Stereoselectivity in Octahedral Complexes. I. Cobalt(III) and Vanadium(III) Complexes of 3-Substituted Camphor

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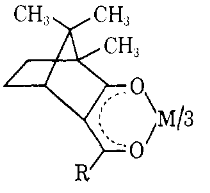
Abstract: Six-coordinate Co(III) and V(III) complexes of (+)- and (−)-3-hydroxymethylenecamphor and (+)-3-acetylcamphor have been investigated. Marked stereoselectivity in formation of the diastereomeric complexes is observed in all cases. For Co(III) complexes it is shown by ORD that the Λ configuration is preferred by (+) ligands, whereas the Δ configuration is more stable for (−) ligands. The same is believed to hold true for the V(III) complexes. Isotropic pmr shifts for the V(III) complexes allow resolution of the resonance signals arising from Δ and Λ species. Integration of these signals provides a means of determining the Δ:Λ ratio, which is 0.31 ± 0.02 for the complex of (+)-3-acetylcamphor at 29°. Assignment of the pmr signals of the V(III) complexes is discussed in terms of the probable mechanism of spin delocalization.

It has been recognized for some time that the diastereomeric complexes formed upon treating transition metal ions with optically active ligands may exist in nonstatistical proportions. This stereoselectivity is particularly pronounced in tris complexes of bidentate ligands.[1] A conformational analysis by Corey and Bailar indicates that the ratio of Δ to Λ diastereomers[2] in tris complexes of 1,2-diamines is governed by their relative inter- and intraligand nonbonded interactions.[3]

Numerous examples of stereoselective behavior in tris complexes of Co(III), Cr(III), Rh(III), and Pt(IV) are known.[1] The ligands generally used are 1,2-diamines or α-amino acids, and the puckered chelate rings formed by these ligands presumably play a significant role in the stereoselective formation of complexes. The question arises as to whether stereoselectivity would be found in tris complexes of ligands which form planar chelate rings. Optically active ligands of this type are not common. One group of ligands that satisfies these requirements is the 3-substituted camphors. The complexes are of structure I and may be prepared from (+)- or (−)-camphor. These ligands are especially suited for stereoselectivity studies because of the expected interligand steric interactions between methyl groups; furthermore the absolute configuration of (+)-camphor is known.[4]



I

Metal complexes of (+)-hydroxymethylenecamphor (I, R = H), hereafter abbreviated +hmc, have been known for many years,[5] and stereoselectivity has been observed for the tris complexes of Co(III) and Cr(III).[6] In a recent reinvestigation of the tris +hmc complexes of Co(III), Rh(III), and Cr(III), Dunlop, Gillard, and Ugo[7] pointed out that +hmc lacks a twofold axis of symmetry, and geometrical isomers may occur in addition to the Δ and Λ optical isomers. Four diastereomeric species are possible: Λ-*cis*-[M(+hmc)$_3$], Λ-*trans*-[M(+hmc)$_3$], Δ-*cis*-[M(+hmc)$_3$], and Δ-*trans*-[M(+hmc)$_3$]. Two diastereomers were isolated for the Co(III) complex by column chromatography and labeled Λ-*cis*-[Co(+hmc)$_3$] and Λ-*trans*-[Co(+hmc)$_3$] on the basis of nmr and ORD data. Only one diastereomer was obtained for the Cr(III) complex, but for Rh(III) the diastereomers Λ-*trans*-[Rh(+hmc)$_3$] and Δ-*trans*-[Rh(+hmc)$_3$] were obtained. In each case the most abundant species had Λ-*trans* geometry. The occurrence of a Δ species for Rh(III) was attributed to the kinetic inertness of the complex once it is formed.

One of the principal difficulties in investigating the stereoselective behavior of metal complexes lies in detecting the species present and measuring their relative abundances. Past work has relied largely upon the classical methods of isomer separation such as fractional crystallization or chromatography. Such techniques are impractical for labile species. Nmr has been used a number of times for detecting *cis* and *trans* geometrical isomers of tris complexes in solution.[8] The relative abundances of the *cis* and *trans* species may be determined by signal integration if their respective resonance signals are well separated. The isotropic pmr shift phenomenon,[9] which serves to amplify chemical shift differences by one or two orders of magnitude, has been used recently to investigate the occurrence of geometrical isomerism in several series of tris complexes of V(III).[10] Nmr spectra of diastereo-

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[1] For a recent review, see J. H. Dunlop and R. D. Gillard, *Advan. Inorg. Chem. Radiochem.*, **9**, 185 (1966).

[2] The nomenclature used in this paper is that proposed by T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961), for tris complexes, where Δ and Λ denote right- and left-hand helicity, respectively, about the C_3 (or pseudo-C_3) axis.

[3] E. J. Corey and J. C. Bailar, Jr., *ibid.*, **81**, 2620 (1959).

[4] F. H. Allen and D. Rogers, *Chem. Commun.*, 837 (1966).

[5] (a) A. W. Bishop, L. Claisen, and W. Sinclair, *Ann.*, **281**, 314 (1894); (b) I. Lifschitz, *Rec. Trav. Chim.*, **41**, 627 (1922); (c) I. Lifschitz, *Z. Physik. Chem.*, **105**, 27 (1923).

[6] (a) I. Lifschitz, *Rec. Trav. Chim.*, **69**, 1495 (1950); (b) S. F. Mason *Quart. Rev.* (London), 17, 20 (1963).

[7] J. H. Dunlop, R. D. Gillard, and R. Ugo, *J. Chem. Soc.*, *A*, 1540, (1966).

[8] (a) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, 84, 2303 (1962); (b) R. C. Fay and T. S. Piper, *ibid.*, **85**, 500 (1963); (c) R. C. Fay and T. S. Piper, *Inorg. Chem.*, 3, 348 (1964); (d) A. Chakravorty and R. H. Holm, *ibid.*, 3, 1521 (1964); (e) A. Chakravorty and K. C. Kalia, *ibid.*, **6**, 690 (1967).

[9] D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonance*, 1, 103 (1965).

[10] (a) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *J. Am. Chem. Soc.*, **89**, 6472 (1967); (b) *Inorg. Chem.*, **6**, 1315 (1967); (c) *ibid.*, **6**, 1607 (1967).

meric complexes are different in principle but are often not resolvably different for diamagnetic systems. It appeared that the pmr shift effect could be used to amplify normally small chemical shift differences between corresponding nuclei on diastereomeric complexes, thus making it possible to assess stereoselectivity in certain paramagnetic complexes without having to isolate the diastereomers.

As part of a general investigation of stereoselectivity in tris complexes of bidentate ligands capable of forming planar chelate rings, we have confirmed the observations of Dunlop, *et al.*,[7] for Co(+hmc)$_3$ and have examined the stereoselective behavior of the Co(III) complexes of −hmc and (+)-3-acetylcamphor (I, R = CH_3, abbreviated +atc). The V(III) complexes of +hmc, −hmc, +,−hmc, and +atc were prepared in order to assess the utility of the isotropic pmr shift effect for stereoselectivity studies.

Experimental Section

Preparation of Ligands. Hydroxymethylenecamphor was prepared using (+)-, (−)-, and (+,−)-camphor according to the procedure given by Bishop, Claisen, and Sinclair.[5a] (+)-3-Acetylcamphor was prepared by Brühl's method.[11]

Preparation of Cobalt(III) Complexes. Co(+hmc)$_3$ and Co(−hmc)$_3$ were prepared by the method described by Dunlop, *et al.*[7] Co(−hmc)$_3$ appears to be identical with Co(+hmc)$_3$ in all respects except for its optical rotatory behavior. Both complexes were separated into *cis* and *trans* forms using an alumina chromatographic column with benzene as the eluent. The *cis* species were obtained only in small quantities and were not investigated further.

Co(+atc)$_3$ was prepared using a procedure similar to that used for Co(+hmc)$_3$. The oily, green crude product was dissolved in a small quantity of ethyl acetate from which it crystallized upon cooling. The crystalline material was dissolved in benzene and chromatographed on alumina to yield analytically pure samples of the *cis* and *trans* forms. These were identified by their nmr spectra; one acetyl methyl resonance was observed for the *cis* complex whereas three signals appeared in this range for the *trans* complex.

Preparation of Vanadium(III) Complexes. In solution the V(III) complexes are extremely sensitive to oxidation by air and must be handled in a rigorously oxygen-free atmosphere. All preparations were carried out *in vacuo* or under nitrogen purified by a chromous chloride train.

V(+hmc)$_3$, V(−hmc)$_3$, and V(+,−hmc)$_3$ were prepared using a procedure analogous to that described in the preparation of tris-(2-methyl-3-oxobutanalato)vanadium(III).[10b] The pale yellow crude products were dried *in vacuo*, then recrystallized several times from small volumes of *n*-heptane or *n*-pentane. Low temperatures (−20°) were necessary to induce crystallization.

V(+atc)$_3$ was prepared by the same procedure, except that a 1:1 water–ethanol mixture was used as the reaction medium. In preparing the deuterium-substituted complex, V(+atc-d_3)$_3$, the following procedure was used. The acetyl methyl group of +atc was deuterated by refluxing +atc for 12 hr in deuterium oxide containing a small amount of ethanol and a trace of sodium carbonate. Deuteration was found by nmr to be about 85% complete. The complex was prepared by adding vanadium trichloride, more ethanol, and more sodium carbonate to the deuterium oxide solution. The work-up is as described above for V(+hmc)$_3$.

Physical Measurements. Electronic absorption spectra were recorded on a Cary Model 14 spectrophotometer. ORD spectra were obtained at 25° on chloroform solutions of the complexes using a Cary Model 60 spectrometer. Magnetic susceptibility measurements on solid samples of the V(III) complexes were made at room temperature by the Gouy method. Nmr spectra were obtained using Varian Models A-60 and HA-100 spectrometers. Chemical shifts were measured by sidebanding. Chloroform was used as the internal reference since the signal of TMS overlapped some of the signals from the complexes. All solution measurements on V(III) complexes were performed under rigorously oxygen-free conditions.

Table I. Results of Elemental Analyses

	Calculated, %		Found, %	
	C	H	C	H
trans-[Co(−hmc)$_3$]	66.45	7.57	66.60	7.57
trans-[Co(+atc)$_3$]	67.69	8.04	67.95	8.06
cis-[Co(+atc)$_3$]	67.69	8.04	67.75	8.03
V(+hmc)$_3$	67.33	7.71	67.15	7.59
V(−hmc)$_3$	67.33	7.71	67.25	7.49
V(+,−hmc)$_3$	67.33	7.71	67.24	7.75
V(+atc)$_3$	68.55	8.14	68.69	8.22

Results and Discussion

Cobalt(III) Complexes. Previous studies have indicated that the most abundant diastereomer of Co(+hmc)$_3$ has Λ-*trans* geometry.[7] Since the configuration (Δ or Λ), adopted by three optically active ligands about a metal ion is often a function of the chirality of the ligands, we prepared Co(−hmc)$_3$ in order to determine whether one of the Δ diastereomers would predominate. The complex was separated into *cis* and *trans* forms by chromatography on alumina. The *trans* complex proved to be in greater abundance as was the case for Co(+hmc)$_3$. A negative Cotton effect is found in the ORD spectrum of *trans*-[Co(−hmc)$_3$] in the region of the ligand field absorption band at 16,500 cm^{-1} which is assigned as the $^1A_1 \rightarrow {}^1E$ transition in effective D_3 symmetry.[12,13] Positive Cotton effects for this transition in tris(β-diketonato)cobalt(III) complexes are diagnostic of the Λ configuration.[13] Thus we may assign the Δ configuration to *trans*-[Co(−hmc)$_3$] if it is assumed that deviation from D_3 symmetry is small. The ORD curves of Λ-*trans*-[Co(+hmc)$_3$] and Δ-*trans*-[Co(−hmc)$_3$] are enantiomeric (see Figure 1). These results clearly demonstrate that the *levo* ligand preferentially stabilizes the Δ complex.

The stereoselective effects of +atc appear to be similar to those of +hmc. Co(+atc)$_3$ may be separated into two species chromatographically, the more abundant one being Λ-*trans*-[Co(+atc)$_3$] as deduced from ORD (see Figure 1) and nmr spectra. Similarly, the lesser abundant product is the Λ-*cis*-[Co(+atc)$_3$] diastereomer.

At present there is no evidence for the existence of Δ-*cis*- or -*trans*-[Co(+hmc)$_3$], Λ-*cis*- or -*trans*-[Co(−hmc)$_3$], or Δ-*cis*- or -*trans*-[Co(+atc)$_3$]. However, this does not preclude the presence of these species in small quantities in solutions with the more stable diastereomers, perhaps in equilibrium with the latter. There is some evidence for an equilibrium of this type in solutions of Cr(+hmc)$_3$,[7] and an equilibrium between Δ and Λ isomers of tris((−)-propylenediamine)cobalt(III) has been effected by means of an activated charcoal catalyst.[14] The occurrence of some of the above diastereomers for the V(III) complexes of +hmc, −hmc, and +atc (*vide infra*) lend support to their existence in the Co(III) complexes.

Vanadium(III) Complexes. The V(III) complexes of +hmc, −hmc, +atc, and +,−hmc were prepared. Results of elemental analyses are given in Table I;

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[11] J. W. Brühl, *Ber.*, **37**, 746 (1904).

[12] T. S. Piper, *J. Chem. Phys.*, **35**, 1240 (1961).

[13] A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

[14] F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

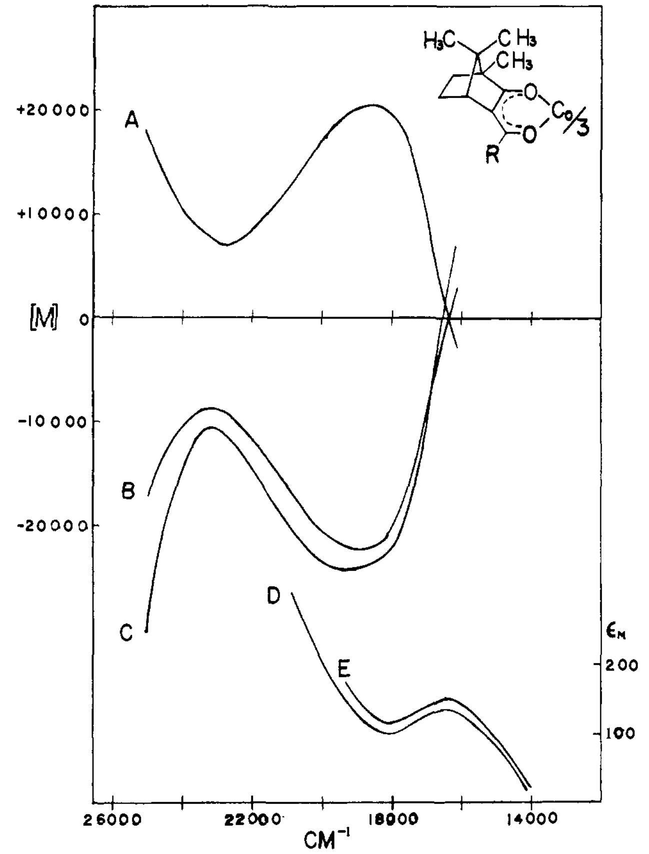

Figure 1. Visible absorption spectra and ORD spectra of Co(III) complexes in chloroform solution: (A) ORD of *trans*-[Co(−hmc)$_3$]; (B) ORD of *trans*-[Co(+hmc)$_3$]; (C) ORD of *trans*-[Co(+atc)$_3$]; (D) visible spectrum of *trans*-[Co(+atc)$_3$]; (E) visible spectrum of *trans*-[Co(−hmc)$_3$].

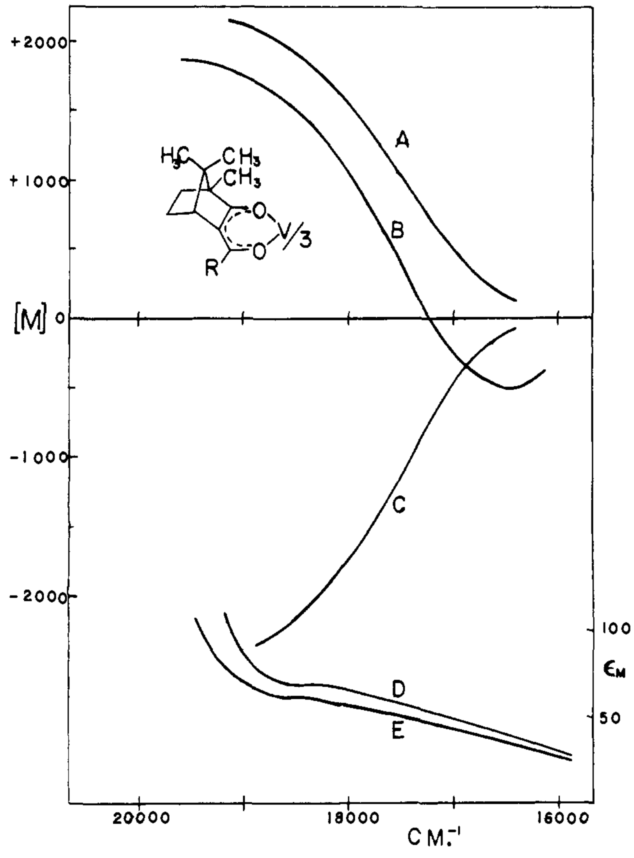

Figure 2. Visible absorption spectra and ORD spectra of V(III) complexes in chloroform solution: (A) ORD of V(+hmc)$_3$; (B) ORD of V(+atc)$_3$; (C) ORD of V(−hmc)$_3$; (D) visible spectrum of V(+hmc)$_3$; (E) visible spectrum of V(+atc)$_3$.

magnetic moments of solid samples at room temperature are all in the range of 2.80–3.00 BM as expected. In solution, these complexes are rapidly oxidized by air, so solutions must be handled in closed containers *in vacuo* or under a blanket of purified nitrogen. No attempts were made to separate the products into *cis* and *trans* forms as was done for the corresponding Co(III) complexes.

The chelate rings are believed to be nearly planar in complexes of structure I, and stereoselectivity must occur as a result of interligand steric interactions between methyl groups. These interactions should be essentially the same for a series of complexes of the same ligand with different metal ions of similar size. If a comparison is made of complexes for which the distribution of diastereomers is thermodynamically controlled, the most abundant diastereomers should have the same absolute configuration. Thermodynamic control is believed to predominate for Co(+hmc)$_3$,[7] and it is expected to occur for the labile complexes of V(III). Thus, for a given ligand the most stable V(III) complex should have the same absolute configuration as the most stable Co(III) complex.

Optical Rotatory Dispersion. The ORD spectra of V(+hmc)$_3$ and V(−hmc)$_3$ in chloroform solution are enantiomeric (see Figure 2). Since each of these solutions contains several diastereomers in different concentrations (*vide infra*), the observed rotations are the combined rotations of the individual species. The occurrence of mirror-image ORD curves indicates that for each component of one solution there exists in the other solution its enantiomer at the same relative concentration.

On basis of the reasoning given above, it is proposed that the predominant diastereomer of V(+hmc)$_3$ has the Λ configuration and that of V(−hmc)$_3$ has the Δ configuration. Similarly, the most stable diastereomer of V(+atc)$_3$ probably has Λ stereochemistry. The ORD curve of V(+atc)$_3$ is similar to that of V(+hmc)$_3$ (see Figure 2).

Nuclear Magnetic Resonance. Tris complexes of V(III) often show large isotropic pmr shifts with well-resolved signals.[10,15,16] If the ligands lack a twofold axis of symmetry, *cis* and *trans* geometrical isomers are possible and may be detected by nmr.[10] If all three ligands are identical, the *cis* complexes possess a C_3 axis, and corresponding atoms on different ligands are related by symmetry. Thus one resonance signal is expected for each kind of proton. On the other hand, *trans* complexes are asymmetric and three resonance signal are expected for each kind of proton. A mixture of *cis* and *trans* isomers is therefore expected to give four resonance signals for each kind of proton. In a statistical mixture the *cis*:*trans* ratio is 1:3, and all four signals will be equally intense. Deviations from the statistical ratio may be measured by signal integration. If, in addition to lacking a C_2 axis, the ligands

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(15) A. Forman, G. N. Murrell, and L. E. Orgel, *J. Chem. Phys.*, 31, 1129 (1959).

(16) D. R. Eaton, *J. Am. Chem. Soc.*, 87, 3097 (1965).

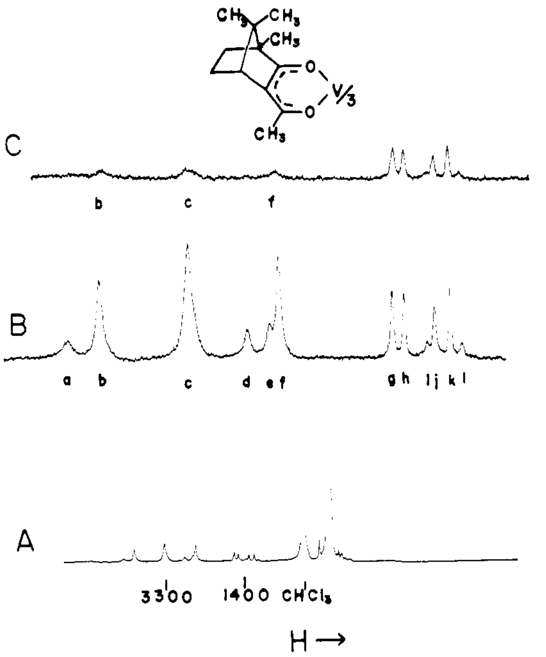


Figure 3. Proton resonance spectra of V(+atc)$_3$ in chloroform solution at 29°: (A) complete spectrum (frequencies show are chemical shifts at 100 MHz relative to chloroform); (B) expansion of low-field region; (C) low-field region of sample partially deuterated at the acetyl methyl.

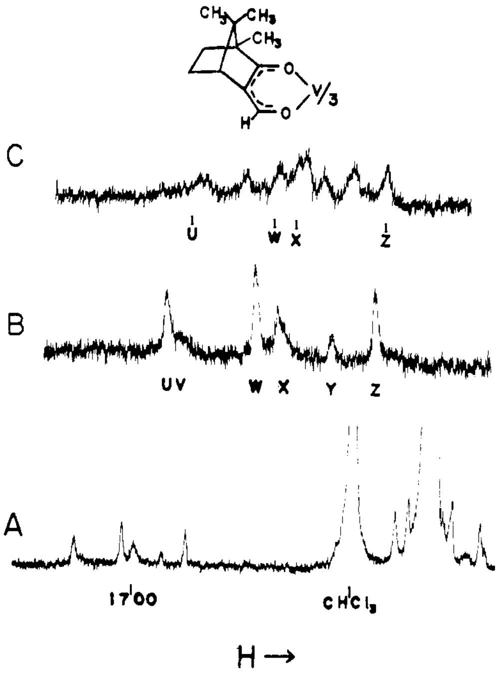


Figure 4. Proton resonance spectra of V(hmc)$_3$ in chloroform solution at 29°: (A) spectrum of V(+hmc)$_3$ at 100 MHz exclusive of high-field region (frequency shown is the chemical shift relative to chloroform); (B) expansion of low-field region of A; (C) low-field region of spectrum of V(+,−hmc)$_3$ (recorded at a slightly different scan rate than B).

are dissymmetric and of same chirality, four diastereomers are possible (see introductory section), and as many as eight resonance signals may be observed for each kind of proton. Integration of the signals would provide a means of determining the Δ:Λ ratio in addition to *cis*:*trans*.

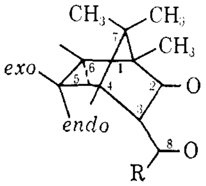
The pmr spectrum of V(+atc)$_3$ at 100 MHz (Figure 3A) consists of an intense multiple signal centered around 600 Hz upfield from the chloroform reference signal and two well-separated sets of signals centered around 1400 and 3300 Hz downfield from chloroform. Of principal interest are the downfield signals, and these are shown expanded in Figure 3B. The ratio of the over-all area of signals a–f to the area of signals g–l is 3:1. Partial deuteration of the acetyl methyl group in this complex results in a marked decrease in signals a–f (Figure 3C). It follows that signals a–f arise from the acetyl methyl and that signals g–l are due to a single kind of proton. The acetyl methyl signals consist of three strong resonances (b, c, f) and three weaker resonances (a, d, e). Signal c contains twice the area of either signals b or f and is believed to consist of two coincident resonances. These four intense signals are assigned to the *cis* and *trans* forms of Λ-[V(+atc)$_3$]. It appears that these *cis* and *trans* species are present in approximately the statistical ratio since all four signals have about the same area. The accuracy of integration is not sufficient to detect small deviations from this ratio. The weaker signals are attributed to Δ-[V(+atc)$_3$]. It is apparent that Δ-*trans*-[V(+atc)$_3$] is present since more than one signal is observed. A fourth weak signal cannot be found, and it is not clear whether the Δ-*cis* diastereomer is absent or whether the fourth resonance lies under one of the stronger signals. The latter possibility would require a nonstatistical *cis*:*trans* ratio for the Λ diastereomers, since the area under one of the strong signals would include the area of the weaker signal. Interligand steric interactions are expected to vary considerably from one diastereomer to another, and there is no apparent reason why the *cis*:*trans* ratio for the Δ and Λ configurations should be equal. The ratio of Δ-*trans*-[V(+atc)$_3$] to Λ-*trans*-[V(+atc)$_3$], obtained from the average of a number of integrations of the acetyl methyl signals, is found to be 0.31 ± 0.02 at 29°. For the Λ-*trans* $\leftrightarrows$ Δ-*trans* equilibrium, $K_{eq} = 0.31$ and $\Delta G = 700$ cal/mole. Attempts to observe the temperature dependence of the equilibrium have failed thus far owing to poor signal resolution at higher temperatures.

Signals g–l consists of four intense resonances (g, h, j, k) and two clearly discernible weaker resonances (i, l). The four strong resonances are assigned to the *cis* and *trans* forms of Λ-[V(+atc)$_3$]; the weaker signals are attributed to Δ-*trans*-[V(+atc)$_3$]. A third weak signal is believed to lie under the strong signal g, because this signal has more intensity than h, j, or k, and, if it is reduced by the intensity of a weak signal, its area matches that of the other three. Again there is no evidence for Δ-*cis*-[V(+atc)$_3$]. The Δ-*trans* to Λ-*trans* ratio from this set of signals is 0.34 ± 0.05.

The pmr spectrum of V(+hmc)$_3$ in chloroform solution at 100 MHz is shown in Figure 4A. In the high-field region the spectrum is qualitatively similar to that of V(+atc)$_3$. In the low-field region appears a set of signals centered around 1700 Hz relative to chloroform. The spectrum of V(−hmc)$_3$ is identical with that of V(+hmc)$_3$ with respect to signal positions and relative intensities, indicating that the solutions are enantiomeric. The low-field resonance signals are shown expanded in Figure 4B. Assignment of the signals is more difficult than for V(+atc)$_3$ because of the overlapping of several signals under envelopes u, v and w, x. The most reasonable assignments consistent with the relative signal areas are as follows. The four peaks u, w, x, and z arise from *cis* and *trans* forms of Λ-[V(+hmc)$_3$]. Resonances v and y are attributed to Δ-[V(+hmc)$_3$]. Integration of envelope w, x indicates it may contain two weak signals having about the same area as y in addition to the two resonances assigned to the Λ diastereomers. Thus it would appear that for V(+hmc)$_3$ all four diastereomers are present. Accurate estimates of the *cis*:*trans* ratios could not be made; however, if it is assumed that signals z and y arise from Λ-*trans*-[V(+hmc)$_3$] and Δ-*trans*-[V(+hmc)$_3$], the Δ-*trans*:Λ-*trans* ratio is about 0.39.

The pmr spectrum of the low-field signals of V(+, −hmc)$_3$, prepared from racemic hydroxymethylenecamphor, is shown in Figure 4C. Assuming a random distribution of ligands, eight enantiomeric pairs of complexes are possible. Since only two of these pairs have a C_3 axis of symmetry, 20 resonance signals are possible for each kind of proton. Although an appreciable number of signals may be discerned, the chemical shift differences are too small to permit an analysis of the spectrum. The pmr spectrum obtained from a 1:1 mixture of V(+hmc)$_3$ and V(−hmc)$_3$ in chloroform is identical in all respects with that of V(+, −hmc)$_3$, indicating that free exchange of ligands occurs during the time interval required to prepare the sample and record the spectrum (<1 hr).

Spin Delocalization in V(III) Complexes. The relative signs and magnitudes of pmr shifts in the V(III) complexes are indicative of the mechanism of spin delocalization. The isotropic shifts observed in other tris(β-diketonate)vanadium(III) complexes are predominately contact shifts arising from the presence of α spin in the lowest unfilled MO of the ligand. A metal-to-ligand charge transfer is responsible for placing spin on the ligand.[10b,15,16] The same spin-transfer mechanism appears to be dominant in the V(III) complexes of hmc and atc.[17] This mechanism is expected to produce large positive π spin densities at carbons 2 and 8 and a smaller negative π spin density at carbon 3 in II.[10b,16]



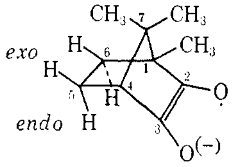
II

The principal evidence for this mechanism derives from the fact that the 8-methyl protons in complexes of atc have negative pmr shifts. A large positive contact shift is expected for the 8-H in complexes of hmc, and several very broad signals around 75–100 ppm upfield of chloroform for V(+hmc)$_3$ are believed to be due to the 8-H. A methyl substituent at carbon 3 is expected to be shifted upfield by this mechanism, and 4-H should appear at high field. Consistent with this expectation is the appearance of several weak signals slightly upfield of the intense resonance attributed to the 1- and 7-methyls. These signals are likely due to 4-H, but the possibility that they arise from 5-*exo*-H cannot be excluded (see below). Relatively small contact shifts are expected for 4-H since it lies nearly in the nodal plane of the p–π orbital of carbon 3. The very strong resonances about 600 Hz upfield of chloroform are attributed to the 1- and 7-methyls which show very small shifts. If dipolar shifts are unimportant in these complexes,[16] observed shifts for the 5- and 6-methylene protons muct be contact shifts which result from spin delocalization through σ bonds. The efficiency of this process is indicated by the magnitudes of long-range epr coupling constants in bicyclic semidiones[18,19] such as the reduction product, III, of camphorquinone. The spin in these systems resides in the lowest unfilled MO, and the observed coupling constants for 5(6)-*exo*-H and 5(6)-*endo*-H are 3.01 and 0.22 G, respectively.[18] Recently, extended Hückel molecular orbital theory has been shown to give good agreement with these values.[20]

Table II. Isotropic Shifts of Low-Field Signals in Tris Complexes of Vanadium(III) at 100 MHz[a]

Complex	C–H	C–CH$_3$
V(+hmc)$_3$	−1865 (z) −2050 (y) −2270 (x)[b] −2365 (w)[b] −2680 (v) −2740 (u)	
V(+atc)$_3$	−1670 (l)	−3100 (f)
	−1760 (k)	−3170 (e)
	−1880 (j)	−3360 (d)
	−1940 (i)	−3840 (c)[b]
	−2140 (h)	−4570 (b)
	−2320 (g)[b]	−4830 (a)

[a] Frequencies shown are in Hz relative to the free ligand resonance, assuming the chloroform reference signal does not receive a significant pmr shift due to solvent–solute association. Alphabetical symbols used to label the resonances correspond to those used in Figures 3 and 4. All measurements were made at 29°. [b] Signal envelope is believed to contain more than one resonance.



III

A simple Hückel MO calculation indicates positive spin density should occur in the p–π orbitals of carbons 2 and 3 in III. Positive spin density is believed to occur also in the p–π orbital of carbon 2 in V(III) complexes of II. Thus by simple analogy, the contact shift of 6-*exo*-H should be much larger than that of 6-*endo*-H.[21] The ligands II do not have the symmetry of semidione III, and negative spin density is believed to occur at carbon 3. The relative magnitudes of contact shifts in other tris(β-diketonato)vanadium(III) complexes indicate that the absolute value of spin density at carbon 3 should be less than that at carbons 2 and 8. Thus the

(17) The results of an extended Hückel MO calculation indicate that the lowest unfilled MO in these ligands is composed mainly of π-oriented atomic orbitals of the chelate ring atoms.

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(21) An extended HMO calculation on II (with the methyls replaced by H and R = H) shows a difference of an order of magnitude in the coefficients of 6-*exo*-H and 6-*endo*-H (*exo* > *endo*) in the lowest unfilled MO which is believed to contain the spin.

5-*exo*-H in II should receive smaller spin density than 6-*exo*-H, and also should show a contact shift of the opposite sign. Much smaller shifts are expected for 5-*endo*-H. The largest observed pmr shifts, excluding those of 8-H and 8-CH_3, in the V(III) complexes of hmc and atc are those of signals u–z and g–l, respectively (see Figures 3 and 4). It has been demonstrated that these signals arise from a single kind of proton, and, on basis of the argument given above, they are assigned to 6-*exo*-H. The other three methylene signals are probably under the envelope of the 1- and 7-methyl resonances.

In summary it can be said that a high degree of stereoselectivity is induced by the ligands in complexes I; the chirality of the predominant diastereomer is determined by the chirality of the ligands. For Co(III) complexes the degree of stereoselectivity is not known. However, for the V(III) complexes it has been shown that stereoselectivity is not complete and that the extent of stereoselectivity may be measured by nmr signal integration in some cases. We are presently engaged in investigating complexes of other dissymmetric ligands with several metal ions in order to assess the effects of increasing or decreasing interligand interactions on the extent of stereoselectivity.

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Kinetics of the Addition of Hydridopentacyanocobaltate(III) to Some α,β-Unsaturated Compounds[1]

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Abstract: The kinetics of the addition of $Co(CN)_5H^{3-}$ to various α,β-unsaturated compounds, $CH_2{=}C(R)X$ (where R = H or CH_3 and X = CN, COOH, COO^-, C_6H_5, $CH{=}CH_2$, α-C_5H_4N, or α-$C_5H_4NH^+$), to yield adducts of the type $Co(CN)_5C(CH_3)(R)X^{n-}$ have been examined. Each reaction was found to exhibit second-order kinetics in accord with the rate law, $k[Co(CN)_5H^{3-}][CH_2{=}C(R)X]$. The values of k, determined in 50 vol. % aqueous methanol, at 25° and 0.5 M ionic strength, ranged from $1.5 \times 10^{-3}\ M^{-1}\ sec^{-1}$ for $CH_2{=}CHCOO^-$ to $4.7 \times 10^{2}\ M^{-1}\ sec^{-1}$ for $CH_2{=}CHC_5H_4NH^+$. The rates of reaction were found to be independent of the concentration of added CN^- and (except for acrylate and 2-vinylpyridine where protonation of the substrate to the more reactive acid form resulted in an increase in rate below pH 8) of the pH of the solution. The significance and mechanistic implications of the kinetic results are discussed.

In this paper we describe an investigation of the kinetics of the addition of hydridopentacyanocobaltate(III), $Co(CN)_5H^{3-}$ (hereafter referred to as CoH), to various α,β-unsaturated compounds, $CH_2{=}C(R)X$, where R = H or CH_3 and X = CN, COOH, COO^-, C_6H_5, $CH{=}CH_2$, α-C_5H_4N, or α-$C_5H_4NH^+$. These reactions yield, initially at least, adducts of the type $Co(CN)_5C(CH_3)(R)X^{n-}$ (hereafter referred to as $CoC(CH_3)(R)X$) in accord with eq 1.

$$Co(CN)_5H^{3-} + CH_2{=}C(R)X \longrightarrow Co(CN_5)C(CH_3)(R)X^{n-} \quad (1)$$

Ever since they were first described by Kwiatek and his coworkers,[2-5] the study of these reactions has attracted considerable interest. Contributing to this interest is the role played by such reactions in the mechanism of the $Co(CN)_5{}^{3-}$-catalyzed homogeneous hydrogenation of unsaturated compounds,[4,5] as well as the more general widespread current interest in the whole class of insertion reactions to which the present examples belong.[6] While most of the earlier investigations of the addition reactions of CoH have been concerned primarily with their stoichiometry and with characterization of the organocobalt adducts, two recent papers, which appeared while the present investigation was in progress, report some kinetic results. The first of these by Jackman, Hamilton, and Lawlor[7] lists half-lives at a fixed concentration of reactants for the reactions of CoH with acrylate and various other α,β-unsaturated acids. The other paper, by Burnett, Connolly, and Kemball,[8] describes a detailed investigation of the $Co(CN)_5{}^{3-}$-catalyzed hydrogenation of 1,3-butadiene including kinetic measurements on the addition of CoH to butadiene and on the subsequent rearrangements of the adduct. The present paper reports some further kinetic measurements on these reactions as well as on the reactions of CoH with a number of other substrates.

Experimental Section

Materials. Butadiene (Matheson CP Grade) was used without purification. The other unsaturated substrates (sources in paren-

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