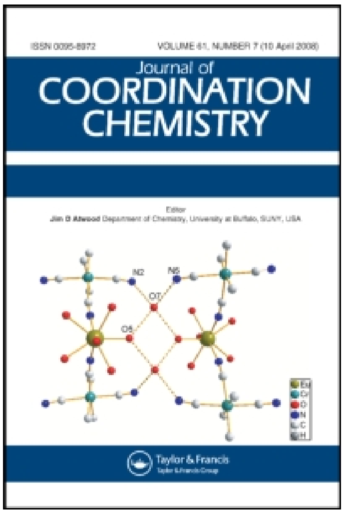

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CHELATION PROPERTIES OF SILICA-BOUND 1,10-PHENANTHROLINE

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Synthesis of 4-formyl-1,10-phenanthroline and its immobilization on silica *via* hydrazone formation with hydrazinophenylsilyl groups on Chromosorb is described. Chelation and chromatographic properties are reported for various transition metal ions.

Keywords: 1,10-Phenanthroline, silica, chelation, chromatography

INTRODUCTION

Chelation provides an effective means for control of metal ion chemistry to achieve and maintain a desired equilibrium level, especially a very low non-interfering level. Chelation also greatly facilitates quantitative separations based upon transfer of metal species between immiscible phases. Recently, increased attention has been given to expanding the role of chelation in separations by devising ways of immobilizing chelating ligands on solid supports. Examples reported from this laboratory include ligands bound by adsorption on styrene–divinylbenzene copolymer (XAD-2)[1] and active carbon[2] and by covalent bonding to silica.[3] Immobilized ligands have proven suitable for use in column applications which inherently provide greater efficiency in separations than batch-techniques and are also faster and more convenient.

In this communication we describe the synthesis of 4-formyl-1,1-phenanthroline, its bonding to a silica support, and the metal ion chelation properties of the resultant material. The results demonstrate a different dimension for chelation by 1,10-phenanthroline, restricted to monochelate formation when immobilized covalently on a solid support. Further study and applications in separations appear promising.

EXPERIMENTAL

Synthesis of 4-Formyl-1,10-phenanthroline

A solution of 2.3 g of 4-methyl-1,10-phenanthroline (G. F. Smith Chemical Co.) in 90 cm^3 of dioxane was added slowly over a 25 minute period to a continuously stirred mixture at 50°C consisting of 1.8 g of selenium dioxide (freshly prepared from selenium and nitric acid) and 20 cm^3 of dioxane contained in a 200 cm^3 flask. Halfway through the addition, the temperature was increased slowly to initiate reflux.

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After heating at reflux for one hour, the mixture was filtered while still hot, and the filtrate was evaporated at low pressure to strip dioxane from the reaction mixture to obtain a yellow oil. The oil was taken up in 50 cm^3 of chloroform and filtered through dry filter paper which retained droplets of aqueous phase and traces of dark selenium. Fresh portions of chloroform were used to wash the filter and then combined with filtrate, which was then extracted with an equal volume of 1% sodium carbonate in water and twice again with distilled water. The aqueous fractions were combined and extracted once with chloroform. The chloroform portions were combined, treated with anhydrous sodium sulfate, filtered, and evaporated to dryness. The resulting dry solid was dissolved in chloroform, filtered to remove traces of red selenium dioxide, and evaporated to a volume of about 5 cm^3. Petroleum ether was added (approximately 15 cm^3) to cause crystallization. A product yield of 1.3 g (53%) was obtained after drying at 90°C. *Anal.*; Calcd. for $C_{13}H_8ON_2 \cdot H_2O$: C, 69.6; H, 4.49; N, 12.49%. Found: C, 71.5; H, 4.26; N, 12.2%. NMR (100 MHz, $CDCl_3$): 10.63δ (s, 1 H, aldehydic proton), 7.2–9.5δ (7 H, aromatic protons). IR: 1700 cm^{-1} (carbonyl stretch).

Preparation of Silica-bound 1,10-Phenanthroline

Chromosorb LC-6, 5-μm particle size (Johns Mansville Co.) was treated with 2 *M* nitric acid at reflux temperature for 3 hours, collected by filtration, washed with deionized water, and dried overnight at 180°C. A 5 g portion was used to prepare silica-bound phenylhydrazine[4] which was then converted to the silica-bound hydrazone of 4-formyl-1,10-phenanthroline by treatment for 3 hours with a solution of 0.50 g of 4-formyl-1,10-phenanthroline in 20 cm^3 of absolute ethanol and 3 drops of glacial acetic acid at reflux temperature. The product was collected by filtration, after cooling, and washed with toluene, then with 2-propanol, and air dried. To deactivate any remaining reactive silanol groups, the product was heated at reflux for 2 hours with 20 cm^3 of 25% (v/v) trimethylchlorosilane in toluene. The final product was washed with toluene, followed by 2-propanol, and then dried at 80°C overnight.

Properties of Silica-bound 1,10-Phenanthroline

Chelation capacities for hydrogen and copper(II) ions, sorption isotherms for iron(II) and zinc(II), and chromatograms for various metal(II) ions were determined using procedures, instrumentation, and detection similar to those described previously.[3,4] The column contained 1.8 g of the Chromosorb-Phen product, was slurry packed, and had a void volume of 3.1 ± 0.1 cm^3 and dimensions 250 × 4.6 mm (i.d.).

RESULTS AND DISCUSSION

In aqueous solutions of pH 1 to 10, 4-formyl-1,10-phenanthroline forms a soluble, orange iron(II) tris-chelate of high stability. Formation is rapid and quantitative between pH 3 and 9. At pH 7 the chelate absorbs maximally at 510 nm with a molar absorptivity of 12,080, only slightly higher than that of the iron(II) chelate of unsubstituted 1,10-phenanthroline. Treatment with hydroxylamine hydrochloride yielded the oxime of the 4-formyl derivative as evidenced by its formation of a very stable, red, water-soluble iron(II) chelate with maximum absorbance at 540 nm and molar absorptivity of 16,340. This observation together with elemental analysis and NMR and IR spectra confirms that the synthesis of 4-formyl-1,10-phenanthroline was successful.

Covalent bonding of 1,10-phenanthroline to the surface of Chromosorb was achieved, as described above, by hydrazone coupling between 4-formyl-1,10-phenanthroline and 4-phenylhydrazine groups on Chromosorb synthesized by silylation with trimethoxy-4-aminophenylsilane followed by diazotization and reduction to the hydrazine. Hydrazone formation was evidenced by the orange-yellow colour taken on by the solid during reaction. Infrared and NMR spectra for the solid were too weak to be considered but chemical measurements, described below, provided quantitative information as to the amount of phenanthroline incorporated per g of Chromosorb.

Titration of the Chromosorb-Phen product with standard perchloric acid in glacial acetic acid yielded only one end-point break, corresponding to the uptake of $33 \pm 2\,\mu$mol of acid per g of solid. Measurement of the uptake of copper(II) at pH 5.0 by the product gave a value of $39 \pm 3\,\mu$mol of copper per g of solid. Lack of close agreement between these two results is indicative of the presence of two or more different kinds of basic sites, at least one of which is too weak to yield a titration break with strong acid but still sufficiently strong enough to bind copper(II) ions. The latter are known to form complexes even with weakly basic ligands. Considering the chemistry of its synthesis, at least three different basic groups could be present on the Chromosorb-Phen product: the bidentate site of the phenanthroline group and the monodentate sites of unreacted amino and hydrazino groups on the phenylsilyl fragment. Another possible site, although very weakly basic, is the hydrazone linkage that binds the phenanthroline group to the Chromosorb. All things considered, it is not surprising that the capacity of the product for copper(II) proved to be slightly greater than that for hydrogen ions.

Further insight into the nature of uptake of metal ions by the product was provided by sorption isotherms measured for sorption of iron(II) and for zinc(II) at room temperature from solutions buffered at pH 3.0. Sorption conformed to the Langmuir rather than Freundlich equation. Values found graphically for the Langmuir parameters b and K are as follows: for Fe(II), $b = 17.9 + 3.6\,\mu$mol/g and $K = 2.4(\pm 0.4) \times 10^4$ L/mol; for Zn(II), $b = 19.6 \pm 3.6$ and $K = 1.7(\pm 0.3) \times 10^5$. As expected from the known solution stability constants of their 1,10-phenanthroline chelates, the Langmuir K value for zinc(II) is about one order of magnitude greater than that for iron(II). The b-values (molar capacity/g solid) for iron(II) and zinc(II) agree closely. These ions, unlike copper(II), tend to complex very weakly or not at all to aniline or phenylhydrazine. Thus, the molar capacities for these are much less than that for either copper(II) or hydrogen ion. The results indicate that an appreciable number of bonded but unreacted anilino and/or phenylhydrazino groups are present in the Chromosorb-Phen product. Assuming that iron(II) or zinc(II) is taken up by chelation to phenanthroline in the usual bidentate fashion and that any given metal ion is chelated by only one bound ligand, there are approximately $19\,\mu$mols of phenanthroline bonded per g.

Chelation of transition metal ions by Chromosorb-Phen was examined chromatographically using dilute solutions of nitric acid as eluents. With 0.10 *M* nitric acid, manganese(II) eluted immediately following the void volume, lead(II) eluted next, followed by iron(II) together with cadmium(II), and then zinc(II). Cobalt(II) could be eluted with difficulty using 0.5 *M* nitric acid, but mercury(II), copper(II) and nickel(II) could not. Higher concentrations of nitric acid were not tried for fear of decomposing the hydrazone and/or silyl groups.

Chromatograms obtained with 0.1 *M* nitric acid for mixtures of metal(II) ions of manganese, lead, iron, cadmium and zinc exhibited broad and poorly resolved peaks, unsuited for chromatographic analysis. Quantitative (baseline) separation was observed only for mixtures of manganese, lead and zinc.

The order of elution for those ions that could be eluted followed the same order as that of the increasing order of formation constants of their 1,10-phenanthroline monochelates. The order of stability (with log β_1, values given in parentheses)[5] is as follows: Mn(II) (4.0), Pb(II) (4.6), Fe(II) (5.7), Cd(II) (5.8), Zn(II) (6.6), Co(II) (7.3), Ni(II) (8.8), Cu(II) (9.3), and Hg(II) (log $\beta_2 = 19.65$).

Slow desorption of metal ions from the Chromosorb-Phen product apparently is the major reason for the chromatographic band broadening observed. Under pseudo-first-order kinetic conditions, a rate constant of $2.7(\pm 0.4) \times 10^{-4}$ $\sec^{-1}$ was found for the release of iron(II) from Chromosorb-Phen on treatment with 0.10 *M* nitric acid, stirred at room temperature. With a half-life approximating 5 min in the sorbed state, iron(II) and similar metal ions cannot be efficiently resolved in a reasonable time for chromatographic analysis of complex mixtures.

Silica-bound 1,10-phenanthroline, although too strongly binding and too slow releasing for metal ion chromatographic application, did prove effective for removing trace levels of transition metal ions from dilute acid solutions. It merits consideration for possible use in purification of reagents and enrichment recovery of trace metals from solution.

REFERENCES

1. J.L. Lundgren and A.A. Schilt, *Anal. Chem.*, 49, 974 (1977).
2. D.J. Hutchinson and A.A. Schilt, *Anal. Chim. Acta*, **154**, 159 (1983).
3. S. Watanesk and A.A. Schilt, *Talanta*, **33**, 895 (1986).
4. N. Simonzadeh and A.A. Schilt, *Talanta*, **35**, 187 (1988).
5. A.A. Schilt, 'Analytical Applications of 1,10-Phenanthroline and Related Compounds', (Pergamon Press, New York, 1969), pp. 28–32.