

Preparation of polymer-bound 2,2'-dipyridylamine and some of its transition metal complexes

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The modification of polystyrene-2% divinylbenzene with 2,2'-dipyridylamine afforded an immobilized chelating system. A number of transition metal complexes of the polymer were prepared and competitive binding studies conducted to demonstrate the versatility of this system. A unique selectivity for Fe^{3+} in organic media was observed in metal ion mixtures.

(Keywords: modified polymer; 2,2'-dipyridylamine; immobilized transition metal complexes; selective chelation)

INTRODUCTION

Anchoring chelating ligands to insoluble supports provides an easy route for the preparation of immobilized transition-metal complexes. A number of polymer-bound chelating ligands, including polydentate amines, crown ethers and porphyrins have been reported¹⁻⁴. Melby¹ demonstrated the selective chelation of specific metal ions from a metal ion mixture by using a number of tetradentate ligands attached to polystyrene-1% divinylbenzene (PS-1% DVB). The most widely studied modified polymeric supports contain phosphine ligands. Significant examples have been reported by Grubbs⁵, Pittman⁶ and others⁷. However, the use of immobilized phosphine transition metal complexes is often limited by leaching of the metal from the polymer⁸.

Although nitrogen heterocycles are among the most versatile chelating systems, little work has been done using these systems. Card and Neckers reported the attachment of bipyridine to PS-2%DVB (PS-bipy), and demonstrated its potential as a polymer-bound chelate⁹ as well as its application as a catalyst^{10,11}. Valera and Hendricker^{12,13} have prepared polymer-bound 1,8-naphthyridine (PS-napy), 1,5-naphthyridine (PS-1,5-napy) and pyrido[2,3-b]pyrazine (PS-ppz) and demonstrated their versatility as polymer-bound chelates by preparing a number of transition metal and lanthanide complexes^{12,13}.

To extend the availability of versatile nitrogen heterocycles attached to a solid support, we report herein the preparation of polymer-bound 2,2'-dipyridylamine, [P]-dpa. Like naphthyridine (napy) and bipyridine (bipy), 2,2'-dipyridylamine (dpa) can be bound to the polymer support smoothly and efficiently and binds to a large number of transition metal ions. Although 2,2'-dipyridylamine is potentially a tridentate ligand, it has been observed to coordinate to a variety of metal ions in a bidentate fashion forming a six-membered chelate ring¹⁴⁻¹⁶. Unlike bipyridine and naphthyridine, 2,2'-dipyridylamine has the added advantage of being a flexible bidentate ligand. To demonstrate the versatility of the polymer-bound 2,2'-dipyridylamine system, a variety

of polymer-bound transition metal complexes were prepared.

EXPERIMENTAL

Chloromethylated polystyrene-2% divinylbenzene beads were purchased from Bio-Rad Laboratories. Aldrich Chemical Company supplied 2,2'-dipyridylamine. All other chemicals and solvents were reagent grade and used without further purification. Elemental analyses were made by Canadian Microanalytical Service Ltd. Infra-red spectra were obtained on a Sirius 100 Fourier transform spectrophotometer modified to record spectra by diffuse reflectance (DRIFT) with a Spectrotech Inc. diffuse reflectance unit. Metal-ion incorporation on the modified polymer was determined by spectrophotometric analysis using a Hewlett-Packard HP8451A diode array spectrophotometer. Metal analysis of some polymer-bound complexes was accomplished by using a Perkin-Elmer HGA 2100 atomic absorption spectrometer.

Polymer-bound 2,2'-dipyridylamine

Method A. Chloromethylated polystyrene (1.34 meq g⁻¹) and a 30-50 fold excess of 2,2'-dipyridylamine were refluxed in dioxane for three days. The resulting yellow beads were collected by filtration, washed with copious amounts of dioxane, dioxane-H₂O, H₂O, THF, THF-H₂O and extracted with THF in a Soxhlet extractor for 24 h. The resin was then dried in a vacuum oven at 80°C for 24 h. Analysis found: C, 85.28%; H, 7.46%; N, 2.29%.

Method B. Chloromethylated polystyrene (1.34 meq g⁻¹) with a 20-fold excess of sodium iodide were refluxed for four days in an acetone-dioxane (3:1) mixture. The reaction mixture was cooled, the resin collected by filtration and extracted with acetone for 24 h in a Soxhlet extractor. The resin was then dried in vacuum at 80°C for 24 h. The dried iodomethylated resin was then swollen in THF and 2,2'-dipyridylamine (5-fold excess) added. The reaction mixture was refluxed for four days and then cooled to room temperature. The yellow resin

was collected by filtration and then extracted with THF for 48 h in a Soxhlet extractor. The resin was washed with copious amounts of 0.1 M HCl in THF, 0.1 M NH₄OH in THF, and THF. This cycle was repeated until the filtrate from at least two complete cycles was colourless. The resin was then washed with THF-H₂O, H₂O, toluene and methanol and dried in vacuum for 24 h at 80°C. Analysis found: C, 84.44%; H, 7.14%; N, 2.74%.

Polymer-bound transition-metal complexes

Typically 200 mg of [P]-dpa was added to a 250 ml Erlenmeyer flask and titrated with a 0.001 M metal-ion solution in THF. The metal-ion solution was added in 5–25 ml portions by pipette and the solution shaken for 5–10 min. This reaction was usually accompanied by an observable decrease in the colour intensity of the solution as well as a colour change of the polymer. The polymer was allowed to settle and a portion of the supernatant solution removed and the concentration determined spectrophotometrically. For example, the chloride salts were monitored at the following wavelengths: Fe³⁺, 394 nm; Cr³⁺, 482 nm; Co²⁺, 682 nm; Cu²⁺, 346 nm and Ni²⁺, 448 nm. The supernatant solution was then returned to the flask and titration continued until no further change in total absorbed metal-ion was observed.

The amount (meq per gram of polymer) of metal-ion incorporation was determined from the expression $(C_i - C_s)V/0.2 \text{ g polymer}$, where C_i represents the initial molar concentration of the solution, the concentration of the supernatant solution is designated C_s and V is the total volume of solution added in millilitres. The results for various metal ions are presented in Table 1.

Competition studies

A series of mixtures containing two metal ions were placed in contact with the modified polymer. The reaction was monitored spectrophotometrically at different wavelengths and the metal-ion incorporation determined as above. Figure 1 shows data for a typical competition reaction.

Table 1 Metal-ion loading

Metal salt	Quantity bound	
	mmol metal per g [P]-dpa	mmol dpa ^a per mmol metal
FeCl ₂	0.62	1.24
Fe(BF ₄) ₂	0.37	2.09
Fe(SCN) ₂	0.39	1.97
CoCl ₂	0.63	1.23
Co(BF ₄) ₂	0.42	1.84
Co(NO ₃) ₂	0.33	2.35
Co(SCN) ₂	0.38	2.03
NiCl ₂	0.65	1.20
Ni(BF ₄) ₂	0.41	1.88
Ni(NO ₃) ₂	0.36	2.14
CuCl ₂	0.64	1.21
Cu(BF ₄) ₂	0.40	1.94
Cu(NO ₃) ₂	0.38	2.03
ZnCl ₂	0.67	1.15
Zn(BF ₄) ₂	0.40	1.95
Zn(NO ₃) ₂	0.39	1.98
FeCl ₃	0.76	1.02
Fe(NO ₃) ₃	0.65	1.18
Fe(SCN) ₃	0.39	1.98
CrCl ₃	0.73	1.05
Cr(NO ₃) ₃	0.48	1.61

^a[P]-dpa (Method B) contains ca. 0.77 mmol dpa per gram of polymer

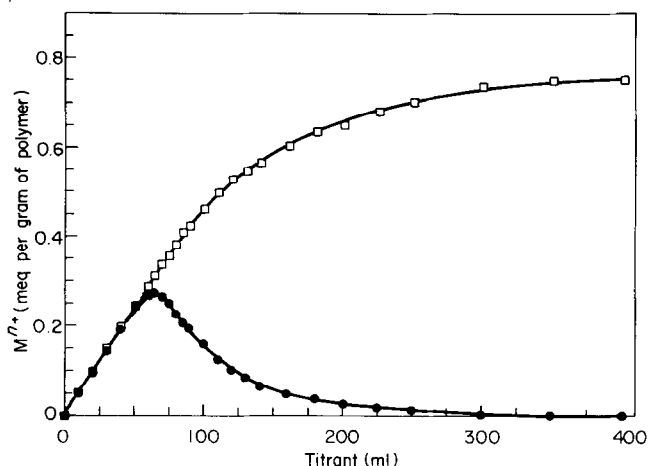


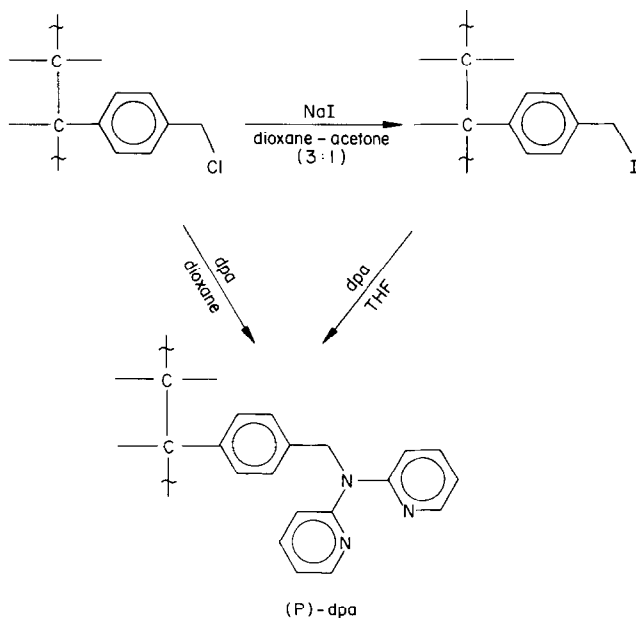
Figure 1 Competitive binding study: equimolar mixture of FeCl₃ (□), and CoCl₂ (●) (1 × 10⁻³ M each)

Stripping and regeneration

After the amount of metal incorporated by the modified polymer was determined, the metal ion was stripped from the polymer using 5 ml of 6 M HCl in THF. The resin was separated by filtration and thoroughly washed with 6 M HCl. The filtrate was then diluted to 1 l and the concentration of the metal ion determined by atomic absorption. This cycle was repeated several times to determine the reusability of the modified polymer.

RESULTS AND DISCUSSION

Chloromethylated polystyrene is readily available and the attachment of a number of polydentate amines and phosphines has been demonstrated⁴. The attachment of 2,2'-dipyridylamine was similarly achieved by employing the following reaction:



Although the chloromethylated resin can be reacted directly with dpa, an excess of amine is important to neutralize the HCl produced and to drive the reaction, since Cl⁻ is a poor leaving group. Conversion of the chloromethyl group to an iodomethyl group allows

attachment of dpa without a large excess of amine since I^- is a much better leaving group.

From elemental analysis the amount of dpa attached to the polymer may be deduced. Results indicate a 48% conversion of the chloromethylated residues to bound dpa for Method A and a 58% conversion for Method B. The latter corresponds to one dpa moiety every 13 phenyl residues.

The infra-red spectrum of [P]-dpa shows, in addition to polystyrene absorptions, new bands at 1620, 1530, 1470 and 1150 cm^{-1} , which are indicative of the attachment of dpa¹⁷. Further evidence for the incorporation of dpa was obtained by computerized Kubelka-Munk spectral subtraction between [P]-dpa and chloromethylated polystyrene.

The swelling factor of [P]-dpa in various solvents has been examined. [P]-dpa swells considerably less (50% in chloroform, THF and benzene) than the chloromethylated polymer. This may be attributed to some expansion of the polymer matrix upon incorporation of the dpa moiety.

A wide variety of transition metal complexes of [P]-dpa can be easily prepared. Tetrahydrofuran is a convenient solvent in which to study metal loading due to its ability to swell the polymer support and to dissolve a large number of metal salts. The results of these studies (Table 1) demonstrate that [P]-dpa is capable of chelating a variety of transition metal ions. Assuming each metal ion is coordinated to one ligand, iron(III) chloride is found to occupy 99% of the available sites in [P]-dpa. Similarly, all the bipy residues were occupied in PS-bipy^{9,10}, whereas in PS-napy only 58% of the napy sites were occupied¹². Increased metal incorporation per millimole of ligand was observed for all MCl_2 salts for [P]-dpa (>80%) compared to both PS-bipy (42%) and PS-napy (50%).

Although all the factors that determine the amount of metal incorporation have not been elucidated, a few important trends have been previously reported¹⁰. For [P]-dpa the metal loading data indicates a counterion dependence that follows the order $Cl^- \gg BF_4^- = SCN^- = NO_3^-$. PS-napy was observed to follow this same order¹², but no trend was apparent from the data reported by Card and Neckers^{9,10}.

With dpa, which is not attached to the polymer support, tetrahedral complexes with covalently bound chlorides of formulation $M(dpa)Cl_2$ have been isolated for $M = Co, Fe, Cu$.^{15,16,18} Formation of tetrahedral $M(dpa)(SCN)_2$ has not been achieved; only the octahedral $M(dpa)_2(SCN)_2$ complex has been isolated ($M = Co, Fe$)^{15,16}. The formation of $Cu(dpa)_2(NO_3)_2$, which contains ionic NO_3^- anions and a square planar cation, has been reported¹⁹. So, the large difference in the amount of metal incorporation observed between the metal chlorides and the other salts reflects the known coordination chemistry of dpa. To obtain similar compounds for the BF_4^- , SCN^- and NO_3^- salts, the polymer would be required to be flexible enough to allow

more than one dpa moiety to coordinate to a metal ion. Based on the metal-loading data, it is reasonable to assign a 1:1 ligand to metal complex for the metal chlorides and a 2:1 complex for the BF_4^- , SCN^- and NO_3^- salts.

The metal ions can be stripped from the polymer-bound chelate with little effect on the ability to regenerate the polymer-bound metal complexes. Regeneration studies were made to establish the reusability of the polymer. Results indicate that after six complete cycles, 90% of the dpa sites were still available for chelation.

A noteworthy selectivity was observed in metal-ion mixtures. In a two component mixture, both metal ions load linearly and independently until 80% of the available sites are occupied, after which competition for the sites begins. Figure 1, which shows the data for $FeCl_3$ and $CoCl_2$ is typical of the competition reactions. From a number of studies the affinity of various metal ions for the dpe moiety was determined to follow the order $Fe^{3+} > Cr^{3+} \gg Co^{2+} > Cu^{2+} > Ni^{2+}$.

Our results suggest that polymer-bound 2,2'-dipyridylamine may have important applications in the quantitative and/or qualitative removal of metal ions, particularly the selective removal of Fe^{3+} , in organic media. Modification of the polymer to yield a material that will swell in solvents that possess higher dielectric constants, such as water, is under study. The catalytic properties of these and other metal complexes are also currently being investigated.

REFERENCES

- 1 Melby, L. R. *Am. Chem. Soc.* 1975, **97**, 4044
- 2 Pedersen, C. J. and Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.* 1972, **11**, 16
- 3 Rollman, L. D. *J. Am. Chem. Soc.* 1975, **97**, 2132
- 4 Drago, R. S., Gaul, J., Zombeck, A. and Staub, D. K. *J. Am. Chem. Soc.* 1980, **102**, 1033
- 5 Grubbs, R., Lau, C. P., Cukier, R. and Brubaker, C., Jr. *J. Am. Chem. Soc.* 1977, **99**, 4517
- 6 Pittman, C. U., Jr. and Hanes, R. M. *J. Am. Chem. Soc.* 1976, **98**, 5402
- 7 Tsutsui, M. and Ugo, R. 'Fundamental Research in Homogeneous Catalysis', Plenum Press, New York, 1977; Carraher, C. E., Jr., Sheats, J. E. and Pittman, C. U., Jr., 'Organometallic Polymers', Academic Press, New York, 1978; Pignolet, L. H. (Ed.) 'Homogeneous Catalysis with Metal Phosphine Complexes', Plenum Press, New York, 1983
- 8 Garrou, P. E. *Chem. Rev.* 1985, **85**, 171
- 9 Card, R. J. and Neckers, D. C. *J. Am. Chem. Soc.* 1977, **99**, 7733
- 10 Card, R. J. and Neckers, D. C. *Inorg. Chem.* 1978, **17**, 2345
- 11 Card, R. J., Liesner, C. E. and Neckers, D. C. *J. Org. Chem.* 1979, **44**, 1095
- 12 Valera, N. S. and Hendricker, D. G. *Polymer* 1980, **21**, 597
- 13 Valera, N. S. and Hendricker, D. G. *Polymer* 1981, **22**, 1007
- 14 McWhinnie, W. R. *J. Chem. Soc.* 1964, 5165
- 15 Goodgame, M. *J. Chem. Soc. A* 1966, 63
- 16 Burbridge, C. D. and Goodgame, D. M. L. *J. Chem. Soc. A* 1967, 694
- 17 Rud'ko, A. P., Chernyuk, I. N., Rozum, Yu. S., Pilyugin, G. T. *Ukr. Khim. Zh.* 1969, **34**, 1275
- 18 Ray, N., Tyagi, S. and Hathaway, B. J. *Chem. Soc., Dalton Trans.* 1982, 143
- 19 McWhinnie, W. R. *J. Inorg. Nucl. Chem.* 1965, **27**, 1619