

Ligand Isotopic Exchange Kinetics of Tris(acetylacetonato)chromium(III) at Elevated Temperatures

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Tris(acetylacetonato)chromium(III) [Cr(acac)₃] undergoes ligand isotopic exchange with ¹⁴C-labeled acetylacetonate (Hacac) in acetonitrile (AN) at >140 °C without decomposition and solvolysis. McKay's exchange rate is proportional to the complex concentration, and the first-order rate constant *k*₀ is dependent on the concentrations of free Hacac and water (e.g., *k*₀ = 8.0 × 10⁻⁵ s⁻¹ at 166.4 °C in 0.030 M Hacac and 0.068 M water in AN). Analysis of the diagrams of *k*₀ vs. free Hacac and water concentrations and the deuterium isotope effect suggested a plausible mechanism. In the region [Hacac] > 0.1 M, free Hacac seems to interact directly with the original complex to give an intermediate, in which the proton transfer from the incoming Hacac to the leaving acac⁻ gives rise to the isotopic exchange. In the region [Hacac] < 0.03 M, the original complex appears to give a unidentate ligand spontaneously and interacts with the free Hacac to give a similar intermediate. Water molecules seem to catalyze the intramolecular proton transfer. This chromium(III) complex gives the smallest ligand isotopic exchange rate among octahedral tris(acetylacetonato) complexes ever studied.

Introduction

Chromium(III) complexes with various unidentate ligands give slow ligand substitution reactions, and the mechanism has been discussed from various viewpoints.¹ Comparatively little information is available, however, concerning the ligand substitution kinetics involving chelating ligands.

The enolate anion of acetylacetonate (Hacac) gives stable complexes with many kinds of metal ion, and their dynamic behavior has been studied by several authors. Fay, Girgis, and Klabunde studied the kinetics of racemization of tris(acetylacetonato)chromium(III), Cr(acac)₃, in chlorobenzene at 96–135 °C and found that the process was intramolecular.² Kutal and Sievers measured the rate of geometrical isomerization of tris(trifluoroacetylacetonato)chromium(III) in the gaseous phase at 118–145 °C and discussed the intramolecular mechanism.³ These authors did not find any sign of intermolecular exchange under their experimental conditions. Kluiber examined the velocity of ligand isotopic exchange of Cr(acac)₃ in chloroform at room temperature but found no appreciable change within 10 min.⁴

As an extension of our studies of ligand isotopic exchange kinetics of various β-diketonato complexes of typical and transition elements,⁵ we have found that Cr(acac)₃ undergoes ligand isotopic exchange with [¹⁴C]Hacac at a measurable rate at temperatures over 160 and 140 °C in the gaseous phase and in acetonitrile (AN), respectively. This paper describes details of the kinetic studies and discusses the mechanism of intermolecular ligand exchange in AN.

Experimental Section

Materials. Cr(acac)₃ was synthesized by the ordinary method⁶ and sublimed in vacuo at 130 °C. Acetylacetonate was dehydrated with calcium sulfate and distilled. The labeled ligands [2,4-¹⁴C]acetylacetonate and [methylene-²H₂]acetylacetonate were prepared by methods previously reported⁷ and by equilibrating Hacac with 99% D₂O,⁸ respectively. The deuterium content of the methylene hydrogens was ca. 85%. The labeled complex Cr([2,4-¹⁴C]acac)₃ was prepared from the labeled ligand by the method of Pinchas et al.⁹ which was suitable for a small-scale preparation. Acetonitrile was distilled in the presence of phosphorus pentoxide.

Kinetic Procedure. Since the experiments were carried out at a temperature over the boiling point of AN, all of the kinetic runs were performed in sealed Pyrex tubes. The complex (to produce 0.0017–0.010 M solution) and Hacac in AN (0.001–5 M solution containing 0.015–0.15 M water, 3 ml) were sealed in Pyrex glass tubes (10 mm in diameter, 80 mm in length). Three to five tubes containing the solutions of same concentrations of the ingredients were simultaneously heated in a silicone oil bath at 155–175 °C. The tubes were withdrawn at appropriate time intervals and individually connected to a vacuum line, and the free Hacac and AN were collected

in small tubes in liquid nitrogen bath to leave pure Cr(acac)₃ in the original tubes. Both Hacac and Cr(acac)₃ were quantitatively recovered, and the recovered species were spectroscopically pure.

The recovered free Hacac and the complex were individually dissolved in anisole containing 0.1% *p*-terphenyl and 0.04% *p*-bis-(5-phenyl-2-oxazolyl)benzene (POPOP) and the radioactivity was measured. The specific counting rate was calculated from the counting rate and the original weight of the compounds.

Measurements. The radioactivity was recorded with a Nuclear Chicago Unilux IIA liquid scintillation counter. The visible and ultraviolet absorption spectra were recorded with a Hitachi 323 spectrometer. The water content of the reaction mixtures was determined by Karl Fischer titration. The D content of the deuterated Hacac was determined by NMR spectroscopy with a Varian A-60 spectrometer.

Calculation of the Exchange Rate. McKay's formula was used throughout the studies, i.e.

$$R = -2.3 [3ab/(3a + b)] [\log(1 - F)]/t \quad (1)$$

where *a* and *b* stand for the concentrations of Cr(acac)₃ and free Hacac, respectively. *t* is the lapse of time in seconds, and *F* the fraction of reaction which is expressed by (x₀ - x_t)/(x₀ - x_∞), x's being the specific counting rates of the species recovered at the time indicated by the subscripts. Hacac is in tautomeric equilibrium between enol and keto form, but the interconversion rate is significantly greater than the present ligand-exchange rate in the given temperature range. Hence the total concentration of free Hacac was taken to be *b*.

Kinetic measurements were made by use of Cr(acac)₃ and [¹⁴C]Hacac and by use of Cr([¹⁴C]acac)₃ and Hacac or [²H₂]Hacac. The *R* values obtained by both systems under identical concentrations of the ingredients gave equal results, except for the deuterated systems.

Results

The absorption spectra of the reaction mixtures before and after the heating were identical with each other. No significant zero-time exchange was observed. The McKay plots gave straight lines in the range *F* < ca. 0.75. Hence no other reactions than the isotopic exchange took place during the heating. The *R* values calculated by measuring the specific counting rate of the recovered Hacac and that of the complex coincided within experimental error. This fact also verifies the absence of other reactions.

Table I shows that *R* is proportional to the complex concentration in the range *a* < 0.010 M, and *R* is expressed by

$$R = k_0 a \quad (2)$$

where *k*₀ is the observed first-order rate constant and can be the measure of rate of the present isotopic exchange.

The *k*₀ values are dependent on both the water and free Hacac concentrations. Figure 1 shows the dependence of *k*₀

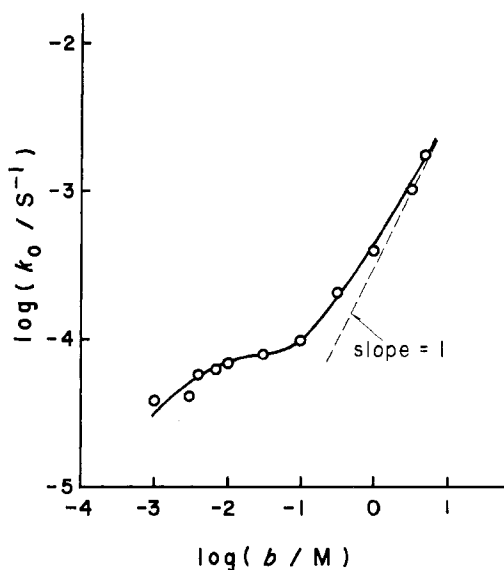


Figure 1. log-log plot of the observed isotopic exchange rate constant k_0 vs. the concentration of the free ligand b in acetonitrile at 166.4 °C ($[\text{H}_2\text{O}] = 0.070 \pm 0.005 \text{ M}$).

Table I. Isotopic Exchange Rate between $\text{Cr}(\text{acac})_3$ and Hacac in Acetonitrile at 166.4 °C

$[\text{Cr}]/10^{-3} \text{ M}$	$[\text{Hacac}]/10^{-3} \text{ M}$	$[\text{H}_2\text{O}]/10^{-3} \text{ M}$	$R/10^{-5} \text{ M s}^{-1}$	$k_0/10^{-5} \text{ s}^{-1}$
1.67	9.71	44	8.93 ± 0.45	5.4 ± 0.3
6.66	9.67	44	38.5 ± 1.5	5.8 ± 0.3
10.1	29.5	68	81.2 ± 2.3	8.0 ± 0.3
3.29	10.0	66	25.3 ± 1.3	7.7 ± 0.4
3.29	9.71	66 ^a		5.3 ± 0.4
3.33	9.40 ^c	91 ^b		7.2 ± 0.3^d
10.3	194	69		5.9 ± 0.2^e
10.0	353	62		8.1 ± 0.4^e
10.3	488	70		11.8 ± 0.2^e
10.1	97.1	67		9.8 ± 0.3
10.1	295	71		21.1 ± 0.8
10.1	295	130		23.2 ± 0.6
10.1	486	87		24.1 ± 2.9
10.3	194	69		23.8 ± 0.5^f
10.0	353	62		29.0 ± 0.3^f
10.3	488	70		39.1 ± 2.4^f

^a D_2O (0.055 M) + H_2O (0.011 M). ^b D_2O (0.055 M) + H_2O (0.036 M). ^c With $[\text{methylene-}^2\text{H}_2]\text{Hacac}$; the deuterium content of the methylene hydrogens is ca. 85%. ^d The corresponding k_0 value with $[\text{H}]\text{Hacac}$ under identical water and free Hacac concentration was estimated by interpolation on line B in Figure 3 to be $10 \times 10^{-5} \text{ s}^{-1}$. ^e At 157.1 °C. ^f At 175.3 °C.

upon the free Hacac concentration on the log-log scale at a given concentration of water. The diagram seems to consist of two parts. In the concentration range $b < 0.03 \text{ M}$, k_0 increases with increase in b and reaches a limiting value k_m . Figure 2 shows such a dependence on a k_0 vs. b plot. When the reciprocal of k_0 was plotted against the reciprocal of b in this concentration region, a linear diagram was obtained. Hence k_0 is expressed by eq 3. From the intercept and the

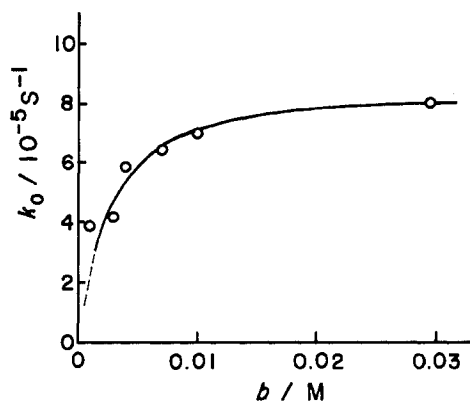
$$k_0 = k_m Ab / (1 + Ab) \quad (3)$$


Figure 2. Influence of the free ligand concentration on the isotopic exchange rate constant k_0 in the $<0.03 \text{ M}$ region at 166.4 °C ($[\text{H}_2\text{O}] = 0.070 \pm 0.005 \text{ M}$).

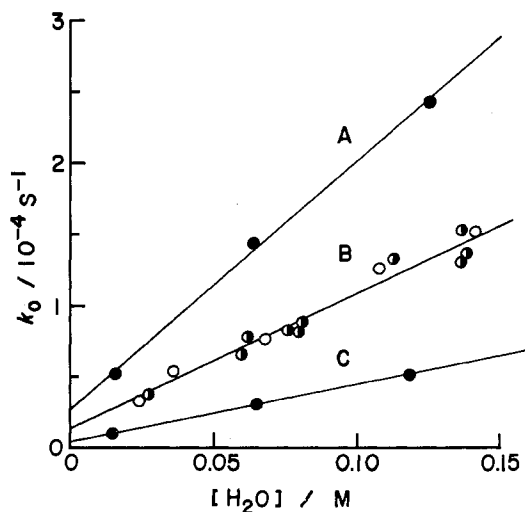


Figure 3. Influence of the water concentration in acetonitrile on the limiting isotopic exchange rate constant k_m ($\approx k_0$) at 175.3 °C (A), 166.4 °C (B), and 157.1 °C (C): open and full circles, $b \approx 0.010 \text{ M}$; half-full circles, $0.012 \text{ M} < b < 0.030 \text{ M}$.

gradient of such a diagram, k_m and A were calculated to be $8.0 \times 10^{-5} \text{ s}^{-1}$ and 630 M^{-1} , respectively, at 166.4 °C.

In the free Hacac concentration range from 0.01 to 0.03 M (where $k_0 \approx k_m$), k_0 is dependent on the water concentration as shown in Figure 3, and eq 4 holds for $[\text{H}_2\text{O}] < 0.15 \text{ M}$.

$$k_0 = k_i + k_w [\text{H}_2\text{O}] \approx k_m \quad (4)$$

When $[\text{H}_2\text{Hacac}]$ (for the ^2H content, cf. footnotes of Table I) was used as free ligand, k_0 decreased significantly (Table I). When the k_0 values involving dissociable protons and deuterons are expressed by $k_{0(\text{H})}$ and $k_{0(\text{D})}$, respectively, the ratio $k_{0(\text{H})}/k_{0(\text{D})}$ was calculated to be ca. 2.0 at 166.4 °C.

On the other hand, in the region $b > 0.1 \text{ M}$, k_0 increases further and the gradient approaches unity (Figure 1). Hence k_0 is written as

$$k_0 = k_m + k_n b \quad (5)$$

Table II. Kinetic Data for the Isotopic Exchange and Racemization of $\text{Cr}(\text{acac})_3$ in Organic Solvents

Reactions	Parameters	Rate constants ^a			$\Delta H^\ddagger / \text{kcal mol}^{-1}$	$\Delta S^\ddagger / \text{cal mol}^{-1} \text{ K}^{-1}$
		157.1 °C	166.4 °C	175.3 °C		
Exchange	$k_i/10^{-5} \text{ s}^{-1}$	0.39 ± 0.30	1.4 ± 0.5	2.8 ± 1.3	38 ± 9	0 ± 2
	$k_w/10^{-4} \text{ M}^{-1} \text{ s}^{-1}$	4.1 ± 0.4	9.4 ± 0.6	17.3 ± 1.8	30 ± 5	-0.5 ± 1.0
	$k_n/10^{-4} \text{ M}^{-1} \text{ s}^{-1}$	1.55 ± 0.15	2.71 ± 0.39	4.66 ± 0.23	22.4 ± 0.7	-25 ± 2
Racemizn	$k/10^{-6} \text{ s}^{-1}$		1.7^b		34.2 ± 0.9	7 ± 2

^a In acetonitrile. ^b In chlorobenzene at 98.2 °C.²

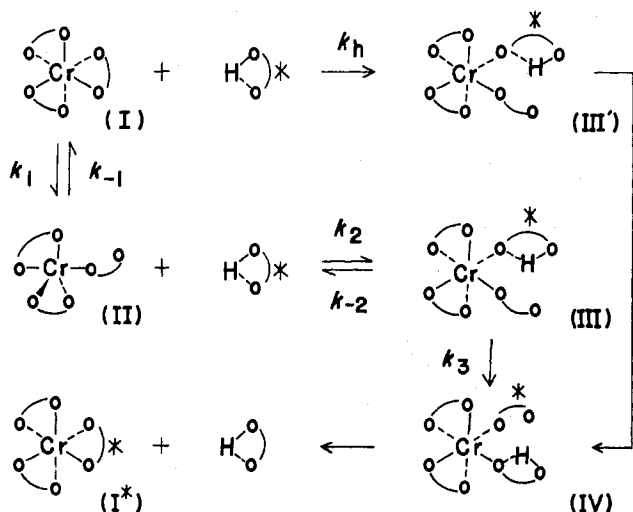


Figure 4. Plausible isotopic exchange mechanism between Cr(acac)₃ and Hacac in acetonitrile. (Asterisks denote ¹⁴C labeling, and arcs represent acetylacetonate. Structural formulas of II, III, III', and IV are provisional.)

In this region, influence of the water concentration is very small as seen in Table I ($[H_2O] = 0.06\text{--}0.13\text{ M}$) and k_h seems to be independent of water concentration.

The activation parameters obtained from the experiments between 155 and 175 °C and the rate constants are summarized in Table II together with those of related reactions. The error was calculated at a 70% confidence level.

Discussion

The dependence of k_0 upon the concentrations of free Hacac and water differs remarkably in the low- and the high-concentration region of free Hacac. The mechanisms of ligand isotopic exchange should be different in these two regions and are discussed separately.

In Low Ligand Concentration Region. Since a significant deuterium isotope effect is observed, proton transfer should be one of the important steps. Equation 3 suggests the presence of a preliminary interaction between the complex and the free Hacac, which approaches saturation when b is more than 0.01 M. If A (630 M⁻¹ at 166.4 °C) stood for the equilibrium constant of a simple intermolecular association between the complex and Hacac, most of the complex would be in the associated form and the ultraviolet absorption spectrum would be changed. Realization of the additivity law between the absorption spectra of the complex and free Hacac rules out such an association.

If the complex I dissociates to give a unidentate ligand and the intermediate II undergoes association with free Hacac to give an associated species III as shown in Figure 4, eq 6 is

$$d[II]/dt = k_1[I] - k_{-1}[II] - k_2[II]b + k_{-2}[III] \quad (6)$$

substantiated. When the rate constant for the change from III and IV is written as k_3 , eq 7 is obtained. When stationary

$$d[III]/dt = k_2[II]b - k_{-2}[III] - k_3[III] \quad (7)$$

states are assumed for the species II and III, both eq 6 and 7 are taken to be equal to zero, to give eq 8 and 9. The

$$[II] = (k_1[I] + k_{-2}[III]) / (k_{-1} + k_2b) \quad (8)$$

$$[III] = k_2[II]b / (k_{-2} + k_3) \quad (9)$$

concentrations of the intermediates II and III should be negligibly small as compared with that of I, and eq 8 is simplified to eq 10. Thus eq 9 is rewritten as eq 11. The

$$[II] = k_1[I] / (k_{-1} + k_2b) \quad (10)$$

$$[III] = k_1k_2[I]b / (k_{-2} + k_3)(k_{-1} + k_2b) \quad (11)$$

rate of isotopic exchange R can be written as eq 12. The

$$R = k_3[III] = k_1k_2k_3[I]b / (k_{-2} + k_3)(k_{-1} + k_2b) \quad (12)$$

exchange rate constant k_0 can be expressed by eq 13, where

$$k_0 = k_1k_3Ab / (k_{-2} + k_3)(1 + Ab) \quad (13)$$

A stands for the ratio k_2/k_{-1} . Equation 13 corresponds to eq 3, and k_m is written as

$$k_m = k_1k_3 / (k_{-2} + k_3) \quad (14)$$

The term Ab indicates the ratio of k_2b/k_{-1} , i.e., ratio of the ease with which intermediate II undergoes association with free Hacac to the ease of restoration of the original complex.

The k_m increases linearly with increase in water concentration less than 0.15 M. This fact can be interpreted either by considering that water participates in the k_3 step and $k_{-2} \gg k_3$ or by assuming the dependence of k_1 upon water concentration. The presence of a significant isotope effect is more reasonably accounted for by the former consideration, and the k_3 step involving proton transfer from the incoming Hacac to the leaving acetylacetonate must play a significant role in determining the rate of present ligand isotopic exchange. The proton transfer may be assisted by the water molecule, and the k_i and k_w terms of eq 4 would correspond to the proton transfer without and with the assistance of the water molecule.

The present kinetic treatment suggests that the change from I to II (Figure 4) is the rate-determining step, and the observed activation parameters mostly reflect those for the k_1 step. Chromium(III) complexes containing the ligands with oxygen as the ligating atom exclusively are believed to undergo ligand substitution mostly via an associative mechanism.¹ The reported activation enthalpies range from 20 to 28 kcal mol⁻¹.¹⁰ The present ΔH^\ddagger values involve large experimental errors due to experimental difficulty (especially that for k_i obtained on the basis of extrapolated intercept). However, they are distinctly larger than the values for the k_h path (vide infra) and the reported values in ref 10. We tend to consider that the cleavage of the Cr-O bond to give II from I takes place by a dissociative mechanism.

In the High Ligand Concentration Region. The linear increase of k_0 with b ($>0.1\text{ M}$) suggests a direct interaction between the free ligand and the original complex (Figure 2). The activation parameters for the k_h path differ significantly from those for the k_i and k_w paths. The remarkably lower ΔH^\ddagger and more negative ΔS^\ddagger indicate an associative attack of the free Hacac upon the original complex to give III', which is similar to III (Figure 4). The ΔH^\ddagger value is also in agreement with the reported values for associative ligand substitution reactions of $[Cr^{III}O_6]$ type complexes.¹⁰ Since k_h is independent of water concentration, the route from III' to I* should proceed without the aid of water. In the low Hacac concentration region the transformation from III to IV accompanied by proton transfer without the aid of water (k_i path) is a minor route, but that from III' to IV seems to proceed much faster. Such a difference might be due to the difference in structure between III and III' or to the presence of a large excess of free Hacac, which can assist the proton transfer through, e.g., an outer-sphere association.

Comparison with Related Reactions. Fay, Girgis, and Klabunde studied the racemization of Co(acac)₃ and Cr(acac)₃ in chlorobenzene in the temperature ranges 79–109 and 96–135 °C, respectively.² Girgis and Fay also studied the racemization and isomerization of *fac*- and *mer*-tris(benzoylacetonato)cobalt(III) in various solvents including chlorobenzene and AN and proposed an intramolecular

bond-rupture mechanism.¹¹ The activation parameters for these changes in chlorobenzene are similar to one another. Thus an intramolecular bond-rupture mechanism can be suggested for the racemization of Cr(acac)₃. The ΔH^\ddagger value for the racemization of Cr(acac)₃ is not very different from our ΔH^\ddagger for the k_i and k_w paths in the low Hacac concentration region (Table II). These ΔH^\ddagger values may reflect the ease of breaking the Cr–O bond, and we may expect a common intermediate II for both racemization and isotopic exchange. The large difference in the first-order rate constants can be accounted for by the contribution of the term $k_3/(k_{-2} + k_3)$ in eq 14.

In the gaseous phase containing 3.5×10^{-5} mol of Cr(acac)₃ and 3.9×10^{-5} mol of [¹⁴C]Hacac l⁻¹, the ligand isotopic exchange was observed in a temperature region over 160 °C. The apparent first-order rate constant with respect to the complex "concentration" is of the order of 10^{-4} s⁻¹ at 190 °C.¹² Not very different data were obtained in a glass vessel and a Teflon-coated metal chamber. Influence of various factors including the pressure and the wall of the vessel should be carefully examined for discussing the mechanism in more detail. However, so far as the observed rate constant is concerned, there seems to be no marked discontinuity between

the isotopic exchange in the gaseous phase and in AN solution.

Among octahedral tris(acetylacetonato) complexes of various metal ions,⁵ the chromium(III) complex gives the most inert example of intermolecular isotopic exchange, i.e., more inert than Co(acac)₃¹³ and [Ge(acac)₃]ClO₄.¹⁴

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Registry No. Cr(acac)₃, 13681-82-8; Hacac, 123-54-6.

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Magnetic Properties of Some Iron(III) Binuclear Complexes in Aqueous Solution

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Magnetic properties of frozen aqueous solutions of two configurationally different iron(III) oxy-bridged dimeric complexes were determined. The compounds may be formulated as *trans*-[(Fe(tetpy))₂O(H₂O)₂]⁴⁺ and *cis*-[(Fe(bmen))₂O(H₂O)₂]⁴⁺, where tetpy and bmen are quadridentate nitrogen ligands with different conjugative capacity, e.g., 2,2':6',2'':6'',2''':-tetrapyridyl and *N,N'*-bis(2-methylpyridyl)ethylenediamine, respectively. The stability of the bridging unit Fe–O–Fe is seen to be [H⁺] dependent only in the case of the *trans* derivative. In weakly acid solutions (pH ~ 5) the oxy-bridged unit of this complex is transformed into a dihydroxy-bridged structure, whose fragmentation occurs only at higher pH values (>6). In contrast, the *cis* derivative retains essentially the original antiferromagnetic character within the whole range of pH explored. The diverse behavior of these complexes in an aqueous medium is briefly discussed in the light of the different stereochemical features.

Introduction

Solution properties of Fe(III) dimeric complexes have received much attention in the last few years either to elucidate the structural features of this type of compound in aqueous medium²⁻⁴ or to investigate their behavior as model systems of naturally occurring materials.^{2c,5} Comparison between solution properties of configurationally different iron(III) derivatives is generally lacking, however, despite the obvious interest in the relationship between stereochemistry and stability as well as reactivity of such compounds.

We have prepared and characterized two novel oxy-bridged Fe(III) binuclear complexes, which exhibit a different configuration depending upon the different conjugative capacity of the quadridentate nitrogen ligands used. In the solid state they may be formulated as *cis*-[(Fe(bmen))₂O(H₂O)₂](SO₄)₂·H₂O (I) and *trans*-[(Fe(tetpy))₂O](SO₄)₂·7H₂O (II) (bmen = *N,N'*-bis(2-methylpyridyl)ethylenediamine and tetpy = 2,2':6',2'':6'',2''':-tetrapyridyl), in which pairs of $S = 5/2$ Fe(III) ions interact antiferromagnetically with $J = -89$ (I) and -83 cm⁻¹ (II), respectively.⁶ Furthermore, evidence has been produced that both dimeric species are stable in acid solution but complex II undergoes a monomer–dimer equilibrium, at variance with complex I,⁶ at pH around neutrality.

In order to explain this peculiar behavior, an extensive study on the magnetic properties of frozen aqueous solutions (25–250

K) at various pH's was undertaken. It is the aim of this paper to present the results of this investigation which definitely indicate that, upon increase in pH, the dimeric complexes behave differently.

Experimental Section

Materials. [(Fe(bmen))₂O(H₂O)₂](SO₄)₂·H₂O and [(Fe(tetpy))₂O](SO₄)₂·7H₂O were prepared as described.⁶ Measurements were performed on freshly prepared aqueous samples using doubly distilled water with a conductivity less than 2×10^{-6} Ω⁻¹ cm⁻¹ (20 °C). Concentrations (based on molecular weights of half the dimers) never exceeded 1.2×10^{-2} and 8.5×10^{-3} M, respectively, since these figures almost represent the maximum solubility in water at room temperature of the complexes.

Methods. Samples for magnetic susceptibility measurements had typical volumes in the range of 0.1 ml. Total volume susceptibilities of the frozen solutions were measured by a novel oscillating-sample version⁷ of the superconducting magnetometer,⁸ within the temperature range of 25–250 K. As previously shown,⁷ the method effectively nulls any contribution from the holder. Paramagnetic and antiferromagnetic contributions show up in the raw data as deviations from the dominant diamagnetic background of the frozen solution. The two contributions can be easily separated when the absolute value of the antiferromagnetic coupling constant J is of the order of 70 cm⁻¹, since in this case the antiferromagnetic contribution in the lowest temperature range explored is negligible. When the coupling constant J is smaller, a trial and error procedure of fitting on raw data must be followed. Paramagnetic and antiferromagnetic contributions were reduced to