October, 1984] © 1984 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 57, 2859—2862 (1984) 2859

Selective Adsorption of Molybdenum(VI) and/or Vanadium(V) Using Cross-linked Polystyrene Resins with Bis(2-hydroxyethyl)amino, Bis(carboxymethyl)amino, and Bis(phosphonomethyl)amino Groups

Masato NISHIZAWA,* Toshiro YOKOYAMA, Tetsuo KIMURA, and Toshishige M. SUZUKI*
Government Industrial Research Institute, Tohoku. 4-2-1, Nigatake, Sendai 983

(Received April 27, 1984)

Styrene-divinylbenzene copolymers containing -$N(CH_2CH_2OH)_2$, -$N(CH_2CO_2H)_2$, and -$N(CH_2PO(OH)_2)_2$ moieties have been synthesized and applied to the selective adsorption of molybdenum and/or vanadium from aqueous solution. The equilibrium adsorption capacity *vs.* pH correlation and exchange kinetics of the resins for Mo^{VI} and V^{V} have been studied. The resin containing bis(2-hydroxyethyl)amino group is particularly effective for the selective recovery of Mo^{VI} and/or V^{V} by column operation due to its high adsorption capacity and faster exchange rate, whereas other resins required much longer time to attain adsorption equilibrium. The bis(2-hydroxyethyl)amino resin was used for the selective recovery of molybdenum from an acid-leaching solution of waste desulfurization catalyst.

In all industrialized countries a significant proportion of the metals consumed by industry should be provided by recycling of used metals. Therefore it is important to achieve a process to recover metals from scrap and industrial wastes. Waste catalysts used in the desulfurization of petroleum contain appreciable amounts of molybdenum and vanadium.[1] We have been searching for highly selective chelating resins in order to recover these metals from acid-leaching solution. Multidentate ligands containing bis(carboxymethyl)amino group(s) are known to form stable complexes with oxomolybdenum(VI) and oxovanadium(V) ions.[2,3] The selective adsorption of these metal ions has been demonstrated by polymer-immobilized iminodiacetic acid[4,5] and *N*-[2-(2-pyridyl)ethyl]ethylenediamine-*N,N'*-diacetic acid.[5]

We have recently prepared cross-linked polystyrene resins containing a series of multidentate ligands as discrete units to attain a high adsorption capacity and selectivity.[6,7] In our preliminary work we found that those resins which contain bis(2-hydroxyethyl)amino and bis(phosphonomethyl)amino moieties have a potential utility for selective adsorption of oxometal ions.[8] In the present paper we deal with a detailed study on the adsorption of Mo^{VI} and/or V^{V} using chelating resins having bis(2-hydroxyethyl)amino (HEA), bis(carboxymethyl)amino (CMA), and bis(phosphonomethyl)amino (PMA) moieties as depicted in Fig. 1 to elucidate the correlation of the adsorption characteristics with the properties of the functional groups. The application of the resins for the selective recovery of molybdenum from the acid-leaching solution of waste catalyst has been studied.

Experimental

Materials. Reagent grade $Na_2MoO_4 \cdot 2H_2O$, $K_2MoO_4 \cdot 5H_2O$, NH_4VO_3, and ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA) were used without further purification. *N,N,N',N'*-Tetrakis(2-hydroxyethyl)ethylenediammonium bis(perchlorate) (THEED·$2HClO_4$)[9] and *N,N,N',N'*-tetrakis(phosphonomethyl)ethylenediamine (EDTPO)[10] were prepared by the reported methods and identified by ^1H-NMR and ^{13}C-NMR spectroscopy. Gel-type of polystyrene-2%-divinylbenzene copolymer beads (200—400 mesh, Kanto Chemical Co.) were used as the polymer matrix of the chelating resins.

Leaching Solution of Desulfurization Catalyst. Metal ions were leached from waste desulfurization catalyst by treatment with 4 M HCl (1 M = 1 mol dm^{-3}) as described previously.[5] The main components in the leaching solution were molybdenum, vanadium, and aluminium, of which the latter two metals originated from crude oil and catalyst support (Al_2O_3), respectively.

Preparation of the Chelating Resins. Polystyrene beads were chloromethylated followed by functionalization with diethylenetriamine (*dien*) to give a *dien*-resin in which *dien* is linked to the polymer uniquely through the imino group.[6,7] The *dien*-resin was used as the starting material for the preparation of *N*-substituted derivatives.

HEA Resin: The *dien*-resin (11 g) was stirred with aqueous ethylene oxide (9.6 g in 100 cm^3) for 3 h under ice-cooling. After standing overnight at room temperature, the resin beads were filtered, washed throughly with water, ethanol, and diethyl ether, and then dried *in vacuo* at 50 °C. Yield: 19.5 g. Nitrogen analysis: 7.3%.

CMA and PMA resins were prepared by carboxymethylation and phosphonomethylation of the *dien*-resin as described previously.[7] Nitrogen analyses of CMA and PMA resins were 7.7 and 6.5%, respectively.

Determination of Adsorption Capacity. A batchwise technique was used to determine the equilibrium adsorption capacity (amount of metal adsorbed on one gram of dry resin) with metal ion always being excess over the resin capacity.

Typically, 100 mg of dry resin was added to 100 cm^3 of metal

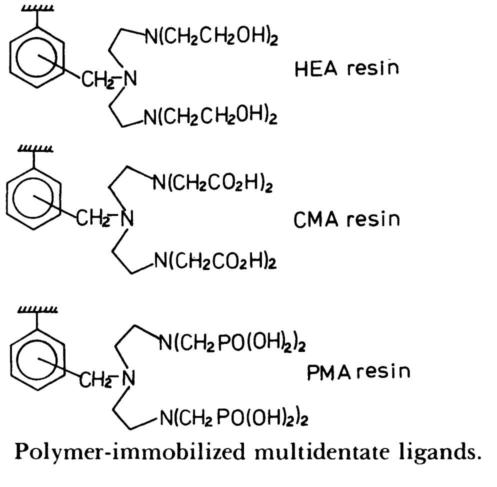

Fig. 1. Polymer-immobilized multidentate ligands.

ion solution of various pH and the mixture was shaken at room temperature. After equilibrium was attained, the concentration of the remaining metal ion in the supernatant was analyzed by atomic absorption spectrometry. The capacity of the resins was calculated by the change in the metal concentration observed.

Adsorption Rate. Time-course experiments for the adsorption of metal ion were carried out under a batchwise procedure: To a buffered metal solution (2—4 mM) was added 500 mg of resin which was swollen with water in advance. While stirring, small portions of the samples were withdrawn at appropriate intervals and analyzed as described above.

Kinetic Runs. Complex formation kinetics of THEED, EDTPO, and EDTA with Mo^{VI} was studied at 25 °C in the pH regions 3.9—5.6, 3.7—6.1, and 4.5—6.8, respectively. The reaction was followed spectrophotometrically at 270 nm by a stopped-flow technique. The kinetic runs were carried out under pseudo-first-order conditions, ligand concentration being in excess (3×10^{-3} M) over Mo^{VI} (1×10^{-4} M). The pH was adjusted with perchloric acid and sodium hydroxide solution at an ionic strength of 0.5 ($NaClO_4$). Plots of log ($A_\infty-A_t$) against time gave straight lines until the reaction reached 85% completion.

Column-breakthrough Experiments. A 5 g sample of chelating resin was swollen with water and poured onto a glass column (ϕ 1.3 cm). The column was conditioned with dilute HCl (pH 1) in advance, then the metal ion solution was passed through the column continuously at a rate of 1.5 $cm^3\,min^{-1}$. The effluent was fractionated into 10 cm^3 portions and the amount of metal ion was determined. The adsorbed molybdenum and/or vanadium was liberated from the column by elution with 1 M sodium hydroxide solution. The resin was regenerated by this procedure and used in the successive operation.

A similar column operation was applied to the actual leaching solution of waste catalyst in which various foreign metal ions other than molybdenum and vanadium were also present. The concentration of the components in the feed solution were 360, 220, 53, 15, 4, and 3 ppm for Mo, V, Al, Co, Ni, and Fe, respectively.

Measurements. The ^1H-NMR and ^{13}C-NMR were obtained with a JEOL FX-100 spectrometer with sodium 3-(trimethylsilyl)-1-propanesulfonate as the internal standard. UV spectra were recorded with a Hitachi 100-60 spectrophotometer. The metal ion concentration was determined with a Shimadzu atomic absorption/flame photometer Model AA-610S. The complexation reaction was followed by a stopped-flow method using a Union Giken RA 601 with a data processor and an X-Y recorder.

Results

Preparation of the Chelating Resins. The chelating resins used in the present study were derived from diethylenetriamine which was immobilized on polystyrene through the imino nitrogen.[6,7] The HEA resin was prepared by treatment of the *dien*-resin with aqueous ethylene oxide solution. *N*-Carboxymethylation and *N*-phosphonomethylation of the *dien*-resin yielded the CMA resin and PMA resin, respectively. Nitrogen analyses indicated that the HEA, CMA, and PMA resins formally contain 1.7, 1.8, and 1.6 mmol of the functional group per gram resin, respectively. All the resins have a satisfactory stability over a wide pH range.

Equilibrium Adsorption. The adsorption capacity *vs.* pH profiles of the resins are given in Figs. 2, 3. The amount of Mo^{VI} adsorbed on one gram of resin are approximately 3 mmol over pH 1—6 irrespective of the functional group. Thus, the ratios of Mo^{VI} capacity to the content of functional group are in the range 1.8—2.0. Previously we reported the capacity of the CMA resin for Mo^{VI} to be 1—1.5 mmol g^{-1} by allowing the resin for 3 h in a metal solution.[5] However a slower adsorption step took place subsequently and the equilibrium was attained after seven days. In any case, the capacities for Mo^{VI} and V^V are markedly decrease in alkaline solution (pH 10) in which pH region the functional groups coordinate to the metal species with difficulty.[11] Therefore adsorbed Mo^{VI} and V^V were readily liberated from the resin on treatment with dilute sodium hydroxide solution. The adsorption capacities

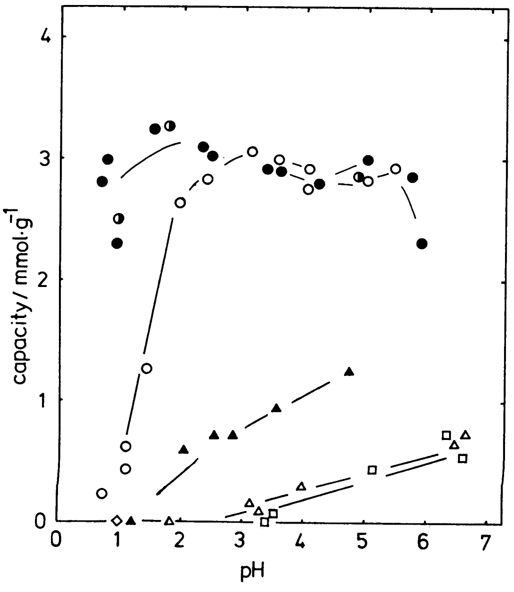

Fig. 2. Adsorption capacity of HEA resin as a function of pH.
-●-: Mo^{VI}, -○-: V^V, -▲-: Cu^{2+}, -△-: Ni^{2+}, -□-: Co^{2+}, -◇-: Al^{3+}, -◐-: Mo^{VI}, in the presence of 1500 ppm of SO_4^{2-}.

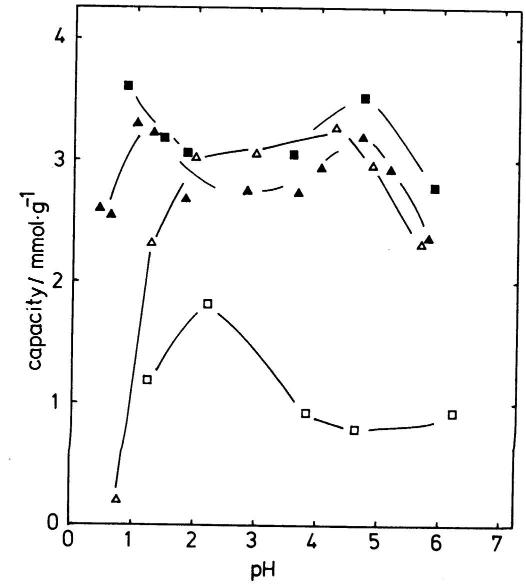

Fig. 3. Adsorption capacity of CMA and PMA resins for Mo^{VI} and V^V as a function of pH.
-■-: Mo^{VI}-CMA resin, -□-: V^V-CMA resin, -▲-: Mo^{VI}-PMA resin, -△-: V^V-PMA resin.

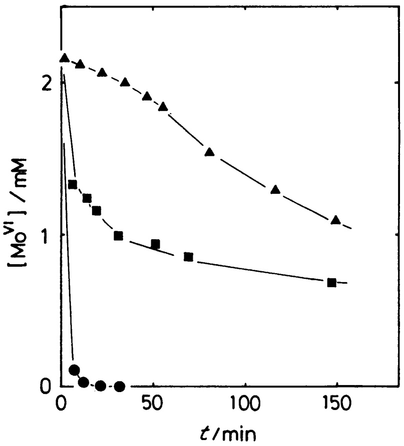

Fig. 4. Adsorption time-course of $\mathrm{Mo^{VI}}$ at pH 4.
-●-: HEA resin, -■-: CMA resin, -▲-: PMA resin.

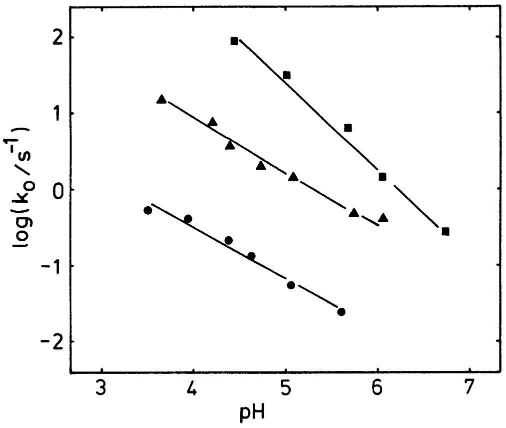

Fig. 5. Conditional first-order rate constant of $\mathrm{Mo^{VI}}$ complex formation as a function of pH.
-●-: THEED, -▲-: EDTPO, -■-: EDTA.

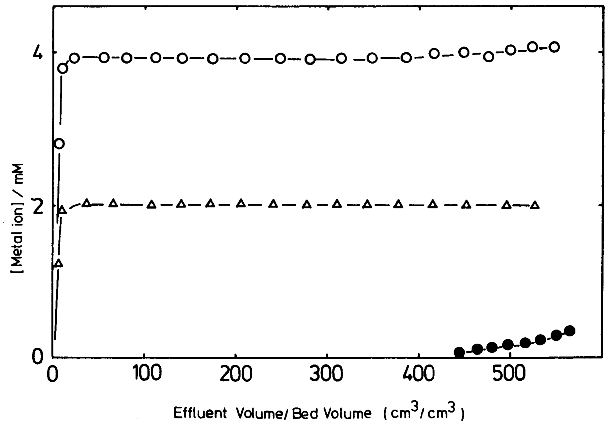

Fig. 6. Breakthrough profile of the acid-leaching solution of waste catalyst.
-●-: Mo, -△-: Al, -○-: V.
Bed resin: HEA resin, 5 g (wet volume 13 $\mathrm{cm^3}$), pH of the feed: 1.0, Flow rate: 1.5 $\mathrm{cm^3\,min^{-1}}$.

of the present resins were reproducible over several adsorption-regeneration cycles. Apparent selectivity was observed for all the resins, the capacities for vanadium at pH below 2.0 is remarkably lower than those for molybdenum. In addition, these resins revealed very little affinity for the common metal cations including $\mathrm{Al^{3+}}$, $\mathrm{Cu^{2+}}$, $\mathrm{Co^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Fe^{2+}}$, at pH lower than 3.0.

Complexation Kinetics. The time-course of $\mathrm{Mo^{VI}}$ adsorption on the present resins was followed by monitoring the concentration in the aqueous phase at pH 4 and the results are shown in Fig. 4. The HEA resin can adsorb the metal ion rapidly and equilibrium was attained within 3 min, while the CMA and PMA resins required much longer time for equilibration under identical conditions. A similar trend was observed at pH 1 for $\mathrm{Mo^{VI}}$ uptake and at pH 4 for $\mathrm{V^{V}}$. As mentioned above, the adsorption of $\mathrm{Mo^{VI}}$ by CMA resin involves two steps, *i.e.*, rapid adsorption took place in the initial 1 or 2 h followed by a second slower step which required extremely long time for equilibration.

The rate of complexation between functional groups and $\mathrm{Mo^{VI}}$ was estimated by model reactions employing ethylenediamine derivatives, THEED, EDTA, and EDTPO. The absorption intensity of aqueous $\mathrm{Mo^{VI}}$ solution at 300—200 nm region increases on addition of the ligands and was monitored spectrophotometrically. Figure 5 shows the profile of the pseudo-first-order rate constants against pH. EDTA coordinates to $\mathrm{Mo^{VI}}$ in one order of magnitude faster than EDTPO and two orders of magnitude than THEED. In every case the rate was enhanced as the concentration of proton increased, however the spectral change became complicated at pH lower than 3.5 due to side reactions.

Column Breakthrough. In the batch experiments present resins showed an apparent selectivity toward $\mathrm{Mo^{VI}}$ at pH lower than 1.5 suggesting the possibility of selective recovery of the metal ion. When a model solution containing equimolar $\mathrm{Mo^{VI}}$ and $\mathrm{V^{V}}$ (4 mM each, pH 1.0) was passed continuously through the column of HEA resin, $\mathrm{Mo^{VI}}$ was quantitatively adsorbed on the resin while $\mathrm{V^{V}}$ was found in the eluate. The amount of $\mathrm{Mo^{VI}}$ adsorbed on one gram of the resin at breakthrough point (breakthrough capacity) is approximately 90% of the equilibrium capacity obtained by batch experiment. Vanadium was then quantitatively collected from the eluate upon subsequent column operation at pH 2—3. Using the column with CMA and PMA resins, on the other hand, both $\mathrm{Mo^{VI}}$ and $\mathrm{V^{V}}$ leaked through the column in the early stage regardless of the pH of the feed solution.

Based on the column experiments we chose HEA resin for selective recovery of molybdenum and/or vanadium from the acid-leaching solution of desulfurization catalyst. Using the column operation described above, molybdenum was quantitatively adsorbed on the resin, while other metals leaked through the column. The breakthrough curves are given in Fig. 6. Small amount of vanadium was cosorbed in a molar ratio Mo/V *ca.* 5/1. The adsorbed ion was liberated in concentrated form, 60-fold over the feed solution, on elution with 1 M sodium hydroxide. Repeated column operation for the eluate greatly improved the Mo/V ratio to be 50/1.

Discussion

EDTA is known to form 1:2 (ligand:metal) complex with oxomolybdenum(VI) ion in the presence of excess metal ion. The facial tridentate coordination of each iminodiacetate arm to the trioxomolybdenum-

(VI) was suggested by ^{1}H- and ^{13}C-NMR studies[12—14] and confirmed in the solid state for $Na_4(MoO_3)_2$-EDTA$\cdot 8H_2O$.[15] The HEA, CMA, and PMA resins formally contain two sets of tridentate ligand, bis(2-hydroxyethyl)amino, bis(carboxymethyl)amino, and bis(phosphonomethyl)amino moieties, respectively. It appears that each of the tridentate ligand units forms a 1:1 complex with Mo^{VI} in a similar fashion to that for the EDTA–Mo^{VI} complex since the metal capacity values in equilibrium are approximately twice the value of the ligand capacity.

The coordination of the hydroxyl arm onto the Mo^{VI} center has been demonstrated by Freeman *et al.*, using *N*-methyl-*N*-hydroxyglycine (MHEG) and *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA).[14] They reported that ^{13}C peaks of 2-hydroxyethyl carbons shift *ca.* $\delta=13$ (hydroxyl carbon) and $\delta=5$ (carbon adjacent to N) down field upon coordination to Mo^{VI}. The ^{13}C-signals of THEED appear at δ 50.5, 57.9, and 58.4 in which the latter two peaks correspond to the 2-hydroxyethyl carbons. On addition of Mo^{VI} (Mo: L=2:1) at pH 5.0 seven peaks are observed in which two peaks at δ 63.0 and 73.9 can be assigned to the coordinated 2-hydroxyethyl carbons. Therefore Mo^{VI} seems to be retained on HEA resin *via* chelate formation with the bis(2-hydroxyethyl)amino moiety.

Although equilibrium capacity is of fundamental importance in characterizing the resin, the rate at which equilibrium is achieved is extremely important from a practical point of view. If the adsorption rate is not sufficiently rapid, the concentration of a metal on the resin is unlikely owing to the short contact time between the resin and the solution. In fact effective column separation of Mo^{VI}/V^{V} was realized only by use of the HEA resin which is superior to other resins with respect to the adsorption rate. On the other hand, CMA and PMA resins were not applicable for column separation due to their slow adsorption rates. In those cases, a batch extraction with a large excess of resin could be conducted over an extended period.

The metal adsorption process of a chelating resin may include the following steps, i) diffusion of the metal ion into the polymer matrix, ii) complex formation with the functional group. The rate for the latter step was estimated by measuring the conditional rate constant of Mo^{VI} complex formation using model ligands. The observed pH dependence of the rates could be accounted for by a mechanism involving protonation to the oxo groups in the activated complexes.[16] The complexation rates are, in any extent, appreciably rapid, especially in the low pH region. Moreover the order of the complexation rate in a homogeneous solution was not in accord with the order of the adsorption rate of the respective resins. Thus, this step is unlikely to play a rate-determining role in the adsorption process.

Since Mo^{VI} was adsorbed on an anion exchange resin at pH 1—2, Mo^{VI} must, principally, exist as anionic form(s) in this pH region. Under acidic conditions, HEA resin is expected to be positively charged due to protonation of the amine nitrogen. The local charge density must be highly concentrated inside the polymer beads where the functional groups are fixed closely, and hence the migration of oxoanion into polymer matrix may be facilitated. On the other hand, the functional group in the PMA resin holds a negative charge on the phosphonomethyl group.[17] Then, the migration of anionic species into the polymer would be retarded due to charge repulsion. Our view is consistent with the observation that PMA resin readily adsorb a wide range of metal cations.[7] Although bis(carboxymethyl)amino moiety itself has a strong affinity toward Mo^{VI},[18] an efficient adsorption of the ion was not achieved by CMA resin. Currently we have no clear explanation for the stepwise adsorption of Mo^{VI} by the CMA resin.

In addition to the high selectivity and rapid adsorption rate toward oxometal ions, HEA resin has little or no affinity for the common cations which are usually contained in the acid-leaching solution. Therefore HEA resin is the most promising agent for practical recovery of oxometal ions from industrial wastes.

The authors thank Professor K. Saito for his permission to use the stopped-flow apparatus at Tohoku University.

References

1) "Proceeding of the Climax Third International Conference on the Chemistry and Uses of Molybdenum," ed by H. F. Barry and P. C. H. Mitchell, Climax Molybdenum Company, Ann Arbor, Michigan, (1979), pp. 73—113.

2) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).

3) K. Saito and Y. Sasaki, *Adv. Inorg. Bioinorg. Mechanisms*, **1**, 179 (1982).

4) N. Rokkawa, *Nippon Kagaku Kaishi*, **1981**, 1227.

5) T. Yokoyama, A. Kikuchi, T. Kimura, and T. M. Suzuki, *Nippon Kagaku Kaishi*, **1983**, 363.

6) T. M. Suzuki and T. Yokoyama, *Polyhedron*, **2**, 127 (1983).

7) T. M. Suzuki and T. Yokoyama, *Polyhedron*, in the press.

8) M. Nishizawa, T. Yokoyama, T. Kimura, and T. M. Suzuki, *Chem. Lett.*, **1983**, 1413.

9) L. Knorr and H. W. Brownsdon, *Chem. Ber.*, **35**, 4470 (1902); D. B. Rorabacher and D. B. Moss, *Inorg. Chem.*, **9**, 1314 (1970).

10) K. Moedritzer and R. R. Irani, *J. Org. Chem.*, **31**, 1603 (1966).

11) S. I. Chan, R. J. Kula, and D. T. Sawyer, *J. Am. Chem. Soc.*, **86**, 377 (1964).

12) R. J. Kula, *Anal. Chem.*, **39**, 1171 (1967).

13) R. J. Kula, *Anal. Chem.*, **38**, 1581 (1966).

14) M. A. Freeman, F. A. Schultz, and C. N. Reilley, *Inorg. Chem.*, **21**, 567 (1982).

15) J. J. Park, M. D. Glick, and J. L. Hoard, *J. Am. Chem. Soc.*, **91**, 301 (1969).

16) S. Funahashi, Y. Kato, M. Nakayama, and M. Tanaka, *Inorg. Chem.*, **20**, 1752 (1981).

17) R. J. Motekaitis, I. Murase, and A. E. Martell, *J. Inorg. Nucl. Chem.*, **33**, 3353 (1971).

18) R. J. Kula, *Anal. Chem.*, **38**, 1934 (1966).