is very similar to the mercury case. Progressing from Cd to Zn, the group 2B metal slips from capping a face to a situation nearer edge capping. In **34** four carbonyls closely approach the zinc atom in a square-planr array with a nearly $D_{2d}$ array about iron. Variation in the electronegativity of M′ (Zn → Hg) is enough to shift the bonding description from nearly ionic to covalent, respectively. This has the effect of changing electronic occupancy but also probably changes the electric field gradient and the asymmetry parameter substantially. The $V_{zz}$, term which is the principal component of the electric field gradient, is most likely changed in sign or direction leading to **37** occurring in quadrant II of Figure 3. The M′ metal in these cases must be a poor enough $\sigma$ donor to effect this change in $e^2qQ$ and $\eta$. With $Zn(NH_3)$ $\sigma$ donation is strong and it is found in quadrant I.

In $[Cd(Fe(CO)_4)_2]^{2-}$ (**37**) we observe a resolved "triplet" Mössbauer spectrum with the two peaks at low $\delta$ being broad and the higher $\delta$ peak being sharp. This spectrum may be fit by the following solutions: as three singlets ($\delta = -0.064$, 0.105, and 0.186 mm $s^{-1}$), as two doublets ($\delta = 0.049$ and 0.145 mm $s^{-1}$; $\Delta = 1.112$ and 0.808 mm $s^{-1}$, respectively), and as a doublet around a singlet ($\delta = 0.105$ ($\Delta$ small) and 0.090 ($\Delta = 1.921$) mm $s^{-1}$). The empirical formula argues against a three-singlet description as well as the asymmetry in the middle peak and the unusual positions of two of the singlets above the $d^8$–$d^{10}$ Fe range. The location and symmetry of the peaks also argue against a doublet around a singlet description. A two-doublet solution for the Mössbauer spectrum of **37** is suggestive of magnetically inequivalent iron atoms. In **37** the one iron atom found in quadrant I may have an electronic description near $d^{10}$-Fe while there is one iron atom obeying the C-P (Figure 1) relationship, which works best for a $d^8$-Fe electronic description. The structure of **37** is nearly identical with its analogue.[6,7] In the electronic crossover $d^8$-Fe → $d^{10}$-Fe one iron atom changes in **37** at a time. In **34** both iron atoms have changed toward $d^{10}$-Fe but are found in quadrant II because of a change in the nuclear description.

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**Registry No.** **1**, 13463-40-6; **2**, 26024-88-4; **3**, 35679-07-3; **4**, 51743-96-5; **5**, 21494-36-0; **6**, 19372-47-5; **7**, 82978-91-4; **8**, 40697-06-1; **9**, 40697-07-2; **10**, 35644-25-8; **11**, 35917-16-9; **12**, 26825-11-6; **13**, 24952-80-5; **14**, 24952-81-6; **15**, 24901-83-5; **16**, 40892-21-5; **17**, 54645-11-3; **18**, 54645-12-4; **19**, 33403-80-8; **20**, 76370-55-3; **21**, 82978-90-3; **22**, 76370-56-4; **24**, 12289-03-1; **25**, 12287-55-7; **26**, 31870-59-4; **27**, 12287-98-8; **28**, 31781-64-3; **29**, 38388-69-5; **30**, 38386-54-8; **31**, 43140-17-6; **32**, 76705-09-4; **34**, 82110-39-2; **35**, 80049-76-9; **36**, 34720-06-4; **37**, 82995-01-5; **38**, 83060-66-6; **39**, 82978-93-6; **40**, 82978-94-7; **41**, 82978-95-8; **42**, 15321-51-4; **43**, 25879-01-0; **44**, 26062-33-9; **45**, 14878-30-9; **46**, 25463-33-6.

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# Clay Column Chromatography for Optical Resolution: Initial Resolutions of Bis(acetylacetonato)(glycinato)cobalt(III) and (Acetylacetonato)bis(glycinato)cobalt(III) on a Δ-Tris(1,10-phenanthroline)nickel(II)-Montmorillonite Column

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Liquid column chromatography was performed on a Δ-tris(1,10-phenanthroline)nickel(II)–montmorillonite column of 1-cm length by 3-cm o.d. at 2 °C for the purpose of resolving racemic neutral cobalt(III) chelates. The investigated chelates were of the type $Co(acac)_n(gly)_{3-n}$ ($n$ = 3, 2, 1, and 0), where acac = acetylacetonato and gly = glycinato. With water as an eluting solvent, $Co(acac)_3$, $Co(acac)_2(gly)$, and $Co(acac)(gly)_2$ were partially resolved, resulting in molecular rotations of $-2.6 \times 10^4$ (at 500 nm), $+4.6 \times 10^3$ (at 450 nm), and $+1.3 \times 10^3$ (at 450 nm) for the initially collected fractions, respectively. The column showed no affinity toward *mer*-$Co(gly)_3$ and did not resolve it to any measurable extent.

## Introduction

A clay adsorbs a metal ion or a metal complex cation at its cation-exchange sites. Recently we investigated the adsorption behavior of tris(1,10-phenanthroline)iron(II) ($Fe(phen)_3^{2+}$) on a colloidal surface of montmorillonite.[1] Each configurational isomer of $Fe(phen)_3^{2+}$ was found to be adsorbed with identical strength. Thus the cation-exchange sites of a clay did not recognize the absolute configuration of a trischelated complex. Notably, however, the adsorption amount of $Fe(phen)_3^{2+}$ was doubled, when the chelate was added as a racemic mixture. The results imply that the sites fully occupied by the one enantiomer (e.g., Λ-$Fe(phen)_3^{2+}$) are still capable of accepting the binding of the other enantiomer (or Δ-$Fe(phen)_3^{2+}$).

The above finding prompted us to investigate the possibility that the clay modified by an optically active metal complex would be able to discriminate the chirality of an approaching molecule. This expectation was supported by the kinetic experiments, in which an adsorption rate of Λ-$Fe(phen)_3^{2+}$ on Δ-$Ni(phen)_3^{2+}$–montmorillonite was compared with that on its counterpart.[2] It was found that Λ-$Fe(phen)_3^{2+}$ was adsorbed on Δ-$Ni(phen)_3^{2+}$–montmorillonite about 4 times faster than on Λ-$Ni(phen)_3^{2+}$–montmorillonite. The difference pointedly illustrates the preference of Λ-$Fe(phen)_3^{2+}$ for Δ-$Ni(phen)_3^{2+}$ to Λ-$Ni(phen)_3^{2+}$ as a stacking partner on the clay surface.

On the basis of the above principles, the liquid column chromatography was performed on a Δ-$Ni(phen)_3^{2+}$–montmorillonite column in order to resolve racemic metal chelates.[3,4]

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As we reported, the column demonstrated the remarkable ability to resolve neutral tris(acetylacetonato)cobalt(III) ($Co(acac)_3$)[3] and $Ru(acac)_3$.[4] The present work describes the further application of the above column for resolving other neutral chelates. The chelates investigated were bis(acetylacetonato)(glycinato)cobalt(III) ($Co(acac)_2(gly)$), (acetylacetonato)bis(glycinato)cobalt(III) ($Co(acac)(gly)_2$), and *mer*-tris(glycinato)cobalt(III) (*mer*-$Co(gly)_3$). As a comparison, $Co(acac)_3$ was also resolved on the same column under identical conditions. The first two glycinato complexes were chosen because there has been no method described for resolving them. In addition, the resolved enantiomer of such a chelate may be used as an intermediate complex, when one aims at the syntheses of asymmetric $\alpha$-amino acids from glycine.[5]

## Experimental Section

Bis(acetylacetonato)(glycinato)cobalt(III) ($Co(acac)_2(gly)$) and (acetylacetonato)bis(glycinato)cobalt(III) ($Co(acac)(gly)_2$) were prepared according to the methods by Laurie.[6] They were identified by the elemental analyses and the electronic spectra in water. Anal. Calcd for $Co(acac)_2(gly)$ ($\lambda_{max}$ 560 nm): C, 43.50; H, 5.44; N, 4.23. Found: C, 40.5; H, 5.6; N, 5.9. Calcd for $Co(acac)(gly)_2$ ($\lambda_{max}$ 535 nm): C, 35.30; H, 4.90; N, 9.15. Found: C, 34.5; H, 5.5; N, 8.9. Since $Co(acac)_2(gly)$ was reported to decompose in the solid state,[6] the compound was kept in water below 2 °C. The electronic spectrum of the stock solution was not altered for at least 2 weeks. Tris(acetylacetonato)cobalt(III) ($Co(acac)_3$) and *mer*-tris(glycinato)cobalt(III) (*mer*-$Co(gly)_3$) were synthesized according to the literature.[7]

The preparation of $\Delta$-$Ni(phen)_3^{2+}$–montmorillonite was described previously.[3] The slurry of the material (~5 g) in water was poured into a 3G3 glass filter to form a column of 1-cm length by 3-cm o.d. with an interstitial space ($I$) of 5 mL, which was estimated from the elution volume of methanol. A single column was employed throughout the present investigations. The solvent (water, methanol, or their mixture) flowed at the rate of 0.06 mL $min^{-1}$ at 2 °C. This temperature was chosen to prevent $Ni(phen)_3^{2+}$ in the column from racemizing.

The concentration of an eluted Co(III) chelate was determined from the electronic spectrum with a Hitachi EPS-3T spectrophotometer. The optical rotatory dispersion (ORD) curve was recorded on a JEOL ORD spectrophotometer, Model ORD/UV-5. X-ray diffraction patterns were measured by a Toshiba XC-40H X-ray diffraction apparatus.

## Results

***mer*-Co(gly)₃.** A $2 \times 10^{-5}$ mol amount of *mer*-$Co(gly)_3$ in 15 mL of water was placed on the column. Figure 1a shows the elution curve of the chelate, when it was eluted by pure water. Initial *mer*-$Co(gly)_3$ appeared at the elution volume ($V$) of 4 mL, which was close to the value of the interstitial space ($I$) of the column ($I$ = 5 mL). The concentration of a recovered chelate had a maximum peak at $V$ = 8 mL. The whole chelate was recovered at $V$ = 24 mL, which was similar in volume to the sum of $I$ and the volume placed initially (5 + 15 = 20 mL). It was concluded from the analyses described above that there was little interaction between the column and *mer*-$Co(gly)_3$. No optical rotation was observed at 250–700 nm, when the ORD curve of each effluent was measured. Thus the present column did not resolve *mer*-$Co(gly)_3$ to any measurable extent.

**Co(acac)(gly)₂.** A $1.2 \times 10^{-4}$ mol quantity of $Co(acac)(gly)_2$ in 15 mL of water was placed on the column. The upper curve in Figure 1b shows the elution curve of the chelate, when water was used as an eluting solvent. The chelate started to elute at $V$ = 5 mL and attained a maximum concentration at $V$ = 21 mL. Within 70 mL of $V$, the whole chelate was recovered from the column. Curve C in Figure 2 shows the

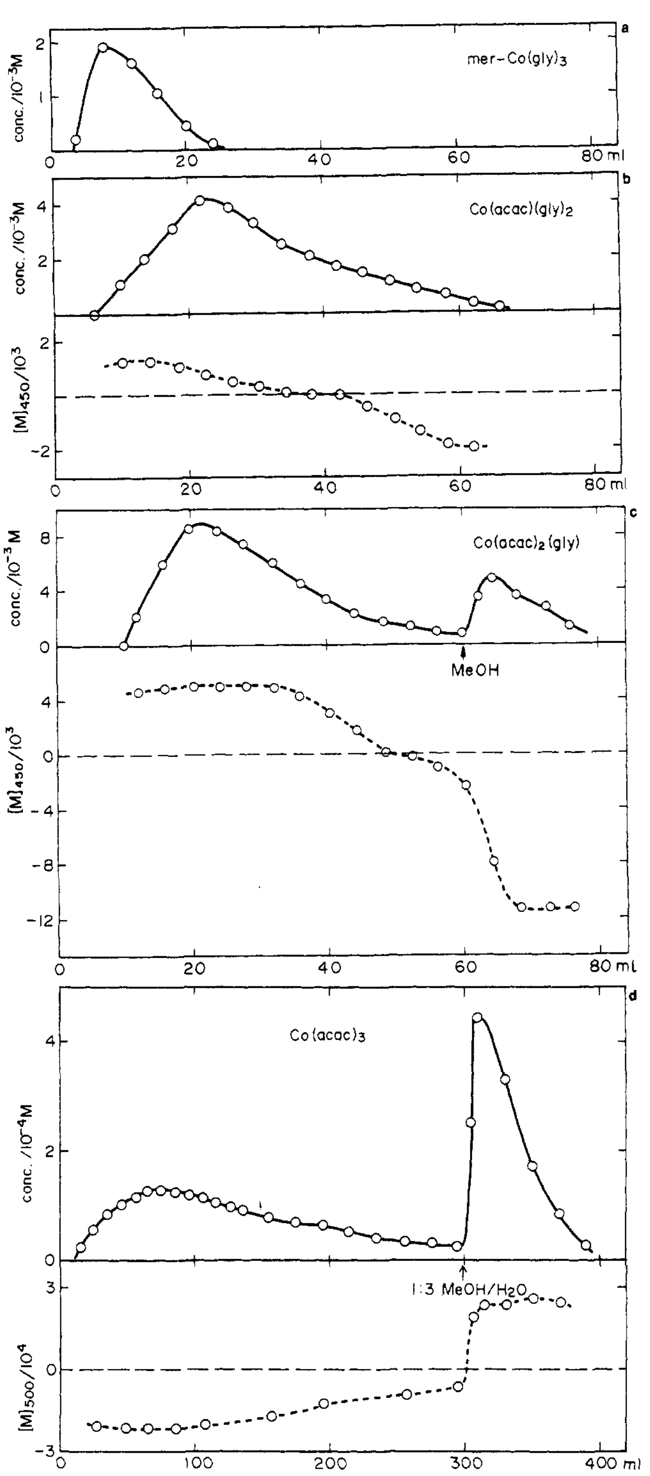

Figure 1. (a) Elution curve of $2 \times 10^{-5}$ mol of *mer*-$Co(gly)_3$ on a $\Delta$-$Ni(phen)_3^{2+}$–montmorillonite column of 1-cm length by 3-cm o.d. at 2 °C. The eluant was water. (b) Elution curve of $1.2 \times 10^{-4}$ mol of $Co(acac)(gly)_2$ on the same column as that in (a): (top) concentration vs. the elution volume ($V$); (bottom) molecular rotation at 450 nm, $[M]_{450}$, vs. $V$. The eluant was water. (c) Elution curve of $2.8 \times 10^{-4}$ mol of $Co(acac)_2(gly)$ on the same column as that in (a): (top) concentration vs. $V$; (bottom) $[M]_{450}$ vs. $V$. The eluant was water for $V$ less than 60 mL and methanol for $V$ larger than 60 mL. (d) Elution curve of $5.2 \times 10^{-5}$ mol of $Co(acac)_3$ on the same column as that in (a): (top) concentration vs. $V$; (bottom) $[M]_{500}$ vs. $V$. The eluant was water for $V$ less than 300 mL and 1:3 (v/v) methanol–water for $V$ larger than 300 mL.

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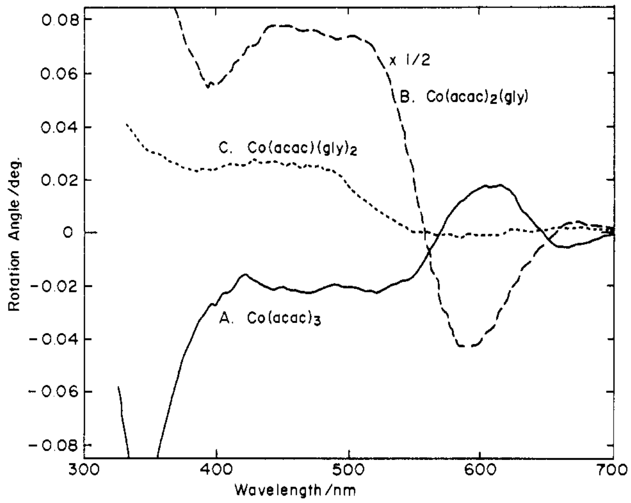

**Figure 2.** ORD curves of the effluents (A) $Co(acac)_3$ at $V = 45$ mL, (B) $Co(acac)_2(gly)$ at $V = 28$ mL, and (C) $Co(acac)(gly)_2$ at $V = 14$ mL.

ORD spectrum of the eluent at $V = 14$ mL. The curve had a large Cotton effect around 540 nm. According to the empirical rules based on the sign of the dominant Cotton effect in the visible spectrum of a trischelated Co(III) complex,[8a] it was tentatively assigned that the solution contained *pseudo*-Δ-$Co(acac)(gly)_2$ as an excess enantiomer. When the molecular rotation at 450 nm, $[M]_{450}$, was plotted against $V$, as can be seen in lower curve of Figure 1b, $[M]_{450}$ changed sign from a positive value to a negative one. The maximum and minimum values of $[M]_{450}$ were obtained to be +1300 and −2000, respectively.

**$Co(acac)_2(gly)$.** A $2.8 \times 10^{-4}$ mol quantity of $Co(acac)_2(gly)$ in 15 mL of water was placed on the column. With water as an eluting solvent, $Co(acac)_2(gly)$ appeared at $V = 10$ mL and had a maximum concentration at $V = 21$ mL. The concentration of the recovered chelate became less than $1 \times 10^{-3}$ M at $V = 60$ mL, where about 20% of the initially placed chelate was still bound with the column. The remaining chelate on the column was recovered by methanol solvent as shown in Figure 1c. Curve B in Figure 2 shows the ORD curve of the water effluent at $V = 28$ mL. The spectrum had a large Cotton effect at 560 nm and a small one above 650 nm. Accordingly the negative peak around 590 nm was more prominent than that observed for $Co(acac)(gly)_2$. On the basis of the same empirical rules as applied for $Co(acac)(gly)_2$[8a] and the comparison of its ORD spectrum with that of Λ-$Co(acac)_2$(L-alaninato),[8b] the solution contained *pseudo*-Δ-$Co(acac)_2(gly)$ as an excess enantiomer. As shown by the lower curve in Figure 1c, $[M]_{450}$ was positive for the initial water effluents until $V$ attained 48 mL. Above $V = 48$ mL, it changed the sign into a negative value. The methanol effluents showed large negative $[M]_{450}$ values. The maximum and minimum values of $[M]_{450}$ for *pseudo*-Δ- and *pseudo*-Λ-$Co(acac)_2(gly)$ were determined to be +4600 and −11 300, respectively.

**$Co(acac)_3$.** A $5.2 \times 10^{-5}$ mol quantity of $Co(acac)_3$ in 15 mL of water was placed on the column. With water as the eluting solvent, the chelate appeared at $V = 10$ mL. The concentration of $Co(acac)_3$ attained a maximum at $V = 70$ mL and decreased very slowly with the increase of $V$ as shown in the upper curve of Figure 1d. At $V = 300$ mL, the concentration of a recovered chelate was less than $2 \times 10^{-5}$ M, although more than 50% of $Co(acac)_3$ was still bound with the column. When the solvent was changed from pure water to a 1:3 (v/v) methanol–water mixture, the remaining chelate was recovered within $V = 400$ mL. Curve A in Figure 2 shows the ORD curve of the water effluent at $V = 65$ mL. The spectrum exhibited a large Cotton effect at 560 nm and a small Cotton effect around 650 nm, indicating that the fraction contained Λ-$Co(acac)_3$ as an excess enantiomer.[9] As shown by the lower curve of Figure 1d, $[M]_{500}$ stayed negative for the water effluents, while it had a large positive value for the methanol–water effluents. The maximum and minimum values of $[M]_{500}$ for Δ- and Λ-$Co(acac)_3$ were determined to be +26 000 and −21 000, respectively. With use of the values +29 000 and −29 000 for the pure Δ and Λ isomers reported,[9] the percentage resolutions were estimated to be 89 and 73% for Δ and Λ isomers, respectively.

**Table I.** Adsorption and X-ray Diffraction Data on a Δ-$Ni(phen)_3{}^{2+}$-Montmorillonite (NiM)–Co(III) Chelate Adduct

| sample | adsorbate | $d(001)$/Å |
|---|---|---|
| NiM (dry) | none | 17.7 ± 0.5 |
| NiM (wet with water) | intercalated $H_2O$ | 18.8 |
| NiM ($5.2 \times 10^{-6}$ mol) in contact with $3.4 \times 10^{-3}$ M $Co(acac)_2(gly)$ | intercalated $H_2O$ | 18.9 |
| NiM ($5.0 \times 10^{-6}$ mol) in contact with $2.3 \times 10^{-3}$ M $Co(acac)_3$ | intercalated $H_2O$ plus $1.1 \times 10^{-6}$ mol of $Co(acac)_3$ | 18.4 |

**X-ray Diffraction Measurements.** To attempt to learn how a chelate was bound to the column, we performed the following X-ray diffraction measurements. About 10 mg of Δ-$Ni(phen)_3{}^{2+}$–montmorillonite was mixed with a 4-mL aqueous solution of $Co(acac)_2(gly)$ or $Co(acac)_3$. The samples were allowed to stand at 2 °C for 6 h. After the solution was centrifuged, the concentration decrease of the chelate in the supernatant was determined spectrophotometrically. No detectable amount of $Co(acac)_2(gly)$ was bound with Δ-$Ni(phen)_3{}^{2+}$–montmorillonite, while 20% of Δ-$Ni(phen)_3{}^{2+}$ in the clay sample was covered by $Co(acac)_3$, supposing one $Ni(phen)_3{}^{2+}$ supplied the sites for one $Co(acac)_3$. X-ray diffraction patterns were measured on the above centrifuged solids. The value of basal spacing obtained ($d(001)$) is listed in Table I, together with the data of dry and wet Δ-$Ni(phen)_3{}^{2+}$–montmorillonites. From the table, $d(001)$ of wet Δ-$Ni(phen)_3{}^{2+}$–montmorillonite is 1.1 ± 0.5 Å larger than that of the dry mixture. This expansion arose from the penetration of water molecules into the interlayer space of the clay. On the other hand, no detectable change in $d(001)$ was observed when $Co(acac)_3$ was adsorbed on wet Δ-$Ni(phen)_3{}^{2+}$–montmorillonite. We therefore obtained no evidence for the intercalation of $Co(acac)_3$ in the interlayer space of Δ-$Ni(phen)_3{}^{2+}$–montmorillonite. One explanation for it is that adsorbed $Co(acac)_3$ was located exclusively on the external surface of the clay.[10]

## Discussion

The resolution of a neutral metal complex such as tris(acetylacetonato)metal(III) is difficult, because it does not

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(8) (a) For the present type of a pseudo-trischelated Co(III) complex, the absorption in the visible region arises from the d–d transitions. Thus it is reasonable to expect that the empirical rules proposed (Von Dreele, R. B.; Fay, R. C. *J. Am. Chem. Soc.* **1971**, *93*, 4936) are also applicable for the Cotton effects of $Co(acac)(gly)_2$ and $Co(acac)_2(gly)$. (b) In the case of $Co(acac)_2$(L-alaninato), the $(+)_D$ isomer was assigned to have the Λ configuration on the basis of the $^1H$ NMR spectroscopic results (Seematter, D. J.; Brushmiller, J. G. *J. Chem. Soc., Chem. Commun.* **1972**, 1277). Since the ORD spectrum of Λ-$Co(acac)_2$(L-alaninato) is almost exactly opposite that of the solution, the latter was assigned to contain Δ-$Co(acac)_2(gly)$ as an excess enantiomer.

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(10) We could not exclude the possibility that the expansion of $d(001)$ was not noticeable, because $Co(acac)_3$ occupied only 20% of the available sites on Δ-$Ni(phen)_3{}^{2+}$–montmorillonite in this experiment. Thus, further experiments are in progress, using an adsorbate that has more affinity than $Co(acac)_3$ to the clay.

form a diastereoisomer with a resolving agent. Such a complex was resolved by the use of a chromatographic column packed with an asymmetric compound. The compounds usually employed are cellulose, lactose, and Sephadex.[11-13] The reported optical purities, however, were relatively low, in the range of 5–20%, in spite of modifications tried for improvement. For example, a column was modified with an optically active molecule[13] or an optically active ion was added in an eluting solvent.[14]

In contrast to the reports cited above, the present chromatography on a $\Delta$-Ni(phen)$_3^{2+}$–montmorillonite column demonstrated remarkably high efficiency in resolving neutral Co(III) complexes. The percentage resolutions attained in resolving Co(acac)$_3$, 73 and 89% for the $\Lambda$ and $\Delta$ isomers, respectively, were about 4 times better than the best value reported in the literature (19.6%).[13] The results are surprising, when one compares the short length of our column (1 cm) with that of the others (300–100 cm). Another advantage in the present method is that the resolution was performed by elution with pure solvents. Accordingly, one gets rid of the difficulty of removing undesired additives from an eluant.

Tris(1,10-phenanthroline)iron(II) and tris(2,2′-bipyridyl)copper(II) are suggested to be adsorbed over a clay surface with their $C_3$ axes perpendicular from electric dichroism[15] and ESR measurements,[16] respectively. $\Delta$-Ni(phen)$_3^{2+}$ may also be adsorbed on the present clay column in the same manner. There are two possible sites at which a cobalt(III) complex interacts with $\Delta$-Ni(phen)$_3^{2+}$ on the montmorillonite clay, which has a well-known layered structure.[17,18] According to a molecular model, at an adjacent site of the Ni(phen)$_3^{2+}$ a $\Lambda$ isomer is more closely stacked with the Ni(II) complex than its counterpart, while at a site over the head of the Ni(II) complex a $\Delta$ isomer fits more closely. Then, it is likely that Co(acac)(gly)$_2$ was resolved at the former site and Co(acac)$_3$ was on the latter one.

**Registry No.** Co(acac)$_2$(gly), 17819-63-5; Co(acac)(gly)$_2$, 17872-14-9; *mer*-Co(gly)$_3$, 30364-77-3; $\Delta$-Ni(phen)$_3^{2+}$, 23385-79-7; montmorillonite, 1318-93-0.

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# Emission Quenching and Photochemistry of Aqueous Pt(CN)$_4^{2-}$

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In a preceding paper (*J. Am. Chem. Soc.* **1982**, *104*, 3596) the emission around 525 nm from concentrated aqueous solutions of Pt(CN)$_4^{2-}$ salts is found to be due to various oligomers, probably a tetramer and higher *n*-mers. We report here that this phosphorescence is efficiently quenched by $O_2$ and $NO_2^-$ and possibly by other excitation energy transfer quenchers. A number of reducible species are also good quenchers, and the effect is attributed to reduction by oligomer excited states. In the particular case of Co(NH$_3$)$_6^{3+}$, concomitant Co(II) production occurs with a quantum yield of 0.62 at room temperature. Although the oligomer excited states should be able to reduce water, no photoproduction of hydrogen is observed.

## Introduction

We have reported on the photophysics of aqueous K$_2$Pt(CN)$_4$ and BaPt(CN)$_4$ solutions, along with a summary of the literature background, including that regarding the crystalline salts.[2] The compounds show emission both *in the solution and* in the solid state. In the latter case, the emission shows components attributable to intramolecular processes associated with the chainlike stacking of Pt(CN)$_4^{2-}$ units. In the case of concentrated solutions, we reported evidence that there is considerable association into dimer, trimer, and higher oligomers, each with a characteristic absorption and emission behavior, and some tentative excited-state assignments were made. Of particular interest here is the phosphorescence of aqueous Pt(CN)$_4^{2-}$ in 0.2–0.4 M solution. The emission is at 510–530 nm, with a lifetime in the range of 500–700 ns, both $\tau$ and $\lambda_{max}$ increasing with increasing concentration. As a matter of brevity, we will refer to this emission as being at 525 nm. This emission band is attributed to phosphorescence from pentamer and higher *n*-mer units, possibly stacked in a manner similar to that in the crystalline state. BaPt(CN)$_4$ is more associated than is K$_2$Pt(CN)$_4$ or, conversely, a given degree of association occurs at a lower concentration. The typical emission maximum for phosphorescence is now at 490 nm.

It has been reported that dilute ($10^{-2}$–$10^{-4}$ M) aqueous Pt(CN)$_4^{2-}$ shows no photochemistry to 254-nm irradiation.[3] The purpose of the present investigation was to determine whether excited states of the oligomers present at high concentrations are reactive either toward net photochemistry or with respect to potential emission quenchers. As to photochemistry, several possibilities were a priori plausible. A number of cyano complexes have been found to show photoelectron production,[4,5] and this was an attractive possibility here. Partially oxidized Pt(CN)$_4^{2-}$ is well-known in the solid state,[6,7] an important stoichiometry being K$_2$Pt(CN)$_4$·0.3Br,

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