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Separation of Some Metal Thiothenoyltrifluoroacetonates and Their Pyridine Base Adducts by Reversed Phase HPLC

Kin-ichi TSUNODA,* Ryu-ichi SEKIGUCHI, and Hideo AKAIWA
Department of Chemistry, Gunma University, Kiryu, Gunma 376

Separated were 1,1,1-trifluoro-4-mercapto-4-(2-thienyl)-3-butene-2-one (thiothenoyltrifluoroacetone, STTA) chelates of Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Co^{3+} by reversed phase high performance liquid chromatography (RP-HPLC). The elution of the STTA chelates of Cd^{2+}, Zn^{2+}, and Ni^{2+} was delayed by the addition of pyridine, α-picoline, or γ-picoline, indicating the formation of the adducts.

The synergistic effect in solvent extraction of a metal chelate has widely been used for improving the extractability of an analyte. In HPLC of metal chelates, the formation of the adducts of neutral ligands may also provide us various analytical merits, for example, a new technique for controlling the separation of metal chelates and/or a chemical modification method for the spectrometric detection. Although Igarashi et al. and Saitoh et al. have reported adduct formation in the separation of some metal-porphine derivatives by RP-HPLC,[1,2] no systematic study has been done on this subject so far. In this paper, we primarily report the separation of STTA chelates of some metal ions and the formation of their adducts of pyridine bases in RP-HPLC.

All the reagents were from Wako Pure Chemical and were used without further purification. Acetonitrile and methanol were HPLC grade and all the others were of guaranteed grade. Deionized water was used throughout. The HPLC consisted of a reciprocating-type pump (Model LC-3A; Shimadzu), a sample injection valve with a 5 x 10^{-3} cm^3 sample loop, a 150 x 4.6 mm i.d. standard octadecyl-bonded silica-gel column (Nucleosil $5C_{18}$; Chromato-packing Center), and a spectrophotometric detector (Model SPD-1; Shimadzu). The temperature of the column was maintained at 35 ℃ by a LC oven (Model CTO-2A; Shimadzu) throughout the measurement. Twenty cm^3 of an aqueous solution containing 4 x 10^{-4} M (mol dm^{-3} = M) metal ion, whose pH was adjusted to pH 6.5 by ammonium hydroxide and 0.1 M KH_2PO_4 - 0.05 M $Na_2B_4O_7$ buffer, was placed in a separatory funnel. An equal volume of chloroform solution containing 5 x 10^{-3} M STTA was added; the mixture was then shaken vigorously for 30 min. After the phases were allowed to separate, an aliquot of the organic phase (5 x 10^{-3} cm^3) was injected into HPLC column. The mobile phase for HPLC was a mixture of methanol, water

and acetonitrile [70:20:10 (v/v) respectively] containing 10^{-4} M STTA. The flow rate of the mobile phase was set at 0.8 cm^3 min^{-1}. The spectrophotometric detection was carried out at 370 nm for metal-STTA chelates and the chromatograms were monitored on a strip chart recorder.

Although Suzuki et al. performed the separation of some metal-STTA chelates by using a polystyrene gel column,[3] an ODS column has not been applied so far to the separation of those chelates. Thus, chromatographic conditions were investigated for their separation by the ODS column. Figure 1 shows the chromatogram of metal-STTA chelates where 10^{-4} M STTA was added to the mobile phase. As shown in the figure, STTA chelates of Zn^{2+}, Ni^{2+}, Cu^{2+} and Co^{3+} were separated on the chromatogram. Moreover, the peak of Cd^{2+}-STTA chelate was also recognized, although it was overlapped with the reagent peak due to STTA. In the absence of STTA in the mobile phase, only the peak of Co^{3+}-STTA chelate appeared at the same retention time as that in Fig. 1, and peaks of other chelates disappeared completely. Hence, further experiments were done on the basis of separation conditions in Fig. 1.

Pyridine, α-picoline and γ-picoline were added to the mobile phase at various concentrations respectively, and the effects of those bases on the retention of metal-STTA chelates were investigated. Figures 2, 3, and 4 show the results. As is seen from Fig. 2, the retention time of Zn^{2+}- and Cd^{2+}-STTA chelates increases with the increase of the pyridine concentration. It should be noticed that Cd^{2+}-STTA is separated from the reagent peak as shown in Fig. 5. As for Ni^{2+}-STTA, slight increase in the retention time is observed. On the other hand, the retention time of Cu^{2+}- and Co^{3+}-STTAs is not changed by the addition of pyridine. In the case of α-picoline, the retention time of Zn^{2+}- and Cd^{2+}-STTAs increases with the increase of α-picoline concentration as shown in Fig. 3. Moreover, Fig. 4 shows that the addition of γ-picoline increases the retention time of Zn^{2+}-, Cd^{2+}-, Ni^{2+}-STTA chelates remarkably, while that of Cu^{2+}-STTA chelate was not affected. The retention time of Co^{3+}-STTA chelate rather decreases with the addition of γ-picoline. These results should be summarized as follows; the retention time of Zn^{2+}- and Cd^{2+}-STTA chelates was affected most strongly by the

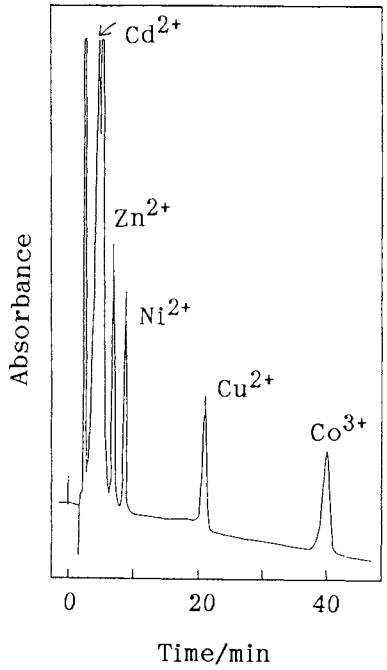

Fig. 1. HPLC separation of metal-STTA chelates.
Column: Nucleosil $5C_{18}$ (5 μm; 150 mm x 4.6 mm i.d.). Mobile Phase: methanol-water-acetonitrile (70:20:10 v/v), 10^{-4} M STTA.

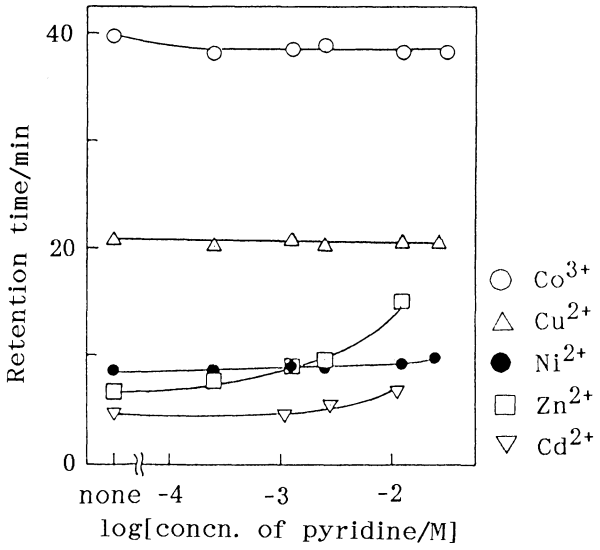

Fig. 2. Effect of pyridine on the retention time of metal-STTA chelates. The various concentrations of pyridine were added to the mobile phase of Fig. 1.

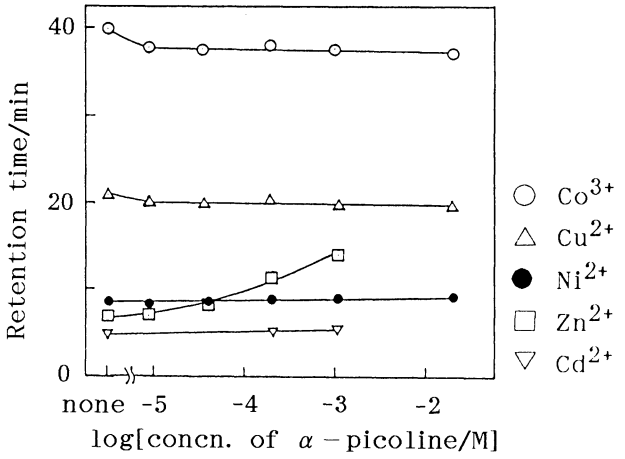

Fig. 3. Effect of α-picoline on the retention time of metal-STTA chelates.

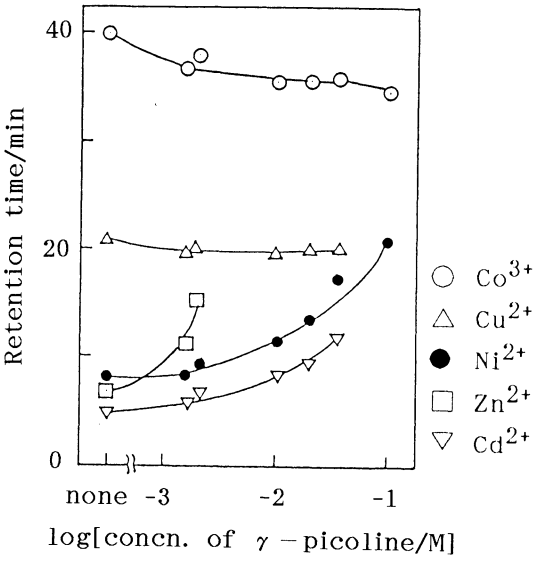

Fig. 4. Effect of γ-picoline on the retention time of metal-STTA chelates.

addition of pyridine bases. The elution of Ni^{2+}-STTA chelate was delayed largely only by the addition of γ-picoline. The retention time of Cu^{2+}- and Co^{3+}-STTA chelates was little affected by the addition of pyridine bases. On the other hand, the effect of the pyridine bases on the retention of metal-STTA chelates increases in the order of α-picoline — pyridine < γ-picoline.

The experimental results mentioned above could be explained mainly by the formation of adducts of pyridine bases. Once an adduct be formed, the retention time of the adduct would be longer than that of the host chelate because the displacement of water with a pyridine base in the complex would cause an increase of its affinity to the stationary phase in RP-HPLC. Thus, the increase in the retention time of Zn^{2+}-, Cd^{2+}-, Ni^{2+}-STTA chelates by the addition of pyridine bases is closely related to the adduct formation. Moreover, the ability of the adduct formation of pyridine bases increases in the order of α-picoline < pyridine < γ-picoline in solvent extraction.[4] Although α-picoline has "about the same pKa value (5.97) as

that of γ-picoline (6.02), α-picoline shows the weakest ability for the adduct formation because of steric hindrance caused by α-methyl group. Thus, the difference between the effects of α-picoline and γ-picoline on the retention behavior of metal-STTA chelates could be attributable solely to their ability of adduct formation. As is seen from Figs. 3 and 4, the increase of the retention time of metal-STTA chelates is much larger in γ-picoline than in α-picoline, strongly indicating the formation of adducts. Furthermore, solvent extraction study also provides us the following information on each metal-STTA chelate; Co^{3+}-STTA chelate does not form its adduct because three STTAs have already coordinated with Co^{3+} and no water molecule exists in the complex to be substituted. In the case of Cu^{2+}-STTA chelate, the adduct is unstable because of Jahn-Teller distortions. Although Ni^{2+}-STTA forms a stable adduct, Ni^{2+} complex is rather inert against the ligand exchange, in general. On the other hand, Zn^{2+} and Cd^{2+}-STTA chelates form adducts of pyridine bases.[5] Thus, the present data reasonably fit with such informations.

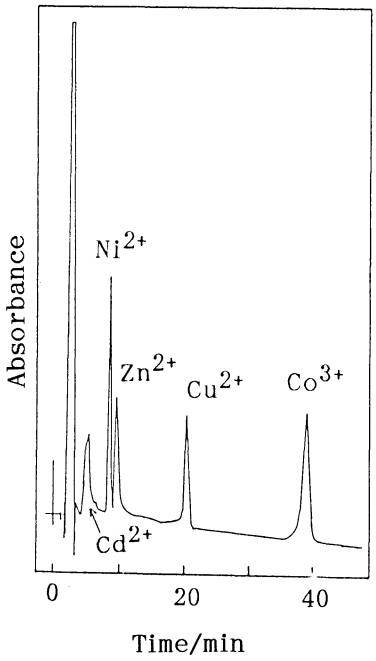

Fig. 5. HPLC separation of metal-STTA chelates with the addition of pyridine to the mobile phase.
Pyridine (2.5×10^{-3} M) was added to the mobile phase of Fig. 1.

In conclusion, the adduct formation should be mainly responsible for the change of the retention of metal-STTA chelates observed in this study. In particular, the adduct formation made it possible to separate Cd^{2+}-STTA from the reagent peak. Further study will be expected to use the adduct formation for controlling the separation of metal chelates in HPLC.

References

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