

PEI AND LPEI AS LIGANDS IN FIRST COORDINATION SPHERE

(a) Ionic Equilibria in Solution

As can be shown in simple test-tube experiments, PEI and LPEI form soluble complexes with most of the "labile" metal ions in aqueous solution. Most typically, Cu^{2+} forms deep blue solutions over a wide pH-range. Strongly acidic solutions ($pH < 1.5$; HNO_3) show the pale blue color of Cu^{2+}_{aq}. The deep blue color develops if NaOH is added to the solution. We have investigated this complex formation by pH-titrations, UV/vis- and ESR-spectroscopy.

An example of a titration curve with $N:Cu^{2+} = 5$ is shown in Fig. 1, together with the curve for PEI alone. The acidity of $HPEI^+$ is strongly increased by the competition of Cu^{2+} and H^+ according to Eq. (1).

$$(PEIH^+)n + Cu^{2+} \longrightarrow (PEI)_nCu^{2+} + nH^+ \qquad (3)$$

The stoichiometric coefficient n can be estimated by variation of the $N:Cu^{2+}$ ratio. In solutions having $N:Cu^{2+} < 5$ precipitation of $Cu(OH)_2$ occurs at $pH \approx 7$, whereas solutions with $N:Cu > 5$ stay clear, even at high pH. The titration curve can best be interpreted if formation of CuN_4 is assumed at intermediate pH-values followed by the appearance of CuN_5 at high pH. This result is strongly corroborated by the UV/vis and the ESR spectra. Figure 2 shows the d-d absorption bands. At low pH ($pH < 2$), the absorption of Cu^{2+}_{aq} ($\lambda_{max} = 813$ nm; $\epsilon = 1.2$ m^2 mol^{-1}) is essentially outside the spectral region studied for the spectrometric titration. Below pH ca. 5, an absorption band occurs at $\lambda_{max} = 615$ nm with $\epsilon = 10$ m^2 mol^{-1}. At higher pH-values ($pH > 5$) a new species is observed with an absorption band at 650 nm having $\epsilon = 7.5$ m^2 mol^{-1}. It therefore seems that except for Cu^{2+}_{aq}, only two absorbing species occur, corresponding to CuN_4 and CuN_5 chromophores, exhibiting the well known "pentamine"-effect.[13]

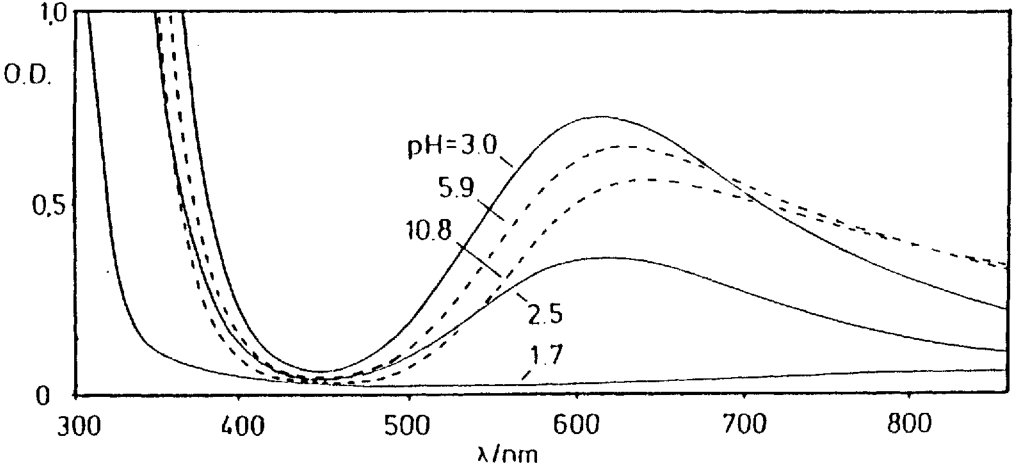

FIGURE 2 Absorption spectra of a solution of $Cu(NO_3)_2$ (4×10^{-3}) and PEI ($N = 8 \times 10^{-2}$ M, $HNO_3 = 1.2 \times 10^{-4}$ M) at various pH-values (titration with NaOH 1.0 M).

i.e., the bathochromic shift of the d-d transition in CuN_5 as compared to CuN_4. In view of the branched structure of PEI, it must be assumed that several slightly different CuN_4 and CuN_5 sites exist in the polymer. The sensitivity of the d-d bands is not high enough, however, to detect such differences.

ESR-spectra of solutions containing the CuPEI complexes yield additional information. Figure 3 shows a series of ESR-spectra of solutions at different pH-values. The N:Cu ratio is 24 in all solutions. The general findings are in complete agreement with the interpretations from the optical spectra. At low pH (pH < 2), the single line spectrum of Cu^{2+}_{aq} ($g = 2.280$) is observed. Raising the pH-value yields a signal exhibiting copper hfs. The strong M_I-dependence which makes the spectrum similar to a powder pattern is a direct confirmation of the binding of Cu^{2+} to the polymer. Metal ions coordinated in first sphere with the polymer or metal complexes coordinated in second sphere (vide infra) exhibit a much slower tumbling rate, as compared to their "free" state. The anisotropic components of the g- and of the A-tensors are therefore averaged out only incompletely.[14] The detailed investigation by evolving factor analysis[15] again yields two species, one below pH ca. 5 with $g_{iso} = 2.103$ and $A_{iso} = 91 \times 10^{-4}\,cm^{-1}$ and one above pH ca. 6 with $g_{iso} = 2.04$ and $A_{iso} = 79 \times 10^{-4}\,cm^{-1}$, corresponding to CuN_4 and CuN_5 respectively. The formation of a CuN_5 rather than a CuN_4OH complex at high pH-values was proven by comparison with the ESR-spectra in fluid and frozen solution of $Cu(trien)^{2+}$ in NaOH or in concentrated NH_3 solution, respectively.[16]

The ESR-spectra exhibit another interesting feature: Even in solutions with a low total Cu^{2+}-concentration ($< 5.10^{-3}$ M), metal/metal interactions are observable for ratios $N:Cu^{2+} < 6$ and pH > 4. Under such conditions PEI can cluster the Cu^{2+}-ions and bring them close together in the polymer coil. No Cu-hyperfine structure is seen in the spectra of such species. Increasing the PEI concentration (Fig. 4) above the indicated values puts an end to the appearance of the unstructured line ($g = 2.174$) in the ESR-spectrum, which is due to exchange coupled Cu^{2+}-ions, as shown by investigations of frozen solution spectra.[16] This effect, due to close packing of the metal ions along essentially one dimension, can be called the "clothes-line" effect.

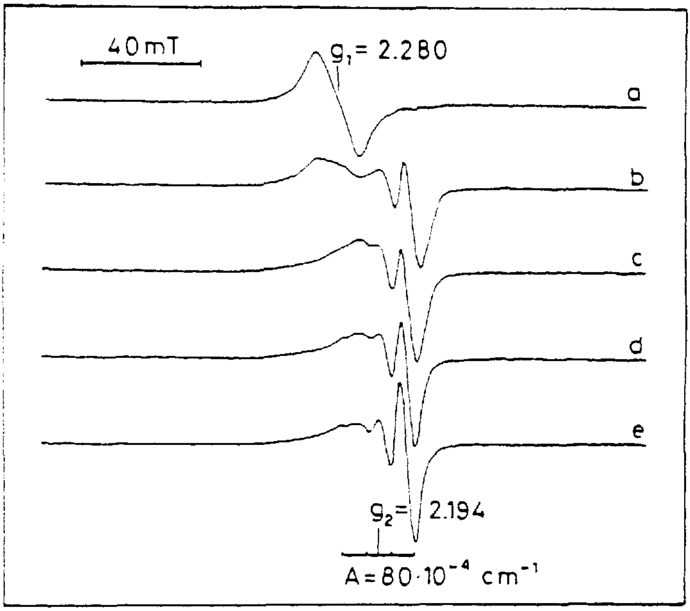

FIGURE 3 ESR spectra of solutions of $Cu(NO_3)_2$ (2.0×10^{-3}) and PEI (N = 4.0×10^{-2} M. HNO_3 = 6.0×10^{-2} M) at various pH values: (a) pH = 1.7. (b) pH = 2.5. (c) pH = 3.0. (d) pH = 5.9. (e) ph = 10.8 (titration with NaOH 1M).

This observation shows the most important difference between solutions of metal complexes of pa and of ppa. The metal ions in ppa solutions are not homogeneously distributed. They are found in high local concentrations within the polymer coils, due to the high number of ligating sites, which is independent of the total ppa concentration. The quantitative treatment of these complex formation equilibria is therefore similar to that of the distribution of a species between two phases. The information on the metal–metal distances obtained from the observed interactions yields an experimental estimate of the volume of the polymer coils.

It cannot be excluded, of course, that metal ions like Cu^{2+} link two or several polymer molecules. While this question requires more refined structural investigations in solution, it can safely be assumed that no extensive crosslinking occurs, because no precipitation is observed, even in concentrated solutions.

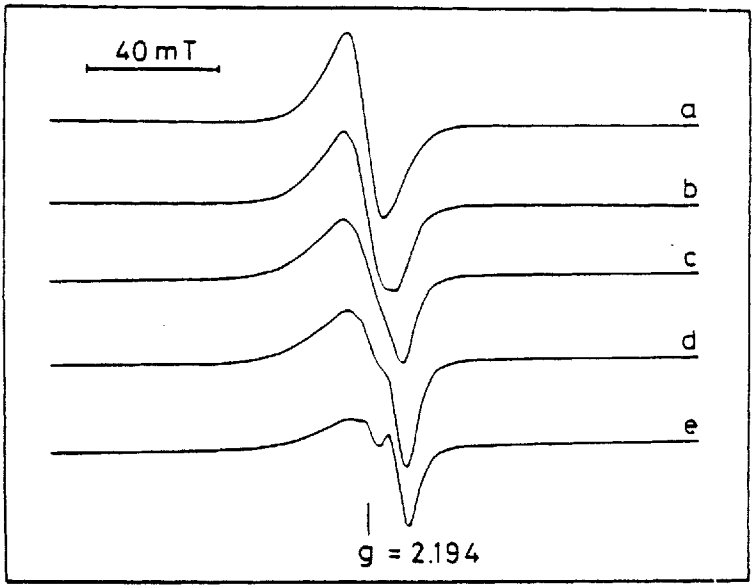

FIGURE 4 ESR spectra of solutions of $Cu(NO_3)_2$ (2.0×10^{-3} M) in solutions of PEI at pH = 7.2: (a) $N:Cu^{2+} = 5$, (b) $N:Cu^{2+} = 6$, (c) $N:Cu^{2+} = 7$, (d) $N:Cu^{2+} = 10$, (e) $N:Cu^{2+} = 23$.

(b) Metal Complexes with Inert M–N Bonds

PEI and LPEI can form complexes with inert metal-ions, e.g., Co(III), Cr(III), Pt(II), etc. as well. Some scattered reports have appeared in the literature.[17,18] We have, so far, carried out only preliminary synthetic experiments with these complexes. Such experiments clearly indicate the formation of inert complexes with PEI. Their exact nature is not yet known, since conventional methods such as NMR-spectroscopy or X-ray diffraction are difficult to apply. The possibility of varying the N:M ratio by simply choosing an appropriate stoichiometry opens up new possibilities, especially concerning the study of metal/metal interactions through the "clothes-line" effect.

Two examples which we have studied somewhat more closely are the reactions of $PtCl_4^{2-}$ and $Ru(bpy)_2Cl_2$ with PEI. The Pt-complex of PEI is obtained by ligand exchange reaction with $PtCl_4^{2-}$. This reaction can easily be followed by the spectral changes between 280 and 500 nm. The rate in buffered solutions is roughly first order in $PtCl_4^{2-}$ and in PEI and increases with increasing pH. The best conditions for complex formation are met in solutions with pH 6–7, which corresponds to a degree of protonation of PEI of ca. 0.15. In more basic solutions, hydroxo complexes of Pt are formed, and at low pH the reaction is considerably slower. Solutions with a N:Pt ratio > 6 do not show any precipitation. Investigations which are still underway in this laboratory give strong evidence for complete formation of PtN_4-species, at least in solutions with N:Pt > 10. Solutions containing this cationic complex are colorless. Their proton accepting capacity is reduced, i.e., the PtN_4-species is blocking at least one protonation site per coordinating PEI unit. No decomposition of the PtN_4-unit is observable within several hours, even in strongly acidic media. In solutions with N:Pt < 10, measurements of the proton accepting capacity indicate formation of PtN_xCl_y-species (y = 1 or 2). This is in agreement with a literature report[18] where the preparation of $Pt(PEI)_2Cl_2$, which is insoluble, is described.

PEI, which is only partially loaded with Pt (in PtN_4-sites), i.e., PEI:Pt > 10, is still capable of binding other labile or non-labile metal ions. For example, it can bind Cu^{2+}. The possibilities for $Cu^{2+} \ldots Cu^{2+}$ interactions are strongly reduced, however, as observed by a different concentration dependence of the ESR-spectra, as compared to PEI as a ligand.

With $Ru(bpy)_2Cl_2$ a complex is obtained in a slow reaction which behaves very similarly to $Ru(bpy)_2(en)^{2+}$ as far as absorption and emission properties are concerned.[19] This behavior indicates a complex $Ru(bpy)_2(PEI)^{2+}$. Further studies with these Ru-species in which quenching reactions along the chain can be studied are underway.

(c) New Materials

Labile as well as inert metals yield solid polymeric materials if the aqueous solutions are evaporated to dryness. These solid polymeric mateials contain metal ions bound coordinatively to the amine groups.

The metal content can again be controlled simply by choosing the appropriate stoichiometry. In this way even materials with two or more different metals can be synthesized. In addition, the counterion can be chosen from a large number of possibilities, including anionic metal species, which form second sphere complexes (vide infra). In this way, enormous variability of different materials can be obtained.

In addition to the conventional use of PEI as a floculating agent in paper manufacture and waste water treatment,[5] some other applications are mentioned in the literature: PEI complexes of transition metals have been used as homogeneous or, bound on a surface, heterogeneous catalysts in different chemical reactions.[20] Another application of PEI is its use in optical sensors for salts of the alkali metals in solution.[21] These systems are based on the possibility of PEI to bind a sensitizer and an emitter in a polymeric film. The energy transfer between the two is strongly dependent on their relative distance. The latter is influenced by the ionic strength of the solution. Applications of PEI complexes with lithium salts have been reported as solid electrolytes for batteries.[22] There is, to our knowledge, so far no report in the literature on applications based on the interaction between the same or different metal ions, bound in high local concentrations within the polymer coils.

POLYETHYLENEIMINE AS SECOND SPHERE COORDINATION AGENT

Supramolecular chemistry has become an important field of chemical research.[23] pa ligands, especially cpa ligands, have been shown to form second sphere complexes in their protonated forms with complex molecules capable of establishing hydrogen bridges.[24] In a series of investigations carried out in our laboratories, we found that PEI is an *excellent* second sphere complexing agent too.

For example, if $HPEI^+$ is titrated with NaOH in the presence of cyano-complexes, the titration curve deviates in the opposite sense from the curve of "free" $HPEI^+$ as compared to that in the presence of Cu^{2+}. This means that the acidic form of PEI is stabilized (Fig. 1) by the interaction with the cyano-complex.

This phenomenon can be interpreted as being due to a second sphere complex formation (Eq. (4)).

$$n\mathrm{HPEI}^+ + \mathrm{M(CN)}_r^{u-} \longrightarrow [\mathrm{M(CN)}_r(\mathrm{HPEI})_n]^{n-u} \qquad (4)$$

The strength of this effect depends on the charge u, and it is quite appreciable for $u = 3$ (Co(III), Cr(III) or $u = 4$ (Fe(II)). The same charge dependence of the stability of supercomplexes was found for the cpa ligands.[24]

Which other phenomena can furnish more information on this second sphere complexation? Electronic spectra are evidently not very well suited, because the chromophoric properties of $M(CN)_6^{u-}$ in water and in the second sphere complex are very similar. In both situations, hydrogen bridging is important and the differences in the spectra are therefore small. Vibrational spectra might yield some information, but this technique has not yet been applied.

Three methods furnish, in addition to the titration effects, *direct evidence* for second sphere complex formation. Two of the three (NMR and ESR) are again based principally on the effect of the tumbling rate on the signal. The third method is based on the reduced reactivity towards ligand exchange when the complex is "shielded" by second sphere complexation.

(i)^{59}Co-NMR of $Co(CN)_6^{3-}$

The nucleus of ^{59}Co (100% natural abundance) has $I = 7/2$. As a quadrupolar nucleus, the linewidths of ^{59}Co-NMR signals are strongly dependent on electric field gradients at the nucleus *and* on the tumbling rates of the atom. In addition, chemical shifts of ^{59}Co are extremely sensitive to changes in its surroundings.[25]

The spectra of solutions containing $Co(CN)_6^{3-}$ in the presence of HPEI$^+$ indeed reveal a species with strongly different NMR characteristics as compared with free $Co(CN)_6^{3-}$.[26] The latter has a relatively narrow line (45 Hz at −0.1 ppm vs. 0.002 M $K_3Co(CN)_6$), with a satellite at −1.7 ppm, which is due to the species $Co(CN)_5(^{13}CN)^{3-}$. In acidic solution a broad line appears with a linewidth of 675 Hz and a chemical shift of −11.8 ppm (Fig. 5). The shape is distinctly non-Lorentzian, indicating a situation outside the extreme narrowing approximation. Solutions containing N:Co < 12 show two signals, a narrow one and a broad one, having the characteristics given above. The appearance of two signals indicates a situation where the exchange process between the free and the polymer-bound $Co(CN)_6^{3-}$ species is relatively slow. This behavior contrasts with the findings of Masuda and Yamatera,[27] who investigated second sphere complexation of $Co(en)_3^{3+}$ with SO_4^{2-}.

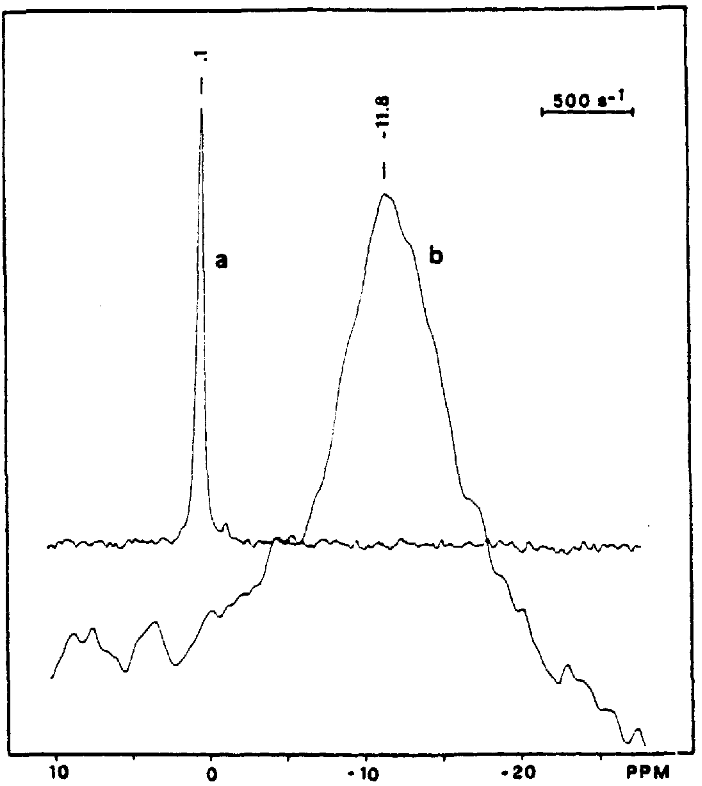

FIGURE 5 ^{59}Co-NMR spectra (MHz) of $K_3Co(CN)_6$(5.3 × 10^{-4} M) in H_2O/10%D_2O solutions containing PEI (N = 8 × 10^{-3} M). (a) pH = 11.5, (b) pH = 2.6.

In these cases rapid exchange, i.e., only one averaged line, was always observed.

An approximate estimate of the relative intensities of the lines of bound and free $Co(CN)_6^{3-}$ in the presence of $HPEI^+$ indicates that the protonated polymer is fully loaded with $Co(CN)_6^{3-}$ at N:Co = 12.[28]

Determination of transverse and longitudinal relaxation times and the measurement of NMR-spectra (^{13}C and ^{59}Co) of species enriched in ^{13}C revealed further details of the formation of the second sphere complexes.[28] Other anionic Co-complexes capable of forming outer sphere complexes with hydrogen bridge donors can doubtlessly also be investigated by the ^{59}Co-NMR method.

(ii) *ESR-Spectroscopy of the Paramagnetic Species* $Cr(CN)_6^{3-}$ *and* $Cr(CN)_5NO^{3-}$

$Cr(CN)_5NO^{3-}$ is a species with $S = 1/2$ and a strong localization of the electronic spin on the NO-ligand.[29] It can therefore be used as a spin label to study the second sphere interaction of cyano-complexes. In agreement with the ^{59}Co-NMR study of $Co(CN)_6^{3-}$ one observes, at high pH (> 10), the narrow line triplet of the fast tumbling free $Cr(CN)_5(NO)^{3-}$. At intermediate pH-values (pH ca. 7) a strong broadening of the signal indicates slow tumbling due to interactions with the polymer.

The chromium complex cannot be studied in acidic solution because of protonation and subsequent ligand substitution (of CN^-).

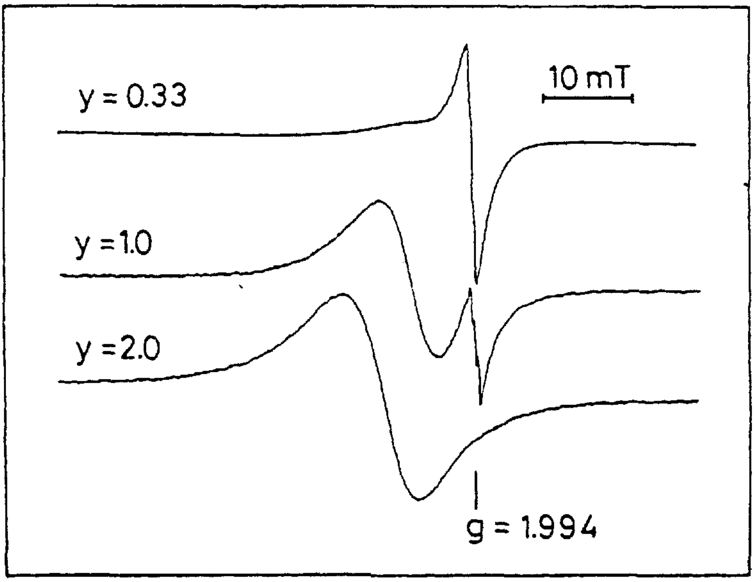

FIGURE 6 ESR spectra of solutions containing $PEI:Cu(NO_3)_2:K_3Cr(CN)_5NO$ in the ratio 15:y:1 at pH = 7.5. ($K_3Cr(CN)_5NO = 5.0 \times 10^{-3}$ M. N = 7.5×10^{-2} M).

The uncharged complex $Cr(CN)_2(H_2O)_3NO$ formed at higher acidities[30] (pH = 2) shows an ESR spectrum virtually identical to that in solution containing no PEI. This observation shows that the second sphere complexation is strongly dependent on electrostatic interactions between the ligand and the complex anion.

In the intermediate pH range around 7, PEI can simultaneously bind $Cr(CN)_5NO^{3-}$ *and* Cu^{2+}. The former in second and the latter in first coordination sphere. The ESR spectra of such solutions clearly show (Fig. 6) an interaction between the two spins at high concentrations within the polymer coil.[31] This system can be used as a synthetic model for the study of spin-probe/spin-label interactions, which is used in biochemistry.[32]

We have also studied the ESR spectra of $Cr(CN)_6^{3-}$ in the presence of PEI. The single line due to the $^4A_{2g}$ ($S = 3/2$) ground state is boadened, too, if the complex binds to PEI. Its widths are 2.5 mT (25 Gauss) at pH = 11.0 and 12 mT (120 Gauss) at pH = 2 in a solution containing PEI:Cr = 20.

A plot of the linewidths against pH is given for several PEI:Cr ratios in Fig. 7. It indicates that the binding Cr-species takes place in a surprisingly narrow pH-region, more like a phase transition, than a non-cooperative equilibrium in solution.

(iii) Photoaquation of $Co(CN)_6^{3-}$

Other evidence of second sphere complexation is a significantly reduced quatum yield of the photoaquation of $Co(CN)_6^{3-}$ in acidic PEI solution, as compared to the "free" $Co(CN)_6^{3-}$.[33] The same observation has been made with the large cpa ligands.[34]

CONCLUSIONS

We have been working with these polymeric ligands partially in an exploratory manner (e.g., preparative work, new materials), partially looking for detailed results (titrations, optical-, NMR- and ESR-spectroscopy). Reports on the latter experiments will appear in due course. This research was always fun for the coordination chemist, because in many respects the systems behave as predicted by simple models but in some cases rather unexpected behavior is observed.

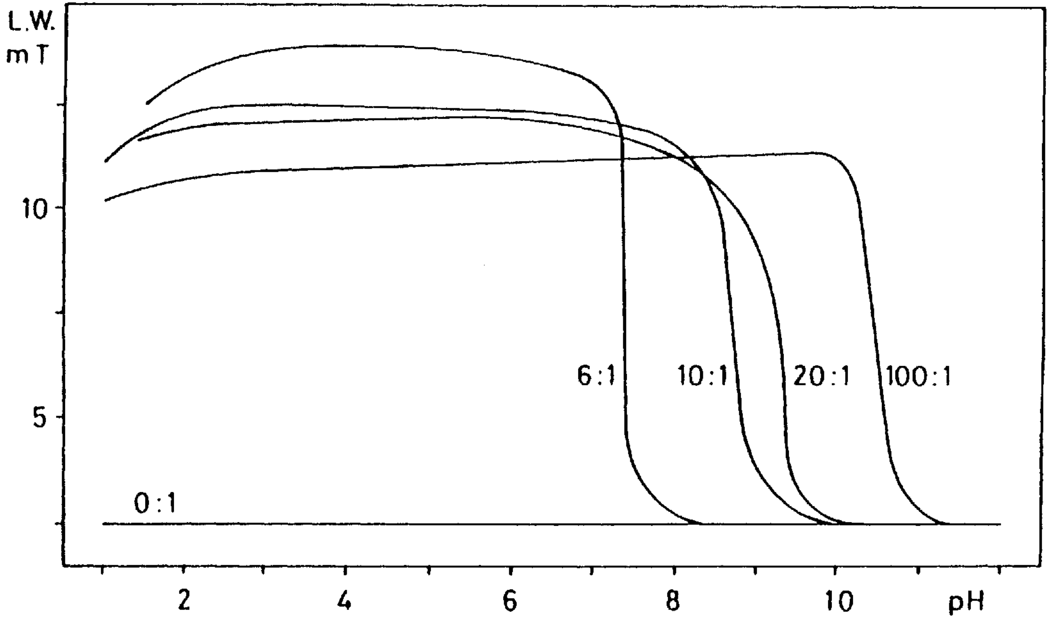

FIGURE 7 Variation of the linewidth (L.W./Hz) as a function of pH in solutions containing $K_3Cr(CN)_6$ and PEI at different ratios ($K_3Cr(CN)_6 = 5.0 \times 10^{-3}$ M).

We are quite confident that further investigations of these systems will yield more insight into the possibilities of interactions between metals and polymers. In addition, these interactions might be a valuable tool to characterize polymers in solution, whereby the transition metal is used as a probe. PEI is capable of being modified in several ways by polymer chemists[35] and the interesting metal ions or metal compounds can be chosen by the coordination chemist. There are numerous possibilities for practical applications of this kind of chemistry ranging from catalysis to sensors and many others, leaving room for innovative research.

LIST OF ABBREVIATIONS

pa	Low molecular weight polyamines
cpa	Cyclic polyamines
ppa	Polymeric polyamines
PEI	Branched polyethyleneimine (polyaziridine)
LPEI	Linear polyethyleneimine
trien	Triethylenetetramine = 2,2,2-tet
en	Ethylenediamine

Acknowledgments

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