

trifluoride from glass apparatus was always accompanied by small amounts of silicon tetrafluoride, although the proportion of impurity seemed to decrease with time, presumably with progressive conditioning of the apparatus. No attempt was made to mix the trifluoride with the matrix gas prior to condensation; instead the trifluoride was vaporized from an ampule cooled to -72°C and cocondensed with the matrix gas on the CsI window.

Phosphorus trifluoride oxide was prepared by the reaction between fluorosulfonic acid and phosphorus pentoxide²⁴ and purified by trap-to-trap distillation in vacuo. The infrared spectrum of the vapor revealed some contamination of the sample by sulfur dioxide and silicon tetrafluoride, but these did not appear to interfere with the matrix isolation of the OPF_3 molecule.

Matrices were formed normally by continuous (rather than pulsed) deposition; the deposition rate was in the order of 3 mmol of matrix gas/h, and deposition took place over periods varying from 30 min to more than 3 h. The photolysis source was a Hanovia Uvitron 125-W high-pressure mercury arc used in conjunction with a 4-cm quartz cell containing water to act as a heat filter.

Infrared spectra were recorded by using a Perkin-Elmer Model 225 spectrophotometer. Calibration was accomplished by superimposing on the measured spectrum sharp vibration-rotation or rotation

lines due to ammonia, atmospheric water vapor, or carbon dioxide;⁴⁵ hence the frequencies of the bands due to the sample were calibrated by interpolation. Such measurements were reproducible within 0.2 cm^{-1} for sharp lines; the resolution was invariably better than 0.5 cm^{-1} . The relative intensities of infrared absorptions were measured either by taking the product of peak height and width at half-height or by tracing the peaks, cutting out, and weighing.

Normal-coordinate-analysis calculations were performed with the aid of an ICL 2980 digital computer by using programs kindly supplied by Professor H. Bürger and Dr. K. Burczyk of the Gesamthochschule Wuppertal.

Acknowledgment. G.P.G. acknowledges with thanks the award of research studentships by the Science Research Council and Linacre College, Oxford.

Registry No. OPF_3 , 13478-20-1; OAsF_3 , 15120-14-6; PF_3 , 7783-55-3; AsF_3 , 7784-35-2; O_3 , 10028-15-6.

(45) IUPAC Commission on Molecular Structure and Spectroscopy, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers", 2nd ed.; Cole, A. R. H., compiler; Pergamon Press: Oxford, 1977.

Contribution from the Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

Clay Column Chromatography: Partial Resolution of Metal(III) Tris(acetylacetonate) on a Δ -Nickel(II) Tris(1,10-phenanthroline)-Montmorillonite Column

AKIHIKO YAMAGISHI

Received October 20, 1981

$\text{M}^{\text{III}}(\text{acac})_3$ ($\text{M} = \text{Co}, \text{Cr}, \text{Ru}$; $\text{acac} = \text{acetylacetonato}$) was partially resolved on a sodium-montmorillonite column, in which the whole cation-exchange site had been replaced by $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ ($\text{phen} = 1,10\text{-phenanthroline}$) stoichiometrically. The efficiency of resolution was outstanding in comparison with that of previously known methods, although the present column was only 2.5 cm in length. The mechanisms for the chirality recognition were discussed on the basis of molecular stacking between $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ and $\text{M}^{\text{III}}(\text{acac})_3$ in the interlamellar space.

A clay adsorbs an inorganic metal ion at its cation-exchange sites. It is believed that the site is usually generated by replacing an Al^{3+} ion in the alumina sheet with a divalent ion like Mg^{2+} or Fe^{2+} .¹ Since there exists no structural asymmetry around such a cation-binding site, a clay cannot discriminate a chiral compound intrinsically. Very recently, however, the present author has revealed that a metal complex with bulky ligands occupies the interlamellar space of clay in a rigorously stereoregular manner.^{2,3} For example, when $[\text{Fe}(\text{phen})_3]^{2+}$ ($\text{phen} = 1,10\text{-phenanthroline}$) was adsorbed on a colloiddally dispersed sodium-montmorillonite, the complex tends to occupy a site as a racemic pair rather than as a single enantiomer.³ Consequently, a solution containing Δ and Λ isomers in unequal amounts improves its optical purity, because the excessive racemate is eliminated as a clay-metal chelate adduct.³ Another consequence of such racemic adsorption is that, when a clay has been modified by an enantiomer of one kind, it becomes stereoselective toward the adsorption of a complex of another kind.⁴ For example, the adsorption rate of $\Delta\text{-}[\text{Fe}(\text{phen})_3]^{2+}$ on a $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ -montmorillonite surface was 4 times faster than that of $\Delta\text{-}[\text{Fe}(\text{phen})_3]^{2+}$, because the

former was a more preferable partner with $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ than the latter.

As the extension of the above findings, we investigated the chromatographic resolution on a column of a clay-chiral metal chelate complex. As a result, it is shown here that metal tris(acetylacetonate) has been efficiently resolved on a $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ -montmorillonite column.

Experimental Section

Materials. $\text{Co}(\text{acac})_3$, $\text{Cr}(\text{acac})_3$, $\text{Ru}(\text{acac})_3$, and $\text{Rh}(\text{acac})_3$ were prepared according to the literature.⁵ The compounds were identified from the electronic spectra. Sodium-montmorillonite (denoted by $\text{Na}^+\text{-M}^-$, M^- being a cation-exchange site) was purchased from Kunimine Industrial Co. (Tokyo, Japan). The material contained 1 molar equiv of cation-exchange site/870 g.

Preparation of a Column. An aqueous solution of $\Delta\text{-}[\text{Ni}(\text{phen})_3]\text{Cl}_2$ (4×10^{-3} mol) was added at 2°C into a solution of a colloiddally dispersed $\text{Na}^+\text{-M}^-$ (7.0 g; 8.0×10^{-3} mol in terms of cation-exchange site) with stirring. The mixture was centrifuged to separate a clay-metal chelate adduct. The precipitate was washed with methanol several times and dried under vacuum for 2 days. The solid was ground into a fine powder (~ 9 g). A slurry of 1-2 g of solid ($\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}\text{-}2\text{M}^-$) in water was poured into glass tubing to form a 2-4-cm column of 1.5-cm o.d. As a pretreatment, water was eluted at the flow rate of $0.2\text{-}0.3\text{ mL s}^{-1}$. After elution with 10-15 mL of

(1) Theng, B. K. G. "The Chemistry of Clay-Organic Reactions"; Wiley: New York, 1974; Chapter 1.
 (2) Yamagishi, A.; Soma, M. *J. Chem. Soc., Chem. Commun.* **1981**, 539.
 (3) Yamagishi, A.; Soma, M. *J. Am. Chem. Soc.* **1981**, 103, 4640.
 (4) Yamagishi, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1128.

(5) Fay, R. C.; Girgis, A. Y.; Klabunde, U. *J. Am. Chem. Soc.* **1970**, 92, 7056 and references therein.

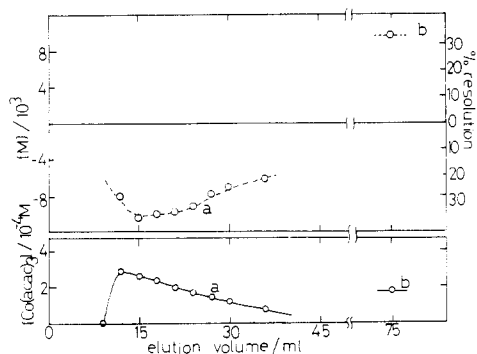


Figure 1. Elution curve of $\text{Co}(\text{acac})_3$ on a Δ - $[\text{Ni}(\text{phen})_3]^{2+}$ -montmorillonite column. Curve a is the elution curve for the water solvent. Plot b is the average value for the methanol effluents. The solid curve (lower) denotes the concentration of $\text{Co}(\text{acac})_3$ in each effluent and the dotted curve (upper) the molecular rotation at 546 nm.

water, the effluent was clear, containing no light-absorbing species at 340–700 nm.

Instruments. Visible spectra were measured with a EPS-3T spectrophotometer. Optical rotatory dispersion (ORD) curves were recorded on a JEOL ORD spectrophotometer, Model ORD/UV-5. Centrifuging of a solution was performed with a Kubota rotor, Type K-80 (maximum rotation: 4×10^3 rotations s^{-1}).

Results

$\text{Co}(\text{acac})_3$. A 1.2×10^{-5} mol quantity of $\text{Co}(\text{acac})_3$ in water was placed on a 2.5-cm column of 1.5-cm o.d. and eluted with water at a flow rate of 0.2–0.3 mL/min. An effluent was collected at every 3 mL and analyzed from the electronic and ORD spectra. About 60 mL of water was passed until the concentration of $\text{Co}(\text{acac})_3$ in an effluent became lower than 2×10^{-5} M. Thereafter the rest of the bound metal chelate was recovered by eluting with methanol. The methanol effluent was collected as a single solution (~ 30 mL).

Figure 1 shows the plots of $[\text{Co}(\text{acac})_3]$ and the molecular rotation at 530 nm, $[M]$, against the elution volume. Apparently the water effluent always showed negative $[M]$, while the methanol effluent showed positive $[M]$. According to the assignment by Fay et al.,⁵ the water and methanol effluents contained Δ and Δ isomers as excess enantiomers, respectively. The vertical axis was scaled also in terms of the percentage resolution defined by $[M]/[M]_0$ with $[M]_0 = -2.9 \times 10^4$ and $+2.9 \times 10^4$ for pure Δ - and Δ - $\text{Co}(\text{acac})_3$, respectively (taken from ref 5). The percentage resolution attained (36% for Δ isomer) was about 2 times better than the best reported value (19.6%).⁶

The water effluent was collected and passed through the same column again. The initial effluent at the second elution (~ 10 mL) contained 86% of Δ - $\text{Co}(\text{acac})_3$ out of the total concentration of 4.0×10^{-4} M (72% resolution). The results indicated that the present column was effective for repeated procedures.

As a comparison with the above column method, the resolution of $\text{Co}(\text{acac})_3$ was investigated by adding colloidal $\text{Na}^+ \text{M}^-$ to a solution of $\text{Co}(\text{acac})_3$ and Δ - $[\text{Ni}(\text{phen})_3]^{2+}$. After the mixed solution was centrifuged, the supernatant was analyzed from the electronic and ORD spectra. As shown in Table I, the following points were concluded: (i) $\text{Co}(\text{acac})_3$ was not adsorbed on a colloiddally dispersed sodium montmorillonite. (ii) When Δ - $[\text{Ni}(\text{phen})_3]^{2+}$ was present in small amounts (runs 1–4), the supernatant contained Δ - $\text{Co}(\text{acac})_3$ as excess enantiomer. (iii) On the contrary, when Δ - $[\text{Ni}(\text{phen})_3]^{2+}$ was present in a large amount (run 5), the supernatant contained Δ - $\text{Co}(\text{acac})_3$ as excess enantiomer. Δ -

Table I. Adsorption of $\text{Co}(\text{acac})_3$ on Sodium-Montmorillonite ($\text{Na}^+ \text{M}^-$) in the Presence of Δ - $[\text{Ni}(\text{phen})_3]^{2+}$ (ClO_4^-)

run	$[\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}]/10^{-4}$ M ^a	[adsorbed $\text{Co}(\text{acac})_3$]/ 10^{-4} M ^b	[excessive enantiomer in the supernatant]/ 10^{-5} M ^c
1	0.0	<0.2	none
2	1.4	0.5	0.4 (Δ)
3	2.9	0.9	0.8 (Δ)
4	4.0	2.1	1.5 (Δ)
5	5.8	2.5	8.0 (Δ)

^a The initial amount of Δ - $[\text{Ni}(\text{phen})_3]^{2+}$ that was present in a solution containing 1.4×10^{-3} M $\text{Co}(\text{acac})_3$ and 1.1×10^{-3} M $\text{Na}^+ \text{M}^-$. ^b The adsorbed amount of $\text{Co}(\text{acac})_3$ in a clay, which was obtained by centrifuging the solution. ^c The excessive enantiomer of $\text{Co}(\text{acac})_3$, which was present in a supernatant solution.

Table II. Chromatographic Data for Partial Resolution of $\text{Cr}(\text{acac})_3$ on Δ - $[\text{Ni}(\text{phen})_3]^{2+}$ -Montmorillonite

fraction no.	eluting solvent	$[\text{Cr}(\text{acac})_3]/10^{-4}$ M	molecular rotation at 578 nm ^a
2	water-methanol	7.9	+3000
3	water-methanol	4.0	+1300
5	methanol	3.9	-1500
6	methanol	1.0	-1700
2' ^b	water-methanol	2.5	+6900

^a (Specific rotation \times mol wt)/100. ^b The second fraction eluted after fraction 2 was placed on the same column again.

$[\text{Ni}(\text{phen})_3]^{2+}$ is adsorbed by $\text{Na}^+ \text{M}^-$, occupying two cation-exchange sites per one chelate. Thus the above results imply that $\text{Co}(\text{acac})_3$ is adsorbed *racemically* with Δ - $[\text{Ni}(\text{phen})_3]^{2+}$, when there remains a free cation-exchange site left on a clay. However, $\text{Co}(\text{acac})_3$ is adsorbed *enantiometrically* with Δ - $[\text{Ni}(\text{phen})_3]^{2+}$, when the whole cation-exchange sites are occupied by Δ - $[\text{Ni}(\text{phen})_3]^{2+}$. Apparently, the results are consistent with the fact that the enantiometric adsorption occurred on a column of Δ - $[\text{Ni}(\text{phen})_3]^{2+} \text{M}^-$.

$\text{Cr}(\text{acac})_3$. A 2.5×10^{-5} mol quantity of $\text{Cr}(\text{acac})_3$ in water was placed on a 2.0-cm column (1.5-cm o.d.) at 2 °C. $\text{Cr}(\text{acac})_3$ was so firmly bound with the column that it was not eluted with water. As 9:1 (v/v) water-methanol was passed, part of the $\text{Cr}(\text{acac})_3$ was recovered; thus every 10 mL of effluent was collected and analyzed from the electronic and optical rotatory dispersion spectra. When the concentration of $\text{Cr}(\text{acac})_3$ in an effluent became lower than 1×10^{-4} M, the solvent was switched to methanol to recover the rest of the bound $\text{Cr}(\text{acac})_3$. The analytical results on each fraction are given in Table II. As was already shown for $\text{Co}(\text{acac})_3$, the resolution was attained by the enantiomeric affinity of $\text{Cr}(\text{acac})_3$ toward Δ - $[\text{Ni}(\text{phen})_3]^{2+}$ -montmorillonite column. The molecular rotation for the initial effluent (+3000) was by far better than the reported value by Fay et al. (+630) for the initial effluent on a D(+)-lactose column (230-cm length \times 3.9-cm o.d.).⁵

$\text{Ru}(\text{acac})_3$. A 1.6×10^{-5} mol quantity of $\text{Ru}(\text{acac})_3$ in water was placed on a 2.5-cm column of 1.0-cm o.d. No ruthenium chelate was recovered by eluting with pure water. When 4:1 (v/v) water-methanol was used as solvent, about 30% of the $\text{Ru}(\text{acac})_3$ was recovered in the first 20 mL of elution. The first effluent was concentrated to a 3-mL solution (solution A). The next 20 mL fraction recovered 10% of the chelate. At the end of this step, the effluent contained less than 10^{-5} M $\text{Ru}(\text{acac})_3$. Thereafter, the rest of the chelate was recovered by eluting with 10 mL of methanol. The last effluent was evaporated to dryness and dissolved in 3 mL of water (solution B).

(6) Yamamoto, M.; Iwamoto, E.; Kozasa, A.; Takemoto, K.; Yamamoto, Y.; Tatehata, A. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 71.

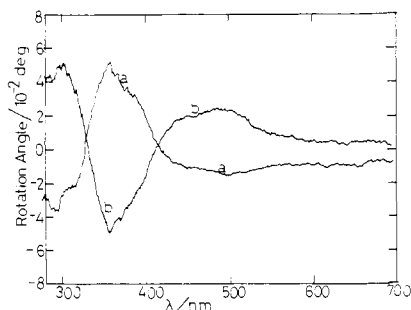


Figure 2. Optical rotatory dispersion curves for the initial and final effluents (denoted by a and b, respectively) for $\text{Ru}(\text{acac})_3$ on a $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ -montmorillonite column. The concentrations were 1.6×10^{-4} M and 3.4×10^{-4} M for curves a and b, respectively.

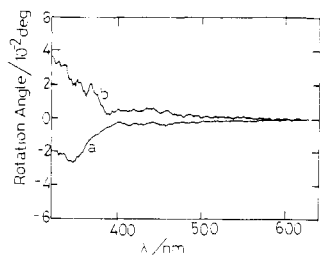


Figure 3. Optical rotatory dispersion curves for the initial and final effluents (denoted by a and b, respectively) for $\text{Rh}(\text{acac})_3$ on a $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ -montmorillonite column.

From the optical rotatory dispersion curves at 400–700 nm (Figure 2), solutions A and B contained excessive Λ - and Δ - $\text{Ru}(\text{acac})_3$ chelates with molecular rotations of -9200 and $+6700$ at 490 nm, respectively.⁷ These values were comparable with those obtained in the first-eluted fraction by Fay and his collaborators (-8000 for $\Lambda\text{-Ru}(\text{acac})_3$).⁵

$\text{Rh}(\text{acac})_3$. A 3.0×10^{-6} mol quantity of $\text{Rh}(\text{acac})_3$ in 4:1 (v/v) water-methanol was placed on a 3.0-cm column of 1.5-cm o.d. When 4:1 (v/v) water-methanol was used as an eluting solvent, all of the $\text{Rh}(\text{acac})_3$ was recovered within the first 20 mL of solvent. In Figure 3 curves a and b show the initial and final 4 mL of effluents, respectively. Although the Cotton effect, which should appear around 420 nm,⁵ was not evident, the negative and positive values below 400 nm for curves a and b may indicate that $\text{Rh}(\text{acac})_3$ was resolved partially on the present column.

Discussion

The resolution of metal tris(β -diketonates) has been a serious experimental difficulty. Since these are molecular substances and contain no functional group, they do not allow stoichiometric combination with optically active resolving agents. As an alternative method, liquid column chromatography has been applied successfully. However, the method has achieved relatively low efficiency so far; for example, in the case of $\text{Cr}(\text{acac})_3$, $[M]_{578}$ for the first-eluted fraction was only one-sixth of the one after recrystallization.⁵ Contrary to the above situations, the present column ($\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}\text{-}2\text{M}^-$) has demonstrated its outstanding features in resolving metal(III) tris(acetylacetonate). For all of the three cases $\text{Co}(\text{acac})_3$, $\text{Cr}(\text{acac})_3$, and $\text{Ru}(\text{acac})_3$, the water-rich solvents always contained the Λ isomer as the excessive enantiomer, while the methanol solvent contained the Δ isomer as such. Such a distinct separation has never been achieved on other known columns. As a consequence, the percentage resolutions attained by the present column were, by far, better than the previous results. The results were even more surprising when

one compared the length of the present column (~ 2.5 cm) with ordinary ones (50–500 cm).

The resolution was achieved by the enantiometric affinity of $M^{III}(\text{acac})_3$ toward preadsorbed $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$. The situations were in marked contrast with the previous finding that the racemic adsorption occurs for metal tris- or bis-(1,10-phenanthroline) complexes like $[\text{Fe}(\text{phen})_3]^{2+}$, $[\text{Fe}(\text{phen})_2(\text{CN})_2]^+$, and $\text{Fe}(\text{phen})_2(\text{CN})_2$ with $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}\text{-}2\text{M}^-$.⁸ The key to the reasons for the reversed chirality recognition in the present cases might lie in the data of Table I. As has been mentioned elsewhere, the racemic adsorption of an iron 1,10-phenanthroline complex is caused by the highest degree of stacking on a clay surface, when the iron 1,10-phenanthroline chelate and $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ are adsorbed side by side on a clay with their C_3 axes perpendicular.⁹ The situations are simply stated by the principle that a left-wing propeller (I) can be stacked with a right-wing propeller (II) more closely than a right-wing propeller (I), when propeller I is placed by the side of propeller II.

Since $\text{Co}(\text{acac})_3$ does not interact with sodium montmorillonite in the absence of $[\text{Ni}(\text{phen})_3]^{2+}$, its adsorption on the present column should be realized by the affinity for $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$. Most probably, the hydrophobic interactions between acetylacetonate and 1,10-phenanthroline ligands are responsible for such an interaction. Accordingly on the present column, $\text{Co}(\text{acac})_3$ may not be in contact with a clay surface directly, but it is located over the $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ layer. Under these situations, $\Delta\text{-Co}(\text{acac})_3$ is more closely stacked with $\Delta\text{-}[\text{Ni}(\text{phen})_3]^{2+}$ than $\Lambda\text{-Co}(\text{acac})_3$, because of the principle that a right-wing propeller (I) can approach a right-wing propeller (II) more closely than a left-wing propeller (I) does, when propeller I is placed over the head of propeller II.

The performances of the present column are compared with the Sephadex column used by Yamamoto et al.⁶ Their column was a 55-cm SP-Sephadex, of 2-cm o.d., whose cation-exchange sites were also completely replaced with $\Delta\text{-Ni}(\text{phen})_3^{2+}$. The column resolved $\text{Co}(\text{acac})_3$ partially at 5–15 °C. Since $\text{Co}(\text{acac})_3$ exhibited the enantiometric affinity toward the column, the mechanism of chirality recognition might be similar to that described above. The maximum percentages resolution, however, attained by their column was 18.4% for $\Delta\text{-Co}(\text{acac})_3$ at 15 °C, which was about half than of the present clay column. Since the cation-exchange capacity of SP-Sephadex (2.3 mequiv/g) is larger than that of $\text{Na}^+\text{-M}^-$ (1.2 mequiv/g), the reason for the observed difference in resolving efficiency might not be sought in the density of adsorption site but in the structure of the site. In the Sephadex column, $\Delta\text{-Ni}(\text{phen})_3^{2+}$ ions are distributed over the three-dimensional network of bridged dextran. Each $\Delta\text{-Ni}(\text{phen})_3^{2+}$ ion is oriented in a random fashion. Under these situations, the chirality recognition may be performed by the interaction of $\text{Co}(\text{acac})_3$ with $\Delta\text{-Ni}(\text{phen})_3^{2+}$ at an individual site. On the contrary, $\Delta\text{-Ni}(\text{phen})_3^{2+}$ in the clay column is located over a silicate sheet with its C_3 axis perpendicular.⁸ Since each $\Delta\text{-Ni}(\text{phen})_3^{2+}$ ion occupies three tetrahedral rings of SiO_4^{4-} , the Ni(II) chelates make a regular two-dimensional lattice over a surface. As a result, the phenanthroline ligands constitute a homogeneous hydrophobic region of about 5 Å thickness over a silicate surface. Such a region may enhance the attractive force by the column toward $\text{Co}(\text{acac})_3$. Since the interaction between a $-\text{CH}_3$ group in acac^- and a phenanthroline molecule is itself very weak (probably less than 1 kcal mol⁻¹), such an enhancement of attractive force may help a column recognize the chirality of an approaching molecule. In conclusion, the cooperative effect of regularly oriented $\Delta\text{-Ni}(\text{phen})_3^{2+}$ ions on

(7) Mason, S. F.; Peacock, R. D.; Prospero, T. J. *Chem. Soc., Dalton Trans.* 1977, 702.

(8) Yamagishi, A. *Inorg. Chem.* 1982, 21, 1778.

(9) Yamagishi, A. *J. Phys. Chem.*, in press.

a silicate sheet is a main factor in realizing the high resolution of the present clay column in comparison with the previous ion-exchange adsorbents.

The above conclusion is supported by the fact that a montmorillonite column whose cation-exchange sites were replaced with Δ -Ni(phen) $_3^{2+}$ to 50% (or Δ -Ni(phen) $_3^{2+}$ -4M $^-$) exhibited much less resolution efficiency (\sim 5%) for Co(acac) $_3$. On such a column, the adsorbed Δ -Ni(phen) $_3^{2+}$ ions are so far apart from each other that the phenanthroline ligands can no longer constitute a hydrophobic region as in the Δ -Ni(phen) $_3^{2+}$ -2M $^-$ column.

Probably the manner of chirality recognition by Δ -[Ni(phen) $_3$] $^{2+}$ is not unique; thus the method will be varied im-

mensely by choosing the kind of preadsorbed chiral complex. For example, if a trivalent complex like [Co(phen) $_3$] $^{3+}$ is adsorbed instead of [Ni(phen) $_3$] $^{2+}$, the resultant column may have a wider interlamellar space, allowing for the penetration of a more bulky complex. This is expected because [Co(phen) $_3$] $^{3+}$ occupies three cation-exchange sites per chelate.

Acknowledgment. Thanks are due to Dr. R. Ohnishi of Hokkaido University for permission to use the JEOL ORD spectrophotometer.

Registry No. Co(acac) $_3$, 21679-46-9; Cr(acac) $_3$, 21679-31-2; Ru(acac) $_3$, 14284-93-6; Rh(acac) $_3$, 14284-92-5; Δ -[Ni(phen) $_3$] Cl_2 , 63985-35-3.

Contribution from Chemistry Department A,
The Technical University of Denmark, DK-2800 Lyngby, Denmark

Negative Oxidation States of Chalcogens in Molten Salts. 2. Raman Spectroscopic, Spectrophotometric, and Electron Spin Resonance Studies on Chloroaluminate Solutions Containing an S_3^- Entity

R. FEHRMANN, S. VON WINBUSH,¹ G. N. PAPATHEODOROU,² R. W. BERG, and N. J. BJERRUM*

Received September 9, 1981

The blue solutions produced by reaction between aluminum and sulfur in basic CsCl-AlCl $_3$ melts have been examined by means of Raman spectroscopic, spectrophotometric, and ESR measurements and are mainly attributed to the presence of S_3^- species. The formal absorptivity of the blue solutions, with an absorption maximum near 16 700 cm $^{-1}$, was measured in the temperature range 390-470 °C and at different sulfur to aluminum formality ratios. The Raman intensity of the $\nu_1 = 529$ cm $^{-1}$ stretching mode was also measured at different sulfur to aluminum formality ratios and in conjunction with the absorption measurements was used to determine the possible number of species formed. The findings have been best interpreted by an equilibrium between the blue S_3^- entity, S(-II) species (present in polymeric chain species of the [AlSCl $_2$] $_n^{\pi-}$ type), and molecular sulfur. No direct evidence for the formation of other sulfur species has been found, but there are indirect indications of a possible existence of other sulfur species. ESR measurements show the presence of the paramagnetic S_3^- radical with $g = 2.023$ and a hyperfine splitting into six lines arising from a direct coupling of the S_3^- with the aluminum atom ($I = 5/2$). The data are discussed in terms of the possible formation of [S $_3$ AlCl $_3$] $^-$ and [S $_3$ AlCl $_4$] $^{2-}$ species in these melts. Finally a single-line ESR spectrum of blue sulfur species in LiCl-CsCl eutectic was attributed to the presence of S_3^- with $g = 2.028$. This "free" radical had its stretching mode at 527 cm $^{-1}$.

Introduction

It is now well recognized that sulfur dissolves in a number of condensed media³⁻⁶ including molten-salt systems such as eutectic LiCl-KCl⁷ and basic CsCl-AlCl $_3$,⁸ forming the blue S_3^- radical. It was, however, found that no blue color could be formed in the most basic NaCl-AlCl $_3$ and KCl-AlCl $_3$ melts in the temperature range up to 400 °C. It was also shown mainly by Raman spectroscopy⁹ that, in melts of CsCl-AlCl $_3$ (e.g., 55-45 mol %), sulfur and excess aluminum (i.e., formality ratio Al:S > 2:3) gave no blue species but only polymeric aluminum chlorosulfide chain species of the type [Al $_n$ S $_{n-1}$ Cl $_{2n+2}$] $^{\pi-}$ ($n \geq 3$).

The present investigation was undertaken to study the formation of different sulfur species as a function of the relative

amounts of reducing and oxidizing materials (Al and S, respectively) with CsCl-AlCl $_3$ as solvent (55.7-44.3 mol %) at temperatures near 400 °C. A few experiments using molten LiCl-CsCl (59.3-40.7 mol %) were also performed in which S_3^- was produced by reaction between sulfur and Li $_2$ S. A main purpose of this study was to investigate the conditions for the formation of S_3^- from sulfur and aluminum and to determine whether blue species other than S_3^- could be formed.

Experimental Section

General Information. One major problem encountered in these types of experiments was determining the total concentration of sulfur in the melt. In the work with the CsCl-AlCl $_3$ solvent semiaccurate sulfur concentrations have been determined by an essentially simple but experimentally difficult technique. This involved application of sealed cells which were almost completely filled with the melt, keeping the content of the vapor phase to minimum. In the experiments performed with the LiCl-CsCl melt a larger gas volume above the melt was allowed.

Chemicals. The anhydrous AlCl $_3$ used was obtained as described previously.¹⁰ CsCl (Suprapur from Merck) and LiCl (Baker Analyzed reagent) were dehydrated by using our normal procedure for alkali chlorides.⁹ Lithium sulfide, Li $_2$ S (CERAC/PURE, 99.9%), was obtained in a closed ampule and used without further purification. The sulfur was from Fluka (99.999%). Aluminum metal was used

- (1) Visiting Professor from State University of New York at Old Westbury.
- (2) Visiting Professor from Argonne National Laboratory.
- (3) Clark, R. J. H.; Cobbold, D. G. *Inorg. Chem.* **1978**, *17*, 3169 and references therein.
- (4) Chivers, T.; Gilmour, E.; Kydd, R. A. *J. Mater. Sci.* **1978**, *13*, 1585.
- (5) Clark, R. J. H.; Franks, M. L. *Chem. Phys. Lett.* **1975**, *34*, 69.
- (6) Holzer, W.; Racine, S.; Cipriani, J. *Adv. Raman Spectrosc.* **1973**, *1*, 393.
- (7) Gruen, D. M.; McBeth, R. L.; Zielen, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 6691.
- (8) Berg, R. W.; Bjerrum, N. J.; Papatheodorou, G. N.; von Winbush, S. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 201.
- (9) Berg, R. W.; von Winbush, S.; Bjerrum, N. J. *Inorg. Chem.* **1980**, *19*, 2688.

- (10) Fehrmann, R.; Bjerrum, N. J.; Poulsen, F. W. *Inorg. Chem.* **1978**, *17*, 1195.