

(s), 1218 (s), 1200 (s), 1180 (s), 1158 (s), 890 (s), 750 (m), 710 (m), 690 (m), 610 (m), and 590 (s) cm^{-1} ; NMR (CDCl_3) δ 6.83 (m, b) ppm.

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Registry No. acac, 17272-66-1; Ni(acac)₂, 3264-82-2; Ni⁺, 14903-34-5; Ni, 7440-02-0; xanthone, 90-47-1; benzophenone, 119-61-9; acetophenone, 98-86-2; propiophenone, 93-55-0; *p*-methoxyacetophenone, 100-06-1; phenanthrene, 85-01-8; fluorenone, 486-25-9; anthracene, 120-12-7; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; 2-nitroso-2-methylpropane, 917-95-3; phenyl-*tert*-butylnitron, 3376-24-7.

NMR of ³¹P Heteroatoms in Paramagnetic One-Electron Heteropoly Blues. Rates of Intra- and Intercomplex Electron Transfers. Factors Affecting Line Widths

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Abstract: Heteropoly complexes are increasingly used as catalysts and specialized redox reagents, making knowledge of electron-exchange characteristics important. Relatively sharp ³¹P NMR signals ($\nu_{1/2} = 1-15$ Hz) are observed at room temperature from the heteroatoms in paramagnetic one-electron heteropoly blue reduction products of α -[PW₁₂O₄₀]³⁻ and α -[P₂W₁₈O₆₂]⁶⁻ in aqueous solution. Line broadenings for equimolar mixtures of the reduction products and their isostructural oxidized parent heteropoly complexes enable calculation of rates of exchange of the delocalized electrons between each reduced complex and its oxidized isomorph. These exchange rates correspond exactly to diffusion-controlled rates for the α -18-tungstodiphosphates and for the α -12-tungstophosphates, although the rate for the former, larger complex is 3 orders of magnitude slower than for the latter. The similarly evaluated electron-exchange rate between α -[P₂Mo₃W₁₅O₆₂]⁶⁻ and its one-electron reduction product, wherein the added electron is delocalized over the three Mo atoms in one end of the ellipsoidal complex, is an order of magnitude slower than that calculated for diffusion control, probably owing to necessity for contact between the Mo₃O₁₃ caps of the exchanging complexes. Extents of broadenings of the two ³¹P NMR lines of 1 ϵ blue α_1 -[P₂MoW₁₇O₆₂]⁷⁻ and its α_2 isomer show that the ³¹P atoms' relaxation mechanism is essentially purely dipolar. Thus, intracomplex exchange rates can be calculated from line widths for electrons hopping among the 12 belt W atoms in α -[P₂W₁₈O₆₂]⁷⁻ and among the 3 cap Mo atoms in α -[P₂Mo₃W₁₅O₆₂]⁷⁻. Electron hopping in the latter isomorph is ~ 25 times slower than in the former.

Many heteropoly anions¹⁻⁴ yield, upon reduction by addition of various numbers of electrons, products which typically retain the general structures of their oxidized parents⁵ and are frequently deep blue in color. These are generally known as "heteropoly blues". The added ("blue") electrons are usually delocalized, according to various time scales, by means of very rapid hopping between certain "addenda" atoms (i.e., W, Mo, V, etc.) in certain regions of the structures. Heteropoly complexes are finding increasing use as catalysts and specialized redox reagents,⁶ making knowledge of electron-exchange characteristics important. Factors involved in NMR study of these complexes attract attention.⁷⁻¹³

This paper reports that unexpected relatively sharp ³¹P NMR lines ($\Delta\nu_{1/2} = 1-15$ Hz) are observed at room temperature for the central heteroatoms in the one-electron heteropoly blue reduction products of α -[PW₁₂O₄₀]³⁻ (Keggin structure) and α -[P₂W₁₈O₆₂]⁶⁻ (Wells-Dawson structure). See Figure 1. This is the first report of any NMR spectra for paramagnetic heteropoly blue species (i.e., those containing odd numbers of delocalized blue electrons). Also reported and discussed below are the ³¹P NMR spectra of one-electron reduction products of α -[P₂Mo₃W₁₅O₆₂]⁶⁻, of α_1 -[P₂MoW₁₇O₆₂]⁶⁻, and of α_2 -[P₂MoW₁₇O₆₂]⁶⁻ (Figure 1).

The absence of a ¹H NMR spectrum for the central protons in the paramagnetic 1 ϵ blue reduction product of Keggin structure metatungstate,^{2,14} [H₂W₁₂O₄₀]⁷⁻, and the reappearance of a slightly shifted proton signal upon further reduction to the diamagnetic 2 ϵ blue, [H₂W₁₂O₄₀]⁸⁻, had made observation of NMR signals from heteroatoms in paramagnetic blue complexes seem improbable.

For solutions of the 12-tungsto-, 18-tungsto-, and 15-tungstophosphates cited, the line widths of the ³¹P NMR signals make it possible to evaluate the rates of electron exchanges between the paramagnetic one-electron reduced species and their fully oxidized diamagnetic isomorphs. Use of ESR data to estimate such exchange rates has been precluded for these unsubstituted Keggin or Wells-Dawson complexes by very large line widths. It is also possible to use the NMR data to estimate the rates of intracomplex electron hopping from W⁵⁺ to W⁶⁺ and, in α -[P₂Mo₃W₁₅O₆₂]⁷⁻, among the Mo atoms.

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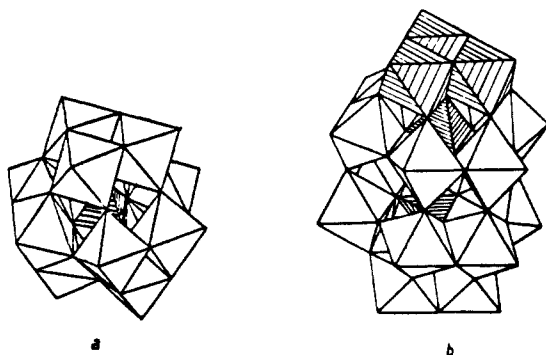


Figure 1. (a) Keggin structure of α -[PW₁₂O₄₀]³⁻. (b) Wells-Dawson structure of α -[P₂W₁₈O₆₂]⁶⁻, α -P₂Mo₃W₁₅O₆₂]⁶⁻, and α_1 - and α_2 -[P₂MoW₁₇O₆₂]⁶⁻. Every vertex of a polyhedron locates the center of an oxygen atom. The P atoms are at the centers of the interior hatched tetrahedra. At the center of each octahedron is a W or Mo atom, displaced significantly off-center toward the unshared oxygen atom of its octahedron. The exterior O atoms are heavily polarized toward the positive W or Mo atoms just beneath the exterior layer of O's, rendering H-bonding to solvent minimal and causing hydrodynamic radii to correspond to the complexes' crystallographic radii. In α -[P₂Mo₃W₁₅O₆₂]⁶⁻ the three MoO₆ octahedra (which are hatched in the figure) form the 3-fold Mo₃O₁₃ cap at the top of the complex illustrated. In α_1 -[P₂MoW₁₇O₆₂]⁶⁻, the MoO₆ octahedron is in one of the two belts of six octahedra about the center of the complex. In α_2 -[P₂MoW₁₇O₆₂]⁶⁻, the MoO₆ octahedron occupies a position in one MoW₂O₁₃ cap.

Experimental Section

All spectra were recorded on an AM300WB NMR spectrometer at 25 °C. The Li⁺ salt of α -[P₂W₁₈O₆₂]⁶⁻, the free acid of α -[PW₁₂O₄₀]³⁻, and the K⁺ salts of α -[P₂Mo₃W₁₅O₆₂]⁶⁻ and of α_1 - and α_2 -[P₂MoW₁₇O₆₂]⁶⁻ were reduced to 1 ϵ blues by constant potential electrolysis,^{15,16} with monitoring of total coulombs passed. For each of the first three of these complexes, a solution was also made which contained an equimolar mixture of the parent oxidized complex and the 1 ϵ reduced complex. This was accomplished by a coulometrically monitored electrolytic reoxidation of each 1 ϵ blue species. Air was rigorously excluded at all times.

The results of the NMR measurements are summarized in Table I.

Discussion

Intercomplex Electron Transfers. In the case of the Keggin complex, the single broad peak, centered for the equimolar mixture exactly between the chemical shifts for the oxidized and reduced species, shows that the electron exchange is more rapid than the NMR time scale. The two peaks with no changes in chemical shifts in the case of the equimolar mixture of the Wells-Dawson 18-tungsto derivatives show that that exchange is much slower than the NMR time scale.

Since oxygen exchange between solvent and these heteropoly species is very slow,¹⁹ the electron exchange must be outer-sphere and second order. Therefore,

$$\text{rate} = k[\text{oxidized heteropoly}][\text{reduced heteropoly}] \quad (1)$$

$$\frac{1}{\tau} = \frac{d[\text{oxidized heteropoly}]}{[\text{oxidized heteropoly}]dt} = k[\text{reduced heteropoly}] \quad (2)$$

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Table I. ³¹P NMR Chemical Shifts and Line Widths for Aqueous Solutions (20% D₂O) at 25 °C^a

formula	overall molarity	chem shifts from 85% H ₃ PO ₄ (ppm), $\nu_{1/2}$ line widths (Hz)	
α -[PW ₁₂ O ₄₀] ³⁻ (oxidized parent)	0.002	-14.6, 0.5	
α -[PW ₁₂ O ₄₀] ⁴⁻ (1 ϵ reduced species)	0.002 ^b	-10.4, 1.0	
equimolar mixture	0.002 ^b	-12.6, 25.8	
structurally identical ³¹ P's shifts (ppm); line widths (Hz)			
formula	overall molarity		
α -[P ₂ W ₁₈ O ₆₂] ⁶⁻ (oxidized parent)	0.02 ^c	-12.7, 0.6	
α -[P ₂ W ₁₈ O ₆₂] ⁷⁻ (1 ϵ reduced species)	0.02 ^c	-0.44, 15 ¹⁷	
equimolar mixture	0.02 ^{c,d}	-12.7, 41	-0.44, 54
shifts (ppm) and line widths (Hz)			
formula	overall molarity	³¹ P near Mo	³¹ P far from Mo
α -[P ₂ Mo ₃ W ₁₅ O ₆₂] ⁶⁻ (oxidized parent)	0.01	-10.4, 1	-12.9, 1
α -[P ₂ Mo ₃ W ₁₅ O ₆₂] ⁷⁻ (1 ϵ reduced species)	0.01	+4.5, 177	-13.5, 7.0
equimolar mixture	0.01	-10.4, 3.9 +4.5, 180	-12.9, 3.6 -13.5, 7.0
α_1 -[P ₂ MoW ₁₇ O ₆₂] ⁶⁻ (oxidized parent)	0.01	-11.4, 1.5	-12.3, 1.5
α_1 -[P ₂ MoW ₁₇ O ₆₂] ⁷⁻ (1 ϵ reduced species)	0.01	+6.3, 900	-3.4, 80
α_2 -[P ₂ MoW ₁₇ O ₆₂] ⁶⁻ (oxidized parent)	0.01	-11.5, 1.5	-12.3, 1.5
α_2 -[P ₂ MoW ₁₇ O ₆₂] ⁷⁻ (1 ϵ reduced species)	0.01	-3.8, 360-410 ^e	-13.4, 8.6

^apH is 1 except for 3-molybdo-15-tungstodiphosphates, for which pH is 2.5. ^bAnalogous measurements for [PW₁₂O₄₀]⁴⁻ and the equimolar mixture at 0.02 overall molarity gave identical chemical shifts and intercomplex rate constants. ^cAnalogous measurements for [P₂W₁₈O₆₂]⁷⁻ at pH 4 gave identical results. ^dAt 90 °C the exchange was not fast enough to make the two peaks coalesce. ^eUncertainty owing to phasing problem caused by small quantity of impurity.

τ is the electron-exchange lifetime. For the Wells-Dawson 18-tungstodiphosphates at the limit of slow exchange²⁰

$$\frac{1}{T_2(\text{mixture})} = \frac{1}{T_2(1\epsilon)} + \frac{1}{\tau} \quad (3)$$

where $1/\pi T_2(\text{mixture})$ is $\Delta\nu_{1/2}$ for the ³¹P of the one-electron blue in the equimolar mixture, and $1/\pi T_2(1\epsilon)$ is $\Delta\nu_{1/2}$ for the ³¹P peak of the pure one-electron blue.

Substitution of the $\Delta\nu_{1/2}$ values and concentrations from Table I into eq 2 and 3 yields $k_{\text{ET}} = 1.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the 18-tungstodiphosphate complexes.

For the Keggin 12-tungstodiphosphates, $\tau < \sqrt{2}/\pi\Delta\nu = 8.7 \times 10^{-4} \text{ s}$ because the two peaks coalesce,²¹ and, upon substituting in eq 2, $k > 1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The numerical value of the rate constant was then estimated from²⁰

$$\frac{1}{T_2(\text{mixture})} = \frac{P(1\epsilon)}{T_2(1\epsilon)} + \frac{P(\text{ox})}{T_2(\text{ox})} + P^2(1\epsilon)P^2(\text{ox})(2\pi\Delta\nu)^2(\tau(1\epsilon) + \tau(\text{ox})) \quad (4)$$

where $P(1\epsilon)$ and $P(\text{ox})$ are mole fractions of one-electron reduced

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and oxidized species, respectively, in the mixture, and each $P = 0.5$. Also, $\Delta\nu =$ the chemical shift difference (expressed in hertz) between the signals from the pure 1ϵ reduced species and the pure oxidized species. It is assumed that $\tau(1\epsilon) = \tau(\text{ox})$.

Substituting numerical values from Table I into eq 2 and 4 yields $k_{\text{ET}} \cong 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the Keggin complexes.

The rate constants predicted for simple diffusion-controlled reactions were calculated by using the diffusion coefficients reported by Pope, Varga, and Papaconstantinou.^{22,23} The hydrodynamic radius of the Keggin structure was taken as 5.6 \AA ²⁴ and that of the Wells-Dawson structure as 10 \AA .²³ For simple diffusion control, the rate constant for the Keggin structure is thus predicted to be $1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, and for the Wells-Dawson structure it would be $1.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

The rate of electron exchange between α -[PW₁₂O₄₀]³⁻ and its one-electron heteropoly blue is thus seen to be diffusion-controlled as also is the electron exchange between α -[P₂W₁₈O₆₂]⁶⁻ and its 1ϵ blue. The rate for the latter case is 3 orders of magnitude slower than that for the Keggin ion although the hydrodynamic radius of the larger ellipsoidal complex is only $\sim 80\%$ greater than that of the Keggin complex.

Owing to the very pronounced inward polarization of their exterior oxygen atoms (see caption, Figure 1), all these heteropoly complexes have extremely low solvation energies and very low van der Waals attractions for one another.^{1,25} Those factors and the anions' significant negative charges probably make long residences of exchanging pairs within aqueous solvent cages not very pronounced. The "blue" electrons transfer between predominantly nonbonding b_2 orbitals of the C_{4v} distorted WO₆ octahedra. For these reasons, little energy barrier to exchange is expected.

The "blue" electron is delocalized over all 12 W atoms^{7,26} in α -[PW₁₂O₄₀]⁴⁻, but it is delocalized only over the 12 belt W's^{7,26} of α -[P₂W₁₈O₆₂]⁷⁻. Any possible resulting geometrical constraint on orientation of the 18-tungstodiphosphate complexes during collision, to enable electron exchange to occur, is insufficient to cause departure from diffusion control.

In the Mo-substituted derivatives, the Mo atoms are reduced preferentially.^{7,16,27,28} In α -[P₂Mo₃W₁₅O₆₂]⁷⁻ the blue electron is delocalized only over the three Mo atoms in one cap of the complex⁷ (Figure 1). For this structure the rate of intercomplex electron transfer is decidedly slower than predicted for diffusion control. The line width for the relevant P atom was carefully measured. It increased only from 177 to 180 Hz upon reduction to the equimolar mixture. Had the exchange been at the diffusion-controlled rate, that line would have broadened to 200 Hz. The observed broadening corresponds to an exchange rate of $\sim 2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, which is about 1 order of magnitude slower than if it were diffusion controlled. This decrease in exchange rate is attributable to a geometrical factor necessitating contact between the molybdenum caps of exchanging complexes.

Intracomplex Electron Transfer. The data for the 1ϵ reduction products of α_1 - and α_2 -[P₂MoW₁₇O₆₂]⁶⁻, wherein the added electron is localized on the Mo in each case, make it possible to estimate intracomplex electron-transfer rates for α -[P₂W₁₈O₆₂]⁷⁻ and α -[P₂Mo₃W₁₅O₆₂]⁷⁻. The ratio of the line widths for the two P atoms in α_1 -[P₂MoW₁₇O₆₂]⁷⁻ is found to be 11.2. Since the ratio of the two P-Mo distances²⁹ raised to the sixth power is 10.9, it is concluded that the relaxation mechanism is essentially dipolar

in character.³⁰ It is assumed that this is also true for α -[P₂W₁₈O₆₂]⁷⁻. The ³¹P line in α -[P₂W₁₈O₆₂]⁷⁻ is narrowed to only 15 Hz, and it appears that the narrowing can be attributed only to electron hopping among the 12 W's in the two belts of the complex, which decreases the nuclear correlation time in contrast to the situation in α_1 -[P₂MoW₁₇O₆₂]⁷⁻ wherein the added electron is localized on the Mo in one belt.

The correlation time for the dipolar interaction, τ_c , is calculated from the equation for $1/T_2$ at the slow motion limit:^{20,30}

$$\frac{1}{T_2} = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{7}{15} \hbar^2 S(S+1) \gamma_s^2 \gamma_1^2 \tau_c r^{-6} \quad (5)$$

wherein $\mu_0 =$ magnetic permeability of vacuum, $\hbar =$ Planck's constant/ 2π , $S =$ electron spin, γ_s and $\gamma_1 =$ magnetogyric ratios of electron and P nucleus, respectively, and $r =$ distance between unpaired electron and the ³¹P nucleus. This yields $1/\tau_c = 2.8 \times 10^9 \text{ s}^{-1}$ for α_1 -[P₂MoW₁₇O₆₂]⁷⁻ and $1/\tau_c = 1.7 \times 10^{11} \text{ s}^{-1}$ for α -[P₂W₁₈O₆₂]⁷⁻. Then^{30,31}

$$1.7 \times 10^{11} = 2.8 \times 10^9 + 1/\tau(\text{hopping}) \quad (6)$$

and $1/\tau(\text{hopping}) = 1.7 \times 10^{11} \text{ s}^{-1}$ for α -[P₂W₁₈O₆₂]⁷⁻.

The rate of hopping of the "blue" electron among the three Mo atoms in the cap of α -[P₂Mo₃W₁₅O₆₂]⁷⁻ is evaluated by the same method, employing the results for α_2 -[P₂MoW₁₇O₆₂]⁷⁻ and again taking the relaxation mechanism as being essentially dipolar for both complexes. The electron-transfer rate between adjacent Mo atoms in the three edge-sharing MoO₆ octahedra in the Mo₃O₁₃ cap is some 25 times slower than the electron-transfer rate between adjacent W atoms in the belts of α -[P₂W₁₈O₆₂]⁷⁻.

Sanchez et al.^{26,27} estimated from temperature dependences of ESR line widths the activation energies of intracomplex electron transfers for [Mo₆O₁₉]³⁻ and for α -[As₂W₁₈O₆₂]⁷⁻, the former of which was found to involve much higher activation energy. Their results are thus in qualitative agreement with those presented herein. The structure of the [Mo₆O₁₉]³⁻ (1ϵ blue) consists of two Mo₃O₁₃ groups, each identical with the Mo₃O₁₃ cap in α -[P₂Mo₃W₁₅O₆₂]⁶⁻. In this heteropoly complex the MoO₆ octahedra are joined so that each shares only edges with its MoO₆ neighbors. Sanchez et al.^{26,27} also reported activation energies for intracomplex electron transfers in several other polytungstate and polymolybdate complexes, but they describe their method of estimation as "difficult". In part it would appear that necessary extrapolations of line widths vs. $1/T$ curves are rather dependent on subjective evaluations.

There have been just two previous studies of electron transfer between heteropoly structures. In 1964 Rasmussen and Brubaker³³ studied, via radioactive tracer experiments, the electron exchange between Keggin structure [⁶⁰Co^{II}W₁₂O₄₀]⁶⁻ and [⁵⁹Co^{III}W₁₂O₄₀]⁵⁻. They found a much slower rate than that reported above for the 12-tungstophosphates. That is not surprising because the exchanging electron in their study was not delocalized over the W atoms but had to penetrate both heteropoly cages to go from the central Co(II) atom to the central Co(III) atom. Probably more significant is the considerable energy barrier involved in interconversion of the small Jahn-Teller distorted^{1,34} Co^{III}O₄ tetrahedron and the larger regular³⁴ Co^{II}O₄ tetrahedron. In 1975, O'Donnell³⁵ studied electron-exchange rates between Keggin structure [PMo^VW₁₁O₄₀]⁴⁻ and [PMo^{VI}W₁₁O₄₀]³⁻ in nonaqueous solvents. Again, the exchanging electron was not delocalized over

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any W atoms. He concluded that exchange rates were faster than predicted for diffusion control and postulated some sort of charge-transfer complex formation between the anions in the nonaqueous solvents.

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New Type of Atropisomerism in Metal Complexes. Preparation and Resolution of (3,4-Diacetyl-2,5-hexanedionato)- bis[(2,2',2''-triaminotriethylamine)cobalt(III)] Ion^{1,2}

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Abstract: A metal complex, (3,4-diacetyl-2,5-hexanedionato)bis[(2,2',2''-triaminotriethylamine)cobalt(III)] ion, was prepared and optically resolved. The optical resolution of the complex confirmed the expected novel twin structure and presented a new type of atropisomer in coordination chemistry. The optical absorption and circular dichroism are discussed in connection with the absorption spectrum of the related complex, (2,4-pentanedionato)(2,2',2''-triaminotriethylamine)cobalt(III) ion, which corresponds to half of the above twin structure.

Recently, several metal complexes having a new type of chiral source (restricted rotation) have been reported that possess chirality different from those of traditional types which are confined mostly to the class of centrodissymmetry.³ Utsuno reported a propeller-like, fixed chiral conformation of pyridine rings in the *trans*-dichlorotetrakis(pyridine)cobalt(III) ion.⁴ We have reported the optical isomerism of a series of Co^{III}(tren) complexes of 3-aryl-2,4-pentanedione, the chirality of which comes from restricted rotation of an aryl group.⁵ Figure 1 shows a typical example. In the present study, a new type of atropisomerism is reported. The twin complex $[\text{Co}(\text{tren})_2\text{tae}]^{4+}$ (Figure 2) is the first example of an atropisomer in binuclear metal complexes.⁶ Although this complex may be only an extension of this series, since a different ligand is introduced into the $[\text{Co}(\text{acac})\text{tren}]^{2+}$ system instead of the aryl group in the above series, it is unique because it contains no unnecessary moiety and therefore shows genuine electronic transitions of the $[\text{Co}(\text{acac})\text{tren}]^{2+}$ chromophore. Thus, the title complex gives important information about the electronic states of $[\text{Co}(\text{acac})\text{tren}]^{2+}$.

Experimental Section

Instruments. Circular dichroism, IR, UV-visible, ¹H NMR, and ¹³C NMR spectra were measured with JASCO Model J-500, Hitachi 295, Hitachi 200-10, Hitachi R-20, and JEOL JNM-FX60 spectrometers, respectively. Elemental analyses were carried out with a YANACO MT02 CHN-order.

Preparations. (a) **(2,4-Pentanedionato)(2,2',2''-triaminotriethylamine)cobalt(III).** A mixture of $[\text{Co}(\text{CO}_3)\text{tren}]\text{ClO}_4 \cdot 1.5\text{H}_2\text{O}$ (5.5 g, 14 mmol)⁷ and 2 N hydrochloric acid solution (20 mL) was stirred for one-half hour. To this solution were added acetylacetone (4 mL) and 1 N sodium hydroxide solution (30 mL). The mixture was kept at 60–80 °C for 2 h under stirring. After the mixture cooled, potassium iodide (18.4 g, 0.11 mol) was added to give a red precipitate, yield 7.6 g (87%). A small amount of the complex was purified by means of cation-exchange chromatography using an SP-Sephadex column and 0.5 N sodium chloride solution as the eluent. After most of the sodium chloride was removed from the eluted solution of $[\text{Co}(\text{acac})\text{tren}]^{2+}$, excess sodium bromide was added to the resulting solution. The precipitate was recrystallized from water: IR 1520 and 1570 cm⁻¹; ¹H NMR δ 2.12, 2.20 (two kinds of methyl protons of the acetylacetonate ring), and 5.73

(methine proton of the acetylacetonate ring). Anal. Calcd for C₁₁H₂₅N₄O₇CoBr₂·3H₂O: C, 25.50; H, 6.03; N, 10.81. Found: C, 25.79; H, 6.28; N, 11.10.

(b) **(3,4-Diacetyl-2,5-hexanedionato)bis[(2,2',2''-triaminotriethylamine)cobalt(III)].** A reaction of $[\text{Co}(\text{CO}_3)\text{tren}]^{2+}$ (1.0 equiv) with H₂tae (0.5 equiv)⁸ similar to the preparation of $[\text{Co}(\text{acac})\text{tren}]^{2+}$ described above gave a solution of crude $[\text{Co}(\text{tren})_2\text{tae}]^{4+}$. Sodium perchlorate (6–8 equiv) was added to the solution. The precipitate was filtered and recrystallized from water, yield 34%. The complex was often contaminated with brown impurities and therefore purified by means of ion-exchange chromatography. IR 1560 cm⁻¹; ¹H NMR δ 2.10, 2.17 (CH₃ of the acac ring), and 2.5–3.8 (CH₂ of the tren chain). Anal. Calcd for C₂₂H₄₈Cl₄Co₂N₈O₂₀·2H₂O: C, 25.40; H, 5.40; N, 10.77. Found: C, 25.10; H, 5.10; N, 10.50.

Optical Resolution of $[\text{Co}(\text{tren})_2\text{tae}]^{4+}$. A previous communication reported the partial resolution of the complex by means of ion-exchange chromatography using a sodium D-tartrate solution as the eluent.⁶ A better result is obtained when the complex is recycled 7 times through an SP-Sephadex column (4.5 cm in diameter and 90 cm in length) using a 0.275 M solution of sodium D-tartratoantimonate(III) as the eluent. Although the eluted fraction does not separate as two bands, we were able to obtain the enantiomeric isomers from the head and tail fractions which show a constant ratio of circular dichroism intensity to absorption coefficient. The head fractions show a negative sign at the lowest energy region ($\Delta\epsilon = -0.57$ at 18.42×10^3 cm⁻¹), and tail fractions show a positive sign ($\Delta\epsilon = +0.55$ at the same position). The concentration of the aqueous solution for the measurement of CD spectra was obtained from the calibration curve of the purified racemate.

Results and Discussion

Characterization of $[\text{Co}(\text{acac})\text{tren}]^{2+}$. The infrared spectrum of the complex showed two strong peaks at 1520 and 1570 cm⁻¹

(1) The following abbreviations were used throughout this paper; tren for 2,2',2''-triaminotriethylamine, acacH for acetylacetone, en for ethylenediamine, tae for tetraacetyethane.

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