

Structural effect of di-Schiff base ligands having pendant arms on ion-pair extraction selectivity of divalent metals

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学 位 論 文 要 旨

Abstract

Structural effect of di-Schiff base ligands having pendant arms on ion-pair extraction selectivity of divalent transition metal cations was investigated by changing ligand structure systematically. Di-Schiff base ligand, *N,N'*-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE), and its analogues were used as complexation reagents for ion-pair extraction of divalent metal cations with picrate anion into nitrobenzene. From the results of numerical analysis concerning the extraction behavior, it was found that these ligands acted mainly as imine-N bidentate ones in these extraction systems except for several cases. The structural effects evaluated by the comparison of the extraction behavior were summarized as follows: (i) The introduction of substituents onto imine-C atoms led to the change in the extraction selectivity originated from steric distortion on the complexation, whereas that onto ethylene-C atoms only caused the enhancement of the extractability without the change of the selectivity. (ii) The closer imine-N distance led to the higher mutual selectivity between each metal cations. (iii) The effects of steric restriction by geometrical and resonance structure resulted in the difference of the shield effect in extracted species and the steric distortion on the complexation, and these contributed the extraction selectivity. (iv) The pendant arms affected only the extractability in the

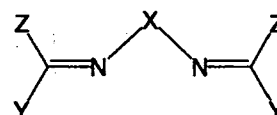
system, originated from the change of lipophilicity and hydrophobicity of them.

Introduction

In ion-pair extraction of metal cations, the coordination sites of metal cations can be saturated with only a neutral ligand used and the charge is neutralized with a counter anion. Therefore, use of a higher selective complexation reagent is one of most important factors to realize their mutual separation, and development of new selective complexation reagents and investigation on ligand structure with respect to the ion recognition ability and extractability have been carried out. In particular, to improve the mutual separation, systematic studies concerning the steric structure around donor atoms in ligands on the extraction selectivity and the extractability are very important.

In the present work, the use of *N,N'*-bis(2-pyridylmethylidene)-1,2-diiminoethane (BPIE) and its analogues shown in Fig. 1 as complexation reagents for ion-pair extraction of divalent metal cations into nitrobenzene with picrate anion was investigated. Since these di-Schiff bases can be synthesized easily from diamines and carbonyl compounds, many kinds of ligands having similar structure can be prepared easily and, therefore, the systematic studies concerning the effect of ligand the structure around donor atoms on extraction selectivity and extractability can be performed easily.

By comparison of extraction behavior of metal cations with these ligands, effects of ligand structure around imine-N atoms on extraction selectivity and extractability in ion-pair extraction system were examined. The four effects of ligand structure, i.e. the effects of substituents around imine-N donor atoms, imine-N distance, steric restriction and pendant arms, were evaluated.



	-X-	-Y	-Z
BPIE	-CH ₂ CH ₂ -	-H	-2-pyridyl
BPEE	-CH ₂ CH ₂ -	-CH ₃	-2-pyridyl
BPBE	-CH ₂ CH ₂ -	-C ₆ H ₅	-2-pyridyl
<i>trans</i> -BPIC	-(<i>trans</i> -1,2-C ₆ H ₁₀)-	-H	-2-pyridyl
<i>cis</i> -BPIC	-(<i>cis</i> -1,2-C ₆ H ₁₀)-	-H	-2-pyridyl
BPIB	-(<i>o</i> -C ₆ H ₄)-	-H	-2-pyridyl
BPMP	-CH ₂ C(CH ₃) ₂ CH ₂ -	-H	-2-pyridyl
BPIBu	-(CH ₂) ₄ -	-H	-2-pyridyl
BPIH	-(CH ₂) ₆ -	-H	-2-pyridyl
BQIE	-CH ₂ CH ₂ -	-H	-2-quinolyl
BQMP	-CH ₂ C(CH ₃) ₂ CH ₂ -	-H	-2-quinolyl

Fig. 1. Chemical structure of ligands used in this study

Experimental

The distribution of metal cations was studied as follows. In centrifuge tube, an aliquot of nitrobenzene (5 cm³) containing 1 × 10⁻³ mol dm⁻³ of a ligand and an equal volume of an aqueous phase containing 1 × 10⁻⁵ - 1 × 10⁻⁴ mol dm⁻³ of M²⁺ (M = Mn, Co, Ni, Cu, Zn, Cd or Pb), 1 × 10⁻³

mol dm⁻³ of sodium picrate (NaPic) as ion-pair reagent, 1×10^{-1} mol dm⁻³ of potassium nitrate and 1×10^{-2} mol dm⁻³ of buffer (chloroacetic acid, acetic acid or 2-(*N*-morpholino)ethanesulfonic acid) having no influence on the extraction, were shaken at $25 \pm 1^\circ\text{C}$ for 1 h. (All of the extraction was equilibrated within 30 min.) After the two phases were separated by centrifugation, the pH and the metal concentration in the aqueous phase were determined and the measured pH was used as equilibrated pH. The metal concentration in organic phase was determined after back-extraction into 1 mol dm^{-3} nitric acid.

Results and discussion

Distribution of metal cations

In all L-NaPic extraction systems, the extracted ratio (%E) for some divalent metals were plotted as a function of the aqueous phase pH equilibrated with organic phase in Fig. 2. Since protonation equilibria of each ligand as side reactions exist in the extraction equilibria, a metal cation showing higher extraction selectivity is extracted in more acidic condition.

As shown in Fig. 2, BPIE-, BPIBu- and BPIH-NaPic systems showed relatively low extractability, originated from its low hydrophobicity of the ligands. In addition, BQIE- and BQMP-NaPic systems showed remarkably low extractability. In BQMP-NaPic system, particularly, only Cu²⁺ was extracted quantitatively. From the results of numerical analysis concerning the extraction behavior, in addition, it was found that these ligands acted

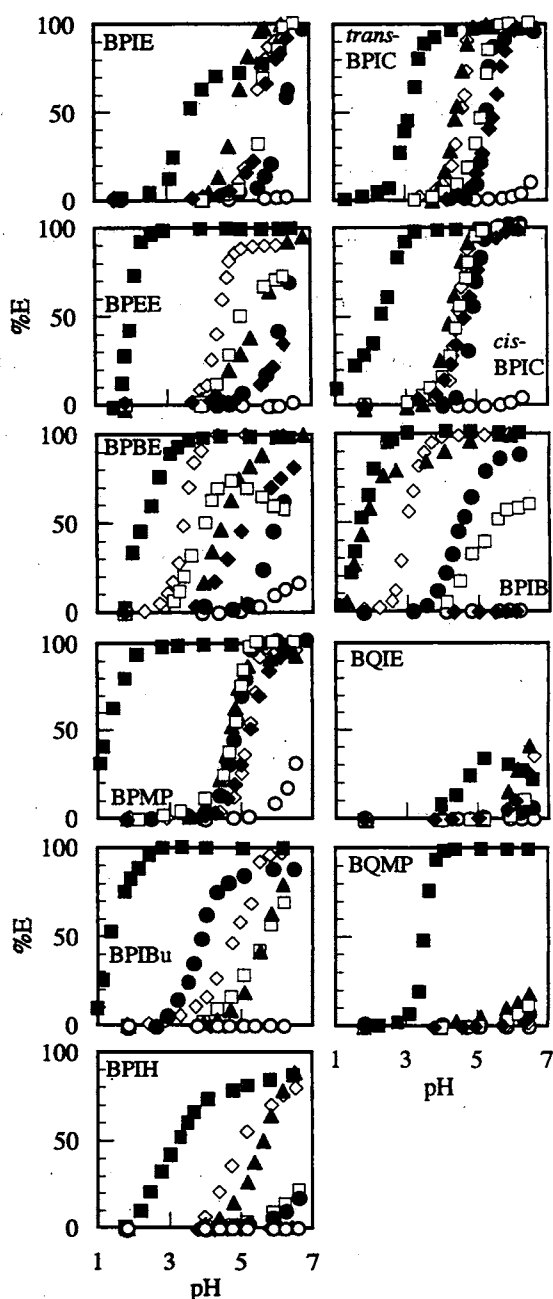


Fig. 2. Extraction behavior of divalent metal cations. (O) Mn²⁺; (◇) Co²⁺; (▲) Ni²⁺; (■) Cu²⁺; (●) Zn²⁺; (□) Cd²⁺; (◆) Pb²⁺.

mainly as imine-N bidentate ones in these extraction systems except for several cases.

Effect of ligand structure on extraction selectivity and extractability

Effect of substituents near imine-N donor atoms on BPIE. As shown in Fig. 2, the higher extractability in BPEE- and BPBE-NaPic systems showed than that in BPIE-NaPic system because the hydrophobicity of BPEE and BPBE are higher than that of BPIE. Furthermore, the extraction selectivity in BPEE- and BPBE-NaPic systems differed from that in BPIE-NaPic system. In other words, the introduction of substituents onto imine-C atom leads to the change of the extraction selectivity. The substituents on the imine-C atoms in BPEE and BPBE may cause steric distortion on the formation of cationic octahedral complex to some extent.

On the contrary, *trans*- and *cis*-BPIC can be regarded as analogues of BPIE substituted on the ethylene-C atoms. These systems showed very similar extraction selectivity to BPIE-NaPic system in spite of their rigid backbone structure due to cyclohexane ring. Namely, it was suggested that the substituents onto the backbone structure in BPIE-type ligand affected hardly in extraction selectivity and contributed only the enhancement of the extractability in ion-pair extraction system.

Effect of the distance between two imine-N donor atoms. Since the studied ligands act as imine-N–imine-N bidentate ones, the imine-N distance seems to be a factor of controlling the extraction selectivity. The order of the distance is BPIB < BPIE < BPMP < BPIBu < BPIH. As shown in Fig. 2, the mutual selectivity between each metals was higher in BPIB-NaPic system and lower in BPMP-NaPic system than BPIE-NaPic system. These results seemed to be originated from the enhanced steric distortion due to the close imine-N distance in BPIB and the flexibility of backbone structure for fitting to any metal cations on the complexation, respectively. In BPMP-NaPic system, however, the higher selectivity for Cu²⁺ was obtained. It is considered that the imine-N distance in BPMP is suitable for the complexation with Cu²⁺. In addition, the imine-N distance in BPIBu and BPIH is too long to form imine-N–M²⁺–imine-N chelate ring, and BPIBu- and BPIH-NaPic systems showed specific extraction behavior.

Effect of structural restriction around the donor atoms. Steric restriction by geometric structure in *trans*- and *cis*-BPIC and by resonance structure in BPIB seemed to affect coordination surroundings on the complexation and to contribute the extraction selectivity. The difference of steric restriction by

geometric structure between *trans*- and *cis*-BPIC resulted in the difference of the shield effect of metal cations. In other words, the cyclohexane ring in *cis*-BPIC seems to shield the metal in extracted species due to its steric configuration, whereas in *trans*-BPIC, the ring seems to orient outside the metal. This difference caused higher selectivity for bulky cations such as Cd^{2+} and Pb^{2+} in *cis*-BPIC-NaPic system than those in *trans*-BPIC-NaPic system. However, the relatively low mutual selectivity in *cis*-BPIC-NaPic system was shown compared with that in *trans*-BPIC-NaPic system since the smaller cations were extracted in similar pH to each other.

On the contrary, in BPIB-NaPic system, the extraction selectivity for the smaller cations such as Co^{2+} , Ni^{2+} and Cu^{2+} was reasonably increased than that in *trans*- and *cis*-BPIC-NaPic systems, whereas extractability of larger cations was decreased. These results were originated from the limitation of steric distortion on complexation due to resonance structure spread in whole of the molecule in BPIB.

Effect of pendant arms. As shown in Fig. 2, the extractability of all metal cations studied in BQIE- and BQMP-NaPic systems was appreciably low compared with those of BPIE and BPMP-NaPic systems, respectively. This result seemed to be led by relatively low lipophilicity of BQIE and BQMP to nitrobenzene compared with that of BPIE and BPMP, respectively, because polarity of 2-quinolyl group is lower than that of 2-pyridyl group. In addition, in BQMP-NaPic system, the selective extraction of Cu^{2+} was achieved. This result seemed to be led by the decrease of extractability originated from 2-quinolyl groups and by the high selectivity for Cu^{2+} shown in BPMP-NaPic systems due to suitable for the complexation of Cu^{2+} . From these results, the pendant arms affected mainly the lipophilicity and hydrophobicity of a ligand, and controlled consequently the extractability of a ligand.

The systematic information of ligand structure on extraction selectivity and extractability obtained in present work can be applied for the development of new chelate reagents having excellent selectivity and extractability.

学位論文審査結果の要旨

本学位論文に関し、平成15年1月16日に第1回学位審査委員会を開催し、口頭発表と面接審査を行った。さらに、2月3日に第2回審査会を開催し、口頭発表後に協議した結果、以下のように判定した。

本論文は、新規に合成した含ペンダントアーム型ジシッフ塩基配位子の *N, N*-ビス(2-ピリジルメチリデン)-1,2-ジイミノエタン (BPiE) および 10 種の構造類縁体を用いて、2 価遷移金属イオン (Mn, Co, Ni, Cu, Zn, Cd, Pb) の抽出挙動の解析を行ったもので、

- 1) イミン窒素近傍にアルキル基を導入した場合、イミン炭素上への導入は選択性の変化をもたらすが、エチレン炭素上への導入はほとんど寄与しない。
- 2) 2つのイミン窒素原子間距離は錯形成における構造的自由度を制御し、距離が短いほど選択性が增大する。
- 3) 幾何構造や共鳴構造による立体的制約の導入は、抽出化学種におけるシールド効果や錯形成における立体的ひずみに起因する選択性の変化をもたらす。
- 4) ペンダントアームは選択性には寄与せず、その親油性および疎水性に基づいて抽出性にのみ寄与する。の四点を明らかにした。

以上のように、本論文は、中性配位子を用いる金属イオンのイオン対抽出において、配位子の化学構造と 7 種の遷移金属イオンの抽出分離特性との相関性を系統的に評価した希少な研究成果として高く評価でき、博士論文に値するものと判断した。