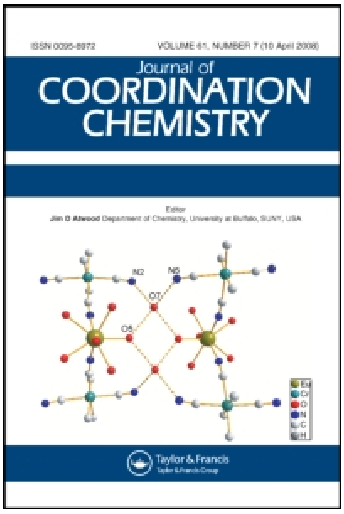


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Metal uptake by a novel bidentate thiosemicarbazide chelating polymer

Azza A. Abo-Hussen[a]; Said S. Elkholy[b]; Maher Z. Elsabee[b]
[a] Department of Chemistry, Faculty of Women, Ain Shams University, Heliopolis, Cairo, Egypt [b] Department of Chemistry, Faculty of Science, Cairo University, Giza, Cairo, Egypt

To cite this Article Abo-Hussen, Azza A. , Elkholy, Said S. and Elsabee, Maher Z.(2004) 'Metal uptake by a novel bidentate thiosemicarbazide chelating polymer', Journal of Coordination Chemistry, 57: 12, 1027 — 1036
To link to this Article: DOI: 10.1080/00958970412331281764
URL: http://dx.doi.org/10.1080/00958970412331281764

J. Coord. Chem., Vol. 57, No. 12, 15 August 2004, pp. 1027–1036

Taylor & Francis
Taylor & Francis Group

METAL UPTAKE BY A NOVEL BIDENTATE THIOSEMICARBAZIDE CHELATING POLYMER

AZZA A. ABO-HUSSEN[a,*], SAID S. ELKHOLY[b] and MAHER Z. ELSABEE[b]

[a]*Department of Chemistry, Faculty of Women, Ain Shams University, Heliopolis, Cairo, Egypt;* [b]*Department of Chemistry, Faculty of Science, Cairo University, Giza, Cairo, Egypt*

(Received 30 October 2003; In final form 15 June 2004)

1-Cyanoethanoyl-4-acryloyl thiosemicarbazide (CEATS) has been prepared and polymerized by a free radical mechanism. The polymer PCEATS has chelating affinity, and metal-uptake capacities were determined for the chlorides of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) in the pH range 1.04–6.0. The extraction experiments show high capacity for Cu(II), (0.26 mmol/g) at pH 5.34 and lower uptake capacities for the other divalent metal ions around pH 5 in buffered solutions, under noncompetitive conditions. However, competitive experiments, performed with solutions containing a mixture of metal chloride salts and acetate buffer, showed a high selectivity for Cu(II) and Cd(II) over other cations. Distribution coefficients determined for the polymer and the metal ions indicate that the Cu(II) complex is more stable than the Cd(II) are and suggest that the stability of the complex decreases rapidly with decreasing pH. Kinetic experiments have shown that uptake of Cu(II), is slow, with $t_{0.5} = 10\,\text{h}$. Ligand regeneration experiments for Cu(II)-loaded PCEATS performed with 2.00 M H_2SO_4 have shown that the capacity for Cu(II) stays at the same level after several cycles of consecutive loading and stripping, indicating that the polymer is chemically stable. ESR spectra of Cu(II)–CEATS resin show that there are two different coordination complexes present in the polymer. IR spectra of the Cu(II) complex confirms the bidentate behavior (S, O; N, O) of CEATS and PCEATS (it is supposed that the cations bridge vicinal CEATS ligands through S, O and N, O atoms); the acetate group completes the octahedral coordination. The obtained data suggest that the polymer behaves as a bidentate ligand via the thiocarbonyl, carbonyl and imide groups. PCEATS and its complexes have an inhibitory effect on both the bacterium *Azotobacter* and the fungus *Fusarium oxysporium*. The effect on the microorganisms is proportional to the amount of free ligand in the complex.

Keywords: Bidentate polymer; PCEATS; Transition metals; UV–vis spectra; IR spectra; Microorganisms; *Azotobacter*; *Fusarium oxysporium*

INTRODUCTION

Recently, there has been growing interest in selective chelating ion exchangers [1–3]. This interest originates from applications in analytical chemistry [4], industry [5], and in solving problems in environmental chemistry [6]. Polymer metal complexes could have catalytic activities [7] and offer excellent models for metalloenzymes [8]. Most of the commercial resins tested in waste-water treatment show high capacity, but poor selectivity for different metal ions. Also, in some cases, the kinetics are slow,

---

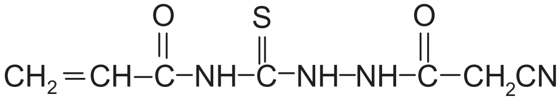
*Corresponding author. E-mail: azza_aly2000@yahoo.com

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970412331281764

owing to the hydrophobic character of the polymer backbone [9,10]. Therefore, immobilization methods are investigated which are straightforward and have good kinetic properties [11–15]. The coordination behavior of metals to the polymers has also been investigated [16–18]. The biological activity of the ligands has been the focus of increasing research [19,20]. It was reported that many ligands have herbicidal and fungicidal activities [21], can be treated as antibiotics [22,23] and can be used in radiopharmaceuticals [24]. The biological activities of most transition metal complexes have been reported [25,26]. Many complexes are active against leukemia and tumors [27–29]. The aim of this study is to investigate the metal uptake behavior of a novel chelating polymer [30] and the biological activity of the loaded-PCEATS towards two kinds of organism chosen for this investigation, a fungus and a bacterium. The fungus (*Fusarium oxysporium*), is considered to be one of the most important fungi that cause *Fusarium*-wilt and rot diseases for many economic crops, *i.e.*, wilt of cotton, wilt of tomato, rot of gladiolus, dry rot of potato and ear rot of maize. On the other hand, the bacterium (*Azotobacter*) has the properties of fixing atmospheric nitrogen and secreting certain growth hormones necessary for improving plant growth and increasing soil fertility [31].

EXPERIMENTAL

l-Cyanoethanoyl-4-acryloylthiosemicarbazide (CEATS) [30],



$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}\overset{\overset{S}{\|}}{C}{-}NH{-}NH{-}\overset{\overset{O}{\|}}{C}{-}CH_2CN$$

readily undergoes free-radical polymerization in both aqueous and nonaqueous media.

Preparation of CEATS

One mole of dry ammonium thiocyanate was dissolved in dried acetonitrile and kept cold in an ice–salt bath (0–5°C). A pre-cooled solution of one mole acryloyl chloride in acetonitrile was added dropwise to the ammonium thiocyanate solution. After complete addition of the acid chloride solution, the reaction mixture was stirred for 1 h at 10°C during which the ammonium chloride by-product completely precipitated. The yellowish acryloyl thiocyanate solution was then filtered. The filtrate was cooled and the appropriate amount of a cold solution of cyanoacetohydrazide (1 mol) in acetonitrile was added dropwise with continuous stirring. After complete addition, yellow crystals of CEATS separated. The crystals were separated by filtration, washed several times with cold ethanol followed by ether and then dried in air (m.p. 185°C). Recrystallization of the monomer was practically impossible, as it undergoes cyclization upon heating. Elemental analysis and spectra confirmed the structure of the monomer. Anal. Calcd. for $C_7H_8O_2N_4S$ (212.23) (%): C, 39.62; H, 3.80; N, 26.40; S, 15.08. Found: C, 39.62; H, 3.77; N, 26.41; S, 15.09. Results were consistent with the calculated values for the proposed formula of the monomer. ^{1}H NMR [δ(ppm, $CDCl_3$)]: 3.2 (2H, s, CH_2): 6.9 (3H, s, $CH_2{=}CH$) and 12 (1H, m, NH).^{13}C NMR (ppm $CDCl_3$): 132 ($-CH_2{=}$) 130

(=CH–), 160 (–C=O), 173 (–C=S), 168 (–C=O), 22 (–CH_2–) 118 (CN) [32]. IR (KBr, cm^{-1}): 3500, 3258 (NH); 2260 (CN); 1720, 1670 (C=O); 1238 (C=S) [33]. Azobisisobutyronitrile (AIBN) (Merck) was used as an initiator and was recrystallized twice from methanol (m.p. 104°C). Other solvents and reagents were analytical grade.

Polymerization Process

The monomer with the required amount of initiator (0.2% of monomer weight) was dissolved in dimethyl formamide (DMF) in a flask fitted with a condenser. The flask was then placed in a water thermostat adjusted to the required temperature (60°C). At the end of the polymerization, the flask was removed from the water thermostat and quickly immersed in an ice–water salt mixture to stop the polymerization reaction. The polymer was then precipitated in cold ethanol, filtered, washed several times with ethanol and finally dried in an air oven at 60°C to constant weight. The degree of conversion was then calculated gravimetrically. The percentage yield is about 10%.

Metal-uptake Experiments

Metal uptake under noncompetitive conditions

The metal-uptake experiments were performed using standard metal chloride solutions (0.16 M) and NaCl/HCl (pH 1.04–2.89) and sodium acetate/acetic acid (NaOAc/HOAc) (pH 3.69–5.73) buffer solutions [34]. The metal solutions and buffer solutions were prepared from analytical grade reagents. All experiments were performed in polyethylene bottles mounted on a shaker at 25°C. The capacities for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} under noncompetitive conditions were determined as a function of pH. Batches of 0.2 g (PCEATS) were used, together with a mixture of 25 cm^3 of metal solution and 25 cm^3 of buffer. After a shaking time of 48 h, the samples were filtered, the solid washed successively with water, ethanol, and diethyl ether, and dried in vacuum at 50°C. For the determination of the Cu^{2+} capacities at pH >5 a lower Cu^{2+} concentration (10 cm^3 of the standard Cu^{2+} solution and 40 cm^3 of buffer) was used to prevent precipitation of Cu(II) hydroxide.

Metal uptake under competitive conditions

Metal-uptake experiments under competitive conditions were performed with a mixture of standard metal chloride (0.16 M) solutions of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} in a pH range 0.9–6.0. Batches of 0.2 g (PCEATS) were used together with 5 cm^3 of each metal solution and 25 cm^3 of buffer. After a shaking time of 48 h the samples were further handled as described above for the noncompetitive experiments.

Determination of the distribution coefficients under noncompetitive conditions

These experiments were performed by mixing 0.1 g of the polymer with 25 cm^3 of $CuCl_2$ or $CdCl_2$ solution (0.001 M) and 25 cm^3 of buffer solution to ascertain the distribution coefficient of the metals as a function of pH according to Roozemond *et al.* [35].

Kinetic Experiments

2.0 g of PCEATS was soaked in 5 cm^3 of NaOAc/HOAc buffer solution, pH 5 for 1 h in order to swell. Then the polymer was immersed in 72.5 cm^3 of M(II), ($CuCl_2$ or $CdCl_2$) solution and 72.5 cm^3 of NaOAc/HOAc buffer (0.6 M) (resulting in 0.016 M $Cu^{2+}$and Cd^{2+} at pH 4.5, 298 K). At appropriate times, 0.5-cm^3 aliquots were removed and diluted to 100 cm^3. The remaining solution was swirled after each sampling, after which the polymer powder was allowed to settle on the bottom of the flask before another sample was taken. The final sample was taken after 48 h. The Cu^{2+} and Cd^{2+} concentrations of the samples were measured by AAS spectroscopy. The values for $t_{0.5}$ (the time needed to achieve loading to half of the final capacity) were estimated from uptake vs. time curves.

Stripping Regeneration Experiments

In the stripping regeneration experiments, 2.00 M H_2SO_4 was tested for its stripping potential. Batches of the ion-exchange materials were loaded with M(II) ($CuCl_2$ or $CdCl_2$) solution (25 cm^3 of the standard metal solution and 25 cm^3 of NaOAc/HOAc buffer) at pH 5.34 for shaking periods of 48 h. The loaded samples were stripped with 2.00 M H_2SO_4 solution (shaking time 48 h).

Metal Analyses and Spectroscopic Characterization of the Loaded Resins

Samples for metal analyses were prepared by heating 0.5 g of the loaded samples with concentrated H_2SO_4 and subsequently with concentrated HNO_3 until clear solutions were obtained. Metal analysis was carried out on a Perkin-Elmer 238 atomic absorption (AAS) spectrometer. To obtain information about the coordination environment of the metal ions when bound to the polymer, IR, UV–vis and ESR spectra of several loaded PCEATS samples were recorded. Infrared spectra were recorded in KBr pellets on a Perkin-Elmer 580 spectrophotometer (4000–200 cm^{-1}) equipped with an IR data station. Electronic spectra (UV–vis) were recorded in the diffuse reflectance mode on a Perkin-Elmer 330 spectrophotometer equipped with a data station. Electron spin resonance spectra were recorded at room temperature using a Jeol FE2xG (Japan) instrument.

Antibacterial and Antifungal Activity of the Polymer and its Metal Chelates

The polymer and its metal complexes were screened for antibacterial and antifungal activity. The media have been prepared for bacterium (*Azotobacter*) and fungus (*Fusarium oxysporium*) [36,37]. For *Azotobacter*, mannitol, 5 g; sucrose, 5 g; K_2HPO_4, 0.25 g; $MgSO_4 \cdot 7H_2O$, 0.1 g; NaCI, 0.1 g; $CaSO_4$, 0.05 g; $CaCO_3$, 0.25 g; $MnSO_4 \cdot 4H_2O$, trace; $FeCl_3 \cdot 6H_2O$, trace; $Na_2MoO_4 \cdot 2H_2O$, trace and agar, 15–20 g were dissolved in 1 dm^3 of distilled water and the pH was adjusted to 7 by addition of 0.1 M NaOH. The media for the fungus were prepared by dissolving sucrose, 30 g; $NaNO_3$, 2 g; KH_2PO_4, 1 g; $MgSO_4 \cdot 7H_2O$; 0.5 g; KCl, 5 g; $FeSO_4$, 0.01 g and agar 20 g in 1 dm^3 of distilled water.

RESULTS AND DISCUSSION

Batch Metal-uptake Capacity

The metal ion capacities of the polymer were measured as a function of pH at high metal concentrations in solution. The capacity determination gave promising results around pH 5. The behavior of PCEATS under noncompetitive conditions shows that uptake of metal ion increases rapidly with increasing pH (Fig. 1). PCEATS shows a high capacity for Cu(II) of 0.260 mmol/g at pH 5.34; for other metals the results were Cd(II), 0.225 mmol/g at pH 5.30; Zn(II), 0.202 mmol/g at pH 5.43; Co(II), 0.147 mmol/g at pH 5.19; Ni(II), 0.110 mmol/g at pH 5.30, indicating that 52.00, 45.60, 40.00, 29.00, and 22.00% of the polymer are complexed, respectively. These results indicate that the uptake capacities of PCEATS for Cd(II), Zn(II), Co(II) and Ni(II) are much lower than for Cu(II).

The results of the noncompetitive metal uptake experiments show that, at lower pH, there is an additional solvation effect due to the higher hydrogen ion concentration and probably a coordinating effect due to the high chloride ion concentration introduced by the buffer. The chloride ion favors formation of anionic chlorometallates, which can be taken up by the resins through anion exchange. This may explain the different metal-uptake results at high and low pH. The increased uptake of Cd^{2+} and Zn^{2+} at low pH is probably due to the relatively high stability in solution of anionic chlorocomplexes, like $CdCl_4^{2-}$,$CdCl_3^-$,$ZnCl_4^{2-}$, and $ZnCl_3^-$ which may be taken up through anion exchange by the hydronated resin [38,39].

The metal-ion capacities of PCEATS under competitive conditions as a function of pH for a number of divalent metal ions are shown in Fig. 2. The resin is highly selective

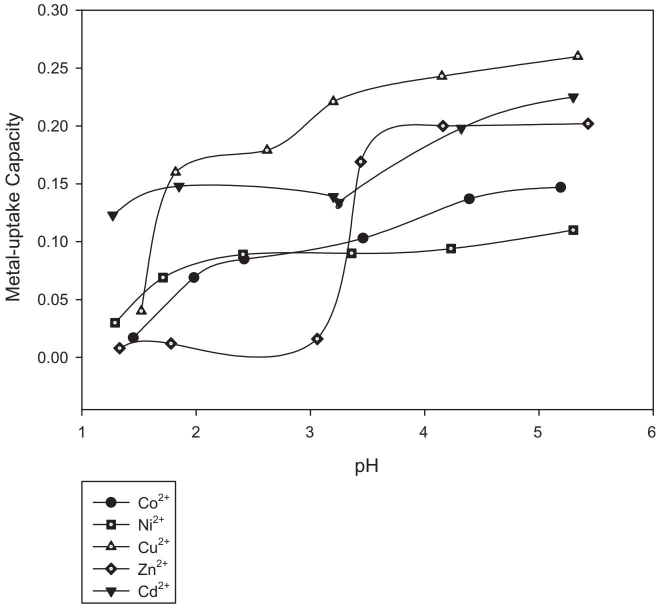


FIGURE 1 Metal-uptake capacity of PCEAT for different divalent cations under noncompetitive conditions.

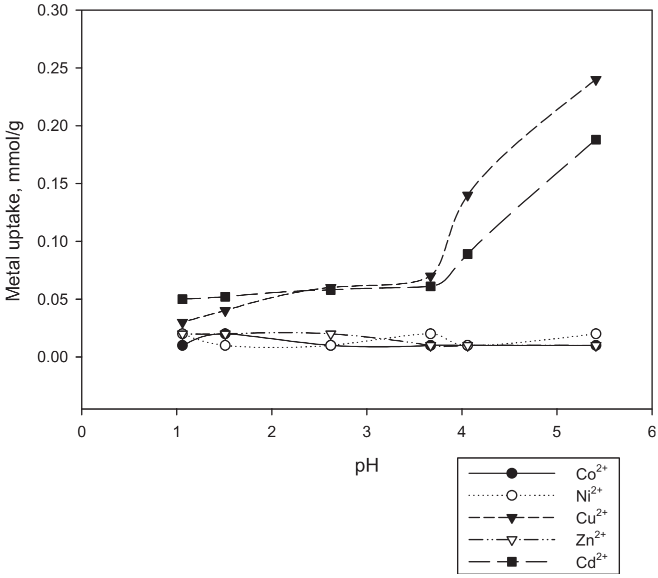


FIGURE 2 Metal-uptake capacity of PCEAT under competitive conditions as a function of pH.

for Cu(II) over the other metal ions. Quotients between capacities follow the sequence 2.22 Cu(II) : 1 Cd(II); 17.14 Cu(II) : 1 Zn(II); 24.00 Cu(II) : 1 Co(II) and 26.99 Cu(II) : 1 Ni(II), respectively. The overall metal-uptake capacity of the polymer at pH 5.72 under competitive conditions is 0.240 mmol/g for Cu (II) and 0.108 mmol/g for Cd(II), which indicates that 69.60% of the resin active binding sites are occupied by metal ions. In these uptake experiments, 48.00% of the binding sites are occupied by Cu^{2+} ions, a result which is in good agreement with the result obtained in the noncompetitive uptake experiments (52.00%). The high ligand occupation for Cu(II) found in these experiments probably indicates formation of 1 : 1 Cu^{2+}-ligand complex on the polymer. The rigidity of the polymer matrix [40] makes it likely that 1 : 1 metal–ligand (a monomer unit) complexes are formed. In these complexes the ligand (PCEATS) is probably bidentate.

As described in the experimental section, the distribution coefficients (*D*) for noncompetitive, metal ion uptake were determined for Cu(II) and Cd(II) at low metal concentrations as a function of the pH,

$$D = \frac{\text{mg Mn/g of dry polymer}}{\text{mg Mn/cm}^3 \text{ of solution}}.$$

These experiments show that the stability of the Cu(II) complex decreases from 1.017 at pH 5.73 to 0.0791 at pH 1.52. This is consistent with the lower uptake capacity for Cu^{2+} at low pH, which indicates the high selectivity of PCEATS for Cu^{2+} and the favorable thermodynamic stability of the complex on the polymer. Distribution coefficients, *D* for the Cd(II) complex (e.g. log $D = 0.9030$ at pH 5.30), confirm the low stability of the formed complex. These results agree with the uptake pattern observed for noncompetitive conditions.

PCEATS shows normal asymptotic metal-uptake behavior [41]. It is assumed that the uptake velocity is proportional to the concentration of free binding sites ($C_{\max} - C_t$) where $C_{\max}$ is the maximum metal concentration in the resin after 48 h and C_t is the actual concentration in the polymer at different times:

$$\mathrm{d}C_t/\mathrm{d}_t = k(C_{\max} - C_t), \tag{1}$$

$$\ln[C_{\max}/(C_{\max} - C_t)] = kt. \tag{2}$$

The apparent first-order kinetics were evident from the straight-line relationship of $\ln[C_{\max}/(C_{\max} - C_t)]$ vs t where k is the rate constant of the reaction determined as the slope of the line. Values after 48 h were found to be 0.0201 and 0.0095 mmol/g with rate constants $k = 6.77 \times 10^{-2}$ ($t_{0.5}$, 10.24 h) and $k = 6.63 \times 10^{-2}$ ($t_{0.5}$, 10.54 h) for Cu(II) and Cd(II) complexes, respectively. The $t_{0.5}$ values indicate that the metal ion uptake by PCEATS is slow. Results of the successive loading–stripping experiments performed with 0.16 M Cu(II) and Cd(II) solutions at pH 4.5 (loading) and H_2SO_4 2.0 M (stripping) show that the metal uptakes were the same for five cycles (0.224/0.226 mmol/g for Cu(II) and 0.186/0.187 mmol/g for Cd(II) (in all cases no metal ion remained in the polymer after stripping), indicating that the polymer structure forms the backbone to the ligand and is chemically stable when treated with 2.00 M H_2SO_4.

Spectroscopic Studies

Electron spin resonance

ESR parameters are not greatly dependent on the pH and the anions present in solution [42]. The solid-state ESR spectra of Cu(II)-loaded resin at pH 5.34 are axial, corresponding to two different Cu(II)-species with $g_{\mathrm{I}} = 2.2491$ and $g_{\mathrm{II}} = 2.3644$ for one of them. The second Cu(II) species unfortunately has a poorly resolved spectrum. The position as well as the shape of the bands indicate the formation of an octahedral structure [43].

Electronic absorption spectra

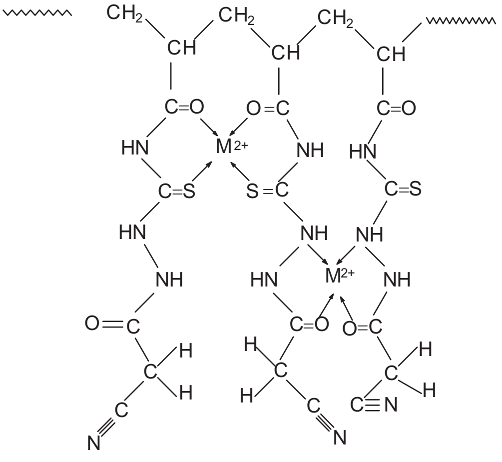
Ligand field spectra of the Cu(II)-loaded samples at different pH values 1.52–5.34 show electronic absorption bands in the region $14–15 \times 10^3\,\mathrm{cm}^{-1}$ ($\varepsilon_{\max} = 0.55 \times 10^4$) with a tail on the low energy side and there is also a very broad band with an absorption maximum at $25 \times 10^3\,\mathrm{cm}^{-1}$ ($\varepsilon_{\max}\, 0.04 \times 10^4$). The broadness of the bands is probably due to the presence of two different Cu(II) species in the resin, as suggested by the ESR spectra. No reasonable ligand-field spectra could be obtained for Ni(II)- and Co(II)-loaded PCEATS, owing to the very low concentrations of Ni(II) and Co(II) in the polymer [44].

Infrared spectra

The spectra reveal many bands assigned to the stretching vibrations of imide, cyanide, carbonyl, thiocarbonyl, and acetate groups. The two strong bands located at 3500 and 3258 cm^{-1} in the spectrum of the polymer can be attributed to the stretching vibrations of the –NH groups. These bands shifted to lower frequencies are on complexation and found at 3423 and 3199 cm^{-1} for the Cu(II) complex and at 3490 and 3210 cm^{-1} for the Cd(II) complex, suggesting involvement of the imide group in complexation. The band corresponding to the stretching vibrations of CN (2262 cm^{-1}) stays at the same position upon complexation, indicating that the cyanide group does not participate in coordination. Bands assigned to the stretching vibration of the carbonyl groups (1670 and 1720 cm^{-1}) are shifted to lower frequencies on complexation and found at 1570 and 1600 cm^{-1} for the Cu(II) complex and at 1540 and 1660 cm^{-1} in the case of the Cd(II) complex. The band at 1300 cm^{-1} can be ascribed to the stretching vibration of the thiocarbonyl group [32]. This band is shifted to a lower frequency and found at 1238 cm^{-1} for the Cu(II) complex and at 1270 cm^{-1} for the Cd(II) complex, supporting complexation of the thiocarbonyl group. It is difficult to assign the bands due to the stretching vibration of the acetate (COO^-), group (since the buffer is sodium acetate/acetic acid) because of overlap with CO groups of the polymer. However, the bands that appear at 937 cm^{-1} for the Cu(II) complex and 925 cm^{-1} for the Cd(II) complex can be assigned to stretching vibrations of the acetate (COO^-) groups [33,45].

Structures Proposed for PCEATS and its Complexes

In the prepared polymer PCEATS, as in the monomer there are two different positions for complexation of the metal. In the monomer, these sites are bidentate (S, O and N, O) while the polymer could be tetradentate (2S, 2O and 2N, 2O) because the pendant groups to the polymer backbone could be arranged as shown in the structure. Octahedral coordination of the metal could be completed by counteranions provided by the buffers, acetate or chloride, which compensate the positive charges of the metal ions. The total ligand (monomer unit)-to-metal ratios should be, therefore, 1 : 1.



Assumed structure of the polymer-metal complex.

TABLE I Percentage of the zone of inhibition by the polymer PCEATS and its complexes for *Azotobacter* and *Fusarium oxysporium*

PCEATS and its complexes	*% of zone of inhibition by Azotobacter*	*% of zone of inhibition by Fusarium oxysporium*
PCEATS	47.22	64.33
Ni(II)	32.55	45.22
Co(II)	28.33	40.66
Zn(II)	17.44	31.99
Cd(II)	10.33	15.33
Cu(II)	10.11	11.11

The Biological Activity of PCEATS and its Complexes

Biological activity measurements show that the polymer and its complexes have an inhibiting effect on both microorganisms (Table I). The inhibition of growth of the fungus will be useful for plants, decreasing the diseases it causes, while the inhibition of the growth of the bacteria will be harmful for the plant, decreasing the fixation of useful atmospheric nitrogen. However, it was found that the effect on the fungus is higher than the effect on the bacteria. The effect of the polymer itself on the microorganisms was found to be higher than the effect of its metal complexes. The sequence of the effect was found to be PCEATS (47.2%) > Ni^{2+} (32.6%) > Co^{2+} (28.3%) > Zn^{2+} (17.4%) > Cd^{2+} (10.3%) > Cu^{+2} (10.1%) for *Azotobacter*, PCEATS (64.3%) > Ni^{2+} (45.2%) > Co^{2+} (40.7%) > Zn^{2+} (32.0%) > Cd^{2+} (15.3%) > Cu^{2+} (11.1%), for *Fusarium oxysporium*. These results show that the effect decreases with the metal-uptake increase, which is in the sequence: Cu^{+2} (52%) > Cd^{2+}(45.6%) > Zn^{2+} (40.4%) > Co^{2+} (29.4%) > Ni^{2+} (22%). It can be deduced therefore that the effect on the microorganisms is proportional to the relative amount of the polymer contained in the complex, reaching the maximum for the pure polymer.

References

[1] P. Hodge and D.C. Sherrington (eds.), *Polymer-supported Reactions in Organic Synthesis* (J. Wiley & Sons, London, 1980).

[2] D.C. Sherrington and P. Hodge (eds.), *Synthesis and Separations Using Functional Polymers* (J. Wiley & Sons, London, 1988).

[3] T. Roher, S. Knaus, H. Graber and D.C. Sherrington, *Macromolecules* **35**, 97 (2002).

[4] M. Streat and J.K. Nair, *Ion Exchange Advances*, *Proceedings of 9IEX 92* (Elsevier Applied Science, London, 1992).

[5] C. Arzanini, E. Entasti and V. Port, *Ion Exchange for Industry* (M. Streat, ed., Ellis Horwood, Chichester, 1988).

[6] S.K. Sahni and J. Reedijk, *Coord. Chem. Rev.* **1**, 59 (1984).

[7] T. Tsuchida and H. Nishida, *Adv. Polym. Sci.* **1**, 24 (1977).

[8] M. Kaneko and E. Tsushido, *J. Polym. Sci., Macromol. Rev.* **16**, 397 (1981).

[9] G.V. Myasoedova and S.B. Savvin, *Crit. Rev., Anal. Chem.* **1**, 17 (1986).

[10] M.J. Hudson, *Ion Exchange Science and Technology*. (A.E. Rodrigues, ed., Martinus Nijhoff, Dordrecht, 1986).

[11] P.M. Van Berkel, P.D. Verweij, W.L. Driessen, J. Reedijk and D.C. Sherrington, *Eur. Polym. J.* **28**, 474 (1992).

[12] A.T. Slark, D.C. Sherrington, A. Titterton and I.K. Martin, *J. Mater. Chem.* **13**, 2711 (2003).

[13] E. Dominguez-Rosado, J.J. Liggat, C.E. Snape and J. Pichtel, *Polym. Degradation Stability* **1**, 78 (2002).

[14] P.D. Verweij, J.S.N. Van-der Geest, W.L. Driessen, J. Reedijk and D.C. Sherrington, *Reactive Polym.* **18**, 191 (1992).

[15] F.S. Angew, *Makromol. Chem.* **39**,144 (1986).

[16] W.G. Haanstra, W.L. Driessen, J. Reedijk, Y. Wang and C.H. Stam, *Inorg. Chim. Acta* **186**, 215 (1991).
[17] W.G. Haanstra, W.L. Driessen, M. Van Roon, A.L.E. Stoffels and J. Reedijk, *J. Chem. Soc., Dalton Trans.* 481 (1992).
[18] R. Liska, *J. Polym. Sci. Part A* **40**, 1504 (2002).
[19] F.L. Urbach, *Metal-Ions in Biological Systems* Vol 13. (H. Siegel, ed., M. Dekker, New York, 1980), p. 73.
[20] G. Stones, G. Argouarch, A.R. Kennedy, D.C. Sherrington and C.L. Gibson, *Org. Biomolec. Chem.* **1**, 2357 (2003).
[21] B. Onoa and V. Moreno, *Transition Met. Chem.* **23**, 485 (1998).
[22] G. Palazzion, L. Cecchi, F. Melani, V. Colotta, G. Filacchioni, C. Martini and A. Lucacchuni, *J. Med. Chem.* **30**, 1737 (1987).
[23] M.I. Page, *Acc. Chem. Res.* **17**, 144 (1984).
[24] M.M. Shoukry, *Talanta* **39**, 1625 (1999).
[25] M.A. Green, H. Luo and P.E. Fanwick, *Inorg. Chem.* **37**, 1127 (1998).
[26] H.A. Azab, F.S. Deghaidy, A.S. Orabi and N.Y. Farid, *J. Chem. Eng. Data* **45**, 709 (2000).
[27] H.A. Scheller, T.H.J. Abel, P.E. Polanyi, P.K. Wenk, B.E. Fisher and H. Siegel, *Eur. J. Biochem.* **107**, 455 (1980).
[28] V.L. Navayanan, M. Nasr and K.D. Paul, *Tin-Based Antitumor Drugs* (Springer, Berlin, 1990).
[29] A.J. Crowe, *Metal-Based Antitumor Drugs*, Vol. 1. (Freund, London, 1989).
[30] S.M. Mokhtar, M.Z. Elsabee, S.S. Elkholy and W.W. Sabaa, *J. Polym. Res.*, **7**, 229 (2000).
[31] L.M. Pinal and R.L. Richard, *Trends in the Chemistry of Nitrogen Fixation* (Academic Press, London 1980).
[32] E. Pretch, J. Clerc, J. Seibl and W. Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds* (Springer-Verlag, Berlin, 1983).
[33] K. Nakamoto (ed.), *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B (J. Wiley & Sons, New York, 1997), 5th ed.
[34] P.M. Van Berkel, W.L. Driessen, F.J. Parlevliet, J. Reedijk and D.C. Sherrington, *Eur. Polym. J.* **33**, 129 (1997).
[35] D.A. Roozemond, F. Den Hond, J.B.J. Veldhuis, H. Strasdeit and W.L. Driessen, *Eur. Polym. J.* **24**, 868 (1988).
[36] G.E. Bossard, *Reaction of Coordinated Dinitrogen Fixation* (J. Wiley & Sons, New York, 1979).
[37] N.S. Subba Rao, *Bio-fertilizers in Agriculture* (Mohan Brimlani for Oxford and IBH-published Co. 1984), 3rd ed.
[38] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Wiley-Interscience, New York, 1988) 5th ed., p. 67.
[39] L.G. Sillén, *Stability Constants of Metal-ion Complexes*, Section I (The Chemical Society, London, 1964), 2nd ed.
[40] P.M. Van Berkel, W.L. Driessen, G.J.A. Koolhaas, J. Reedijk and D.C. Sherrington, *J. Chem. Soc., Chem. Commun.* 147 (1995).
[41] H. Strasdeit, J.B.J. Veldhuis, R. Hoogendoorn, H. Verhoogt, J.H. Sluys, W.L. Driessen and J. Reedijk, *Proc. Int. Conf. Coord. Chem.* **24**, 635 (1986).
[42] P.M. Van Berkel, P.D. Verweij, W.L. Driessen and J. Reedijk, *Eur. Polym. J.* **28**, 747 (1992).
[43] A. Abragam and B. Belamy, *Paramagnetic Resonance of Transition Ions* (Clarendon, London, 1970), p. 492.
[44] A.B.P. Lever, *Inorganic Electronic Spectroscopy* (Elsevier, Amsterdam, 1984), 2nd ed.
[45] J.R. Ferraro, *Low-Frequency Vibrations of Inorganic and Coordination Compounds* (Plenum Press, New York, 1971).