Chiral Chelates with Chiral Ligands. The Stereoisomers of Tris[(+)-3-acetylcamphorato]cobalt(III)[1]

By CHARLES S. SPRINGER, Jr.,[*2] ROBERT E. SIEVERS, and BINYAMIN FEIBUSH

The equilibrium mixture of the four diastereoisomers of tris-[(+)-3-acetylcamphorato]cobalt(III) at 60° in C_6H_6 has been found to contain 45.2 mol % Λ-trans, 31.3 mol % Δ-trans, 16.4 mol % Λ-cis, and 7.0 mol % Δ-cis isomer. These values indicate that, contrary to previous statements in the literature, the 3-acylcamphorato ligand exhibits only slight thermodynamic stereoselectivity in tris complexes. The four isomers have been separated and characterized individually by ¹H nmr, ORD, and CD. A study of their CD curves reveals that a significant vicinal effect is extant in the visible region of the spectrum and that it is roughly additive to the configurational effect.

The two main factors which historically have been of interest in the study of chiral chelates with chiral ligands are (1) the extent of stereoselectivity[3] exhibited by the chelate and (2) the contribution to the optical activity of the metal transitions made by the presence of chirality in the ligand, the vicinal effect.[4]

The majority of bidentate chiral ligands which have been employed in such studies are 1,2-diamines or α-amino acid anions. Another type of bidentate chiral chelating ligand has been intimately connected with the development of such studies since their very beginnings. This is the β-keto enolate produced by the acylation of camphor in the 3 position (the (+) form is shown).
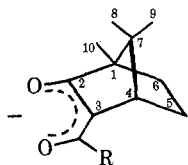
The formyl derivative (R = H), abbreviated in the literature as oca, for oxymethylenecamphor, or hmc, for hydroxymethylenecamphor, was first prepared and used as a ligand in 1894.[5] The spectra and mutarotations of the complexes of a number of metals with the benzoyl (R = C_6H_5) derivative were reported by Lowry and coworkers.[6] Although they claimed the detection of stereoisomers of the bis(benzoylcamphor)beryllium-(II)[6b,e] and tris(benzoylcamphor)aluminum(III)[6e,f] complexes, the first systematic investigations into the stereoselectivity caused by these bulky chiral ligands were begun by Lifschitz.[7] He reported the preparation

of only one isomer each of the Co(III) and Cr(III) tris complexes using the (+)hmc ligand. These were (−)Co((+)hmc)₃ and (+)Cr((+)hmc)₃.[7b] If only one chiral form of the ligand is used, there are four possible diastereomers, for example, Λ-*trans*-M((+)hmc)₃, Λ-*cis*-M((+)hmc)₃, Δ-*trans*-M((+)hmc)₃, and Δ-*cis*-M((+)-hmc)₃.

Since Lifschitz observed no Cotton effect in the visible region of the spectra of compounds such as Co-((+)hmc)₂·2H₂O and Ni((+)hmc)₂·2H₂O,[7b] he concluded that any ligand such as this, in which the asymmetric carbons are not contained in the chelate ring, is incapable of causing a vicinal effect. Thus, he reasoned that the Cotton effect observed in the visible region of the spectrum of Cu((+)hmc)₂[7a] indicated a tetrahedral structure.[7b] In 1938, Pfeiffer and his coworkers observed no Cotton effect in the visible spectrum of Ni((+)hmc)₂ and, following Lifschitz's reasoning, assumed it to have a planar structure.[8] French and Corbett disagreed, on the basis of the observed paramagnetism and uv Cotton effect.[9] Mellor showed that the Cotton effect was due to a ligand transition and that both Ni((+)hmc)₂ and the bis(benzoylcamphor)nickel-(II) complex exhibited visible spectra typical of octahedral nickel(II).[10] He concluded that vicinal effects could not be operative when the metal ligand bonds were "ionic." Lifschitz reinvestigated these systems in 1950 and reported the partial isolation of a (−)Cr-((+)hmc)₃ isomer.[11] He could observe no Cotton effect in the visible region of a "racemic" mixture of the (+) and (−) isomers and felt that this confirmed his earlier conclusion regarding the lack of a vicinal effect.

Mason and his coworkers used circular dichroism to assigned the Λ[12] configuration to the (−)Co((+)hmc)₃ and (+)Cr((+)hmc)₃ complexes.[13] Dunlop, Gillard, and Ugo reported the separation of the (−) cobalt species into cis and trans isomers in 1966.[14] They were

(1) Presented, in part, at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 16, 1969.

(2) Author to whom correspondence should be addressed at the State University of New York at Stony Brook.

(3) We use the term "stereoselectivity" in the same sense as that of Dunlop and Gillard, who defined it as "the behavior of molecular diastereoisomers;" J. H. Dunlop and R. D. Gillard, *Advan. Inorg. Chem. Radiochem.*, 9, 185 (1966).

(4) The term "vicinal effect" was first used for metal complexes by Y. Shimura, *Bull. Chem. Soc. Jap.*, 31, 315 (1958). See also J. Fujita and Y. Shimura, "Spectroscopy and Structure of Metal Chelate Compounds," K. Nakamoto and P. J. McCarthy, Ed., Wiley, New York, N. Y., 1968, Chapter 3, p 156.

(5) A. W. Bishop, L. Claisen, and W. Sinclair, *Ann.*, 281, 314 (1894).

(6) (a) H. S. French and T. M. Lowry, *Proc. Roy. Soc., Ser. A*, 106, 489 (1924); (b) H. Burgess and T. M. Lowry, *J. Chem. Soc., London, Trans.*, 125, 2081 (1924); (c) I. J. Faulkner and T. M. Lowry, *ibid.*, 127, 1080 (1925); (d) T. M. Lowry, H. Burgess, I. J. Faulkner, and R. C. Traill, *Proc. Roy. Soc., Ser. A*, 132, 387 (1931); (e) T. M. Lowry and R. C. Traill, *ibid., Ser. A*, 132, 398 (1931); (f) T. M. Lowry and R. C. Traill, *ibid., Ser. A*, 132, 416 (1931).

(7) (a) J. Lifschitz, *Recl. Trav. Chim. Pays-Bas*, 41, 627 (1922); (b) J. Lifschitz, *Z. Phys. Chem.*, 105, 27 (1923); (c) J. Lifschitz, *ibid.*, 114, 485 (1925).

(8) P. Pfeiffer, W. Christeleit, T. Hesse, H. Pfitzner, and H. Thielert, *J. Prakt. Chem.*, 150, 261 (1938).

(9) H. S. French and G. Corbett, *J. Amer. Chem. Soc.*, 62, 3219 (1940).

(10) D. P. Mellor, *J. Proc. Roy. Soc. N. S. W.*, 75, 157 (1942).

(11) J. Lifschitz, *Recl. Trav. Chim. Pays-Bas*, 69, 1495 (1950).

(12) The symbols Λ and Δ, as used in this paper, are consistent with the recently published nomenclature proposals: *Inorg. Chem.*, 9, 1 (1970). Thus, Λ signifies the absolute configuration in which the chelate rings have a left-handed helical relationship when viewed along the C_3 or pseudo-C_3 axis of a tris-bidentate chelate.

(13) (a) R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc., London*, 331 (1962); (b) S. F. Mason, *Quart. Rev., Chem. Soc.*, 17, 20 (1963); (c) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965). The cobalt complex is incorrectly designated (+)Co((+)hmc)₃ in this paper.

(14) J. H. Dunlop, R. D. Gillard, and R. Ugo, *ibid., A*, 1540 (1966).

unable to isolate Lifschitz's (−) chromium isomer but assigned the (+) isomer the trans structure and reported the isolation of the Λ-trans and Δ-trans isomers of Rh((+)hmc)₃, thus affording the first example of a Δ configuration in the (+)-3-acylcamphor series. They concluded that stereoselectivity in tris complexes of the (+) forms of the ligands produced the order of stability Λ-trans > Λ-cis > Δ-trans > Δ-cis and that Δ isomers could only be isolated in systems under kinetic control. Chen and Everett reported an investigation of the complexes of Co(III) and V(III) with (+)- and (−)hmc and (+)atc, the acetyl derivative (R = CH₃).[15] Their results with (+)hmc agreed with those of Dunlop, Gillard, and Ugo and they reported that the two (+) cobalt isomers which they detected with the (−)hmc ligand had the expected Δ-trans and Δ-cis structures; *i.e.*, the (−) form of the ligand stabilizes the Δ configuration. Their results with (+)atc were entirely analogous to the (+)hmc findings. They detected no evidence for the existence of the Δ-trans or Δ-cis isomers of the cobalt complexes with the (+) ligands. However, their nmr studies of the labile paramagnetic V(III) chelates indicated that the Λ-trans, Λ-cis, and Δ-trans isomers of the V((+)atc)₃ complex did coexist in equilibrium and that all four isomers of the V((+)hmc)₃ complex could be detected. Lintvedt and Fatta have reported infrared spectral and molecular weight investigations of a large number of hmc complexes and have shown that the Ni(hmc)₂ and Co(hmc)₂ complexes are trimeric with octahedral coordination and that the Cu(hmc)₂ complex has a planar structure.[16]

We have accomplished the preparation, isolation, and characterization of all four diastereomers of the Co((+)atc)₃ complex. In so doing, we have discovered that, contrary to the almost complete agreement in all of the relevant literature cited above, the tris chelates of the 3-acylcamphorato ligands show only slight stereoselectivity and do indeed exhibit a significant vicinal effect.[17]

Experimental Section

Preparation of the Ligand.—(+)-3-Acetylcamphor was prepared from (+)-3-bromocamphor[18] and ethyl acetate according to the organozinc syntheses of Bruhl.[19] The product is a colorless liquid at room temperature and was purified by triple distillation under reduced pressure, the last distillation being under a nitrogen atmosphere: bp 74° (0.45 mm), 76° (0.60 mm), 79° (0.70 mm), 81–83° (0.80 mm), 86–89° (1.30 mm) [lit.[19] 115–117° (10 mm), 118–118.5° (11.2 mm), 127–128° (15.5 mm)]. The neat ligand possessed an ir spectrum generally similar to that reported for solid H(hmc).[16] Some of the details of this spectrum as well as those of the nmr spectrum will be discussed in the Results. The ORD curve of the ligand was also recorded; [α]²⁵D +50.2° (CH₃OH).

Preparation of the Complex.—Tris[(+)-3-acetylcamphorato]-cobalt(III) was prepared from Na₃[Co(CO₃)₃]·3H₂O and H-((+)atc) according to the method of Gillard.[14] After the reaction was completed, the reaction mixture was filtered to remove the

(15) Y. T. Chen and G. W. Everett, *J. Amer. Chem. Soc.*, **90**, 6660 (1968).
(16) R. L. Lintvedt and A. M. Fatta, *Inorg. Chem.*, **7**, 2489 (1968).
(17) King and Everett have recently reinvestigated the Co((+)atc)₃ system and have succeeded in separating all four isomers by thin layer chromatography. Their isomeric abundance values are in good agreement with ours but their conclusions concerning the degree and source of stereoselectivity differ somewhat: R. M. King and G. W. Everett, Jr.; *ibid.*, **10**, 1237 (1971).
(18) The absolute configuration of (+)-3-bromocamphor has been determined by anomalous dispersion X-ray diffraction techniques: F. H. Allen and D. Rogers, *Chem. Commun.*, 837 (1966).
(19) J. W. Bruhl, *Chem. Ber.*, **37**, 746 (1904).

brown, gummy side product. The upper deep green benzene layer of the filtrate contained the complex and was separated from the lower colorless aqueous layer. The benzene layer was then rapidly passed through a very small column of acid-washed alumina to remove any soluble Co(II) impurities. The nmr of the concentrated benzene layer was studied to determine the relative proportions of the stereoisomers. (See the Results.) The relative areas of the various peaks were measured by the weighing of paper cutouts or by planimetry.

Chromatography of the Complex.—A typical separation and purification of a reaction mixture, treated as stated above, will be given. For a reaction mixture containing approximately 7 g of complex in approximately 25 ml of benzene, a chromatographic column of 4-cm diameter was tightly packed under benzene with approximately 500 g of acid-washed alumina (Merck No. 71695). Benzene was allowed to run out until the liquid level was just at the top of the column (height approximately 40 cm). The reaction mixture was added to the column and benzene was run out from time to time to keep the liquid level just at the top of the column. As soon as all of the complex was absorbed at the top of the alumina, the rest of the column was filled with freshly distilled benzene to produce a head approximately 115 cm above the bottom of the column. Maintaining this head, a flow rate of approximately 10 ml/min was obtained. As the elution proceeded, the initial green band separated into two new bands. The faster moving band was approximately 3 times larger than the more strongly absorbed band. The leading portion of the larger band developed a distinct brownish green tint while the trailing portion became deep green. The opposite was noted for the smaller band; *i.e.*, the trailing portion had the brownish green tint. After approximately 0.5 hr, the breakthrough of the leading band occurred. It was collected in two approximately equal fractions as was the second band which broke through after approximately 8.5 hr. The latter band was completely eluted after approximately 11 hr. The isomeric contents of the fractions could be monitored by nmr spectroscopy. Each band was found to contain two isomers. The two isomers in the larger band were labeled α and β in the order in which they came off the column; *i.e.*, β was the more strongly absorbed isomer. Similarly, the γ isomer was eluted before the δ isomer in the second band. A second chromatographing of each fraction on a smaller column was sufficient to allow collection of reasonable amounts of the pure isomers. The single band produced by each fraction was itself collected in two fractions of approximate relative ratios of 3:1 or 1:3, as the case required. Thus, the first fraction of the αβ band was collected in two fractions, the first one of which comprised three-fourths of the total. It contained pure α. In the same way, pure samples of the β, γ, and δ isomers were also collected. Quantitative separation was not achieved and, therefore, measurement of the relative amounts of the various isomers was achieved by integrating the nmr spectrum of the reaction mixture as described above.

Characterization of the Isomers.—The four isomers melted with decomposition in sealed, evacuated tubes at the following temperatures: α, 196–198°; β, 200–202°; γ, 150–154° (did not decompose until 187°); δ, 193–196° (all temperatures are uncorrected). Elemental microanalyses were conducted by Galbraith Laboratories and the results are presented in Table I.

TABLE I

ELEMENTAL ANALYSES FOR THE ISOMERS OF Co((+)atc)₃

	% C	% H	% Co
Calcd	67.69	8.04	9.22
Found			
α	67.96	7.95	8.98
β	67.06	7.96	9.62
γ	67.03	7.85	8.26
δ	67.22	8.17	8.72

The infrared spectra of the four isomers (as recorded in Nujol mulls on a Perkin-Elmer Model 137 instrument) were nearly identical and were in agreement with the spectrum reported for Co(hmc)₃.[16] For example, the C≐O and C≐C stretching frequencies of Co(hmc)₃ were reported at 1615 and 1481 cm⁻¹, respectively, and the analogous assignments for the Co((+)atc)₃ isomers are as follows: α, 1605, 1485 cm⁻¹; β, 1610, 1495 cm⁻¹; γ, 1625, 1510 cm⁻¹; δ, 1625, 1505 cm⁻¹.

Nuclear Magnetic Resonance Spectra.—The ¹H nmr spectra of the isomers were recorded on Varian A-60 or HR-100 spectrom-

TABLE II
^{1}H NMR SPECTRAL DATA FOR H((+)atc) IN CCl$_4$[a]

	Exo			Endo			Anti		
	δ[b]	J, Hz	Rel area	δ[b]	J, Hz	Rel area	δ[b]	J, Hz	Rel area
3-H	2.80	0	0.85	3.24	4.4, 1.2	1.2	...	...	...
4-H	2.68	3.9	0.85	2.47[c]	c	c	2.74[c]	c	c
Acetyl–olefin methyl	1.87	0	3.2	2.20	0	2.9	2.25	0	2.8
8-, 9-, and 10-methyl	0.95	0	2.7	1.00	0	3.0	0.88	0	6.0[f]
	0.90	0	6.0[d]	0.82	0	6.0[e]	0.58	0	2.6

[a] Concentration approximately 20%, by volume; temperature ambient. [b] In ppm, downfield from TMS. [c] The 4-H multiplets for the endo and anti isomers could not be resolved. The combined peak is a doublet with a splitting of 3.6 Hz. The higher field component is somewhat more intense than the low-field member. The 4-H protons are spin coupled with the exo 5 protons with a coupling constant of approximately 3.9 Hz. In addition, the 4-H proton in the endo isomer is spin coupled with the exo 3 proton. [d] Arbitrary area standard for those peaks assigned to the exo isomer. [e] Arbitrary area standard for those peaks assigned to the endo isomer. [f] Arbitrary area standard for those peaks assigned to the anti isomer.

eters and will be discussed in detail in the Results. All chemical shifts reported are the average values from several spectra and were measured by the side-band technique.

Visible-Region Electronic Absorption, Optical Rotatory Dispersion, and Circular Dichroism Spectra.—The electronic absorption spectra of the four isomers in benzene were obtained on a Cary Model 14 recording spectrophotometer from 650 to 300 nm. The benzene solution ORD spectra were obtained on a Cary Model 60 recording spectropolarimeter over the same wavelength range. Beer's law compliance was noted from the fact that the straight line through the two values of α_{500} for two different concentrations of the α isomer also passed through the origin of a plot of α_{500} vs. concentration. The CD spectra were also obtained on the Cary 60.

Thermal Equilibration of Isomers.—A solution of 21.8 mg of α-Co((+)atc)$_3$ in 488.8 mg of Spectrograde benzene was degassed and sealed in an nmr tube in vacuo. The solution was heated in a thermostated bath at 60° until the nmr spectrum, which was monitored on the thermally quenched sample at intervals, showed no further change (after approximately 60 hr). No evidence of decomposition was noted. The nmr spectrum of the resultant mixture was analyzed for the relative amounts of the isomers in the same manner as was the reaction mixture.
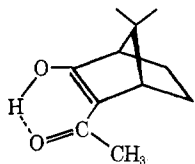
Results

The ligand, (+)-3-acetylcamphor, can exist in three tautomeric forms: a β-keto enol form which has two diastereomers[20]

anti   syn
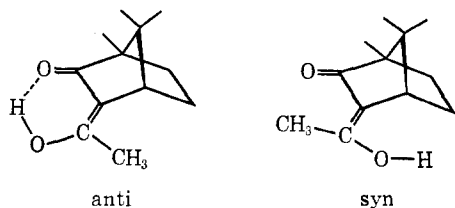
a β-diketone form which has two epimeric diastereomers

exo   endo
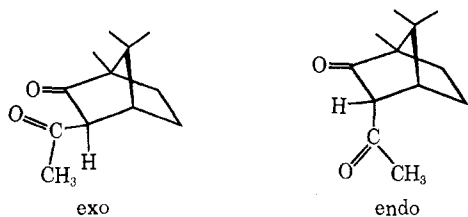
and another β-keto enol form

(20) The nomenclature used here is analogous to that used by Daniel and Pavia for H(hmc): A. Daniel and A. A. Pavia, *Tetraheron Lett.*, 1145 (1967).

The H(hmc) analog of this last tautomer has been calculated to be of high energy on the basis of strain effects.[21,22]

The infrared spectrum of neat H((+)atc) shows four strong absorptions in the carbonyl–olefin stretching region at 1750, 1710, 1695, and 1635 cm^{-1}. The band at 1750 cm^{-1} can reasonably be assigned to the 2-carbonyl stretches of the exo and endo isomers which would not be expected to be very different from that of camphor (1750 cm^{-1} [16]). The band at 1710 cm^{-1} is most likely the carbonyl stretch of the anti isomer analogous to that of *anti*-H(hmc) (1711 cm^{-1}) while the band at 1635 cm^{-1} is the accompanying C=C stretch [H(hmc) analog, 1628 cm^{-1}].[16]

The relevant ^{1}H nmr spectral data and assignments for H((+)atc) in CCl$_4$ are given in Table II. The spectrum is closely analogous, in the 3- and 4-hydrogen region (2.3–3.4 ppm downfield from TMS), to that reported for H(hmc) in the same solvent.[20] Thus, the assignments in this region are made by analogy. The 4 protons are spin coupled to the exo 5 protons.[23] The 3 proton (exo) in the endo isomer is spin coupled with the 4 proton (4.4 Hz) and with the exo 5 proton (1.2 Hz) which is related to it by a "W" configuration.[24] The relative amount of the anti isomer was obtained by subtracting an amount equal to the area under the 3-H peak of the endo isomer (−3.24 ppm) from the area under the combined 4-H peaks of the endo and anti isomers (−2.47 ppm). The relative amount of the exo isomer was obtained from the area under the 3-H peak at −2.80 ppm. The mole percentages of the isomers thus obtained are as follows: exo, 40%; anti, 33%; endo, 27%.

The assignments in the acetyl–olefin and 8-, 9-, and 10-methyl regions are made from relative area considerations based on the various 3- and 4-hydrogen peaks. Three peaks present in the acetyl–olefin methyl region of the spectrum of the ligand indicate that essentially the same isomeric content also obtains in benzene solution. A well-resolved nmr spectrum of the neat ligand could not be obtained because of its high viscosity. Thus, its isomer content is not known. The relative amounts of syn and anti isomers of H(hmc) have been reported to be solvent dependent.[20−22]

Our results are in agreement with those of Lintvedt and Fatta, who, in reinvestigating the low-field spectral region previously studied by Garbisch,[21,22] found no *syn*-H(hmc).[16] It is interesting to note that the ratio

(21) E. W. Garbisch, *J. Amer. Chem. Soc.*, **85**, 1696 (1963).
(22) E. W. Garbisch, *ibid.*, **87**, 505 (1965).
(23) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963), and references cited therein.
(24) K. M. Baker and B. R. Davis, *Tetrahedron*, **24**, 1663 (1968).

TABLE III
^{1}H NMR SPECTRAL DATA FOR THE ISOMERS OF Co((+)atc)$_3$

| | 8-, 9-, and 10-methyl region | | Acetyl methyl region | |
Isomer	C$_6$H$_6$	CCl$_4$	C$_6$H$_6$	CCl$_4$
α	65.2^a (6.0),^{b} 42.6 (3.1)	62.3 (2), 59.3 (1), 55.3 (1), 53.3 (2), 50.3 (3)	120.2 (1), 116.3 (1), 114.6 (1)	124.8 (1), 123.3 (2)
β	65.4 (1.3), 63.1 (1.0), 58.4 (1.5), 56.0 (2.1), 51.7 (1.2), 44.3, 42.4, 41.0 (3.0)	57.6 (2), 55.8 (1), 49.1 (3), 46.3 (3)	119.7, 119.1 (2.0), 117.1 (1.3)	127.3, 126.9 (2.0), 121.3 (0.9)
γ	61.6 (3), 54.2 (3), 41.7 (3)	58.0 (3), 50.1 (3), 47.3 (3)	118.3 (3)	123.5 (3)
δ	67.5 (3), 64.3 (3), 42.7 (3)	59.7 (3), 54.6 (3), 50.1 (3)	118.9 (3)	124.3 (3)

^{a} Chemical shifts are given in hertz downfield from TMS. ^{b} Relative areas are given in parentheses.

of the concentrations of the exo isomer to the endo isomer reported by Daniel and Pavia for H(hmc) in CCl$_4$, 1.7, and in a CCl$_4$–DMSO mixture (where the syn isomer is favored over the anti isomer), 1.6,[20] is essentially the same for H((+)atc) in CCl$_4$, 1.5. Thus the major difference caused by the substitution of a methyl group for a proton in the R position of 3-acylcamphor seems to be a relative destabilization of the anti isomer.

The four possible stereoisomers of a M((+)atc)$_3$ complex are shown in Figure 1. Since only one chiral
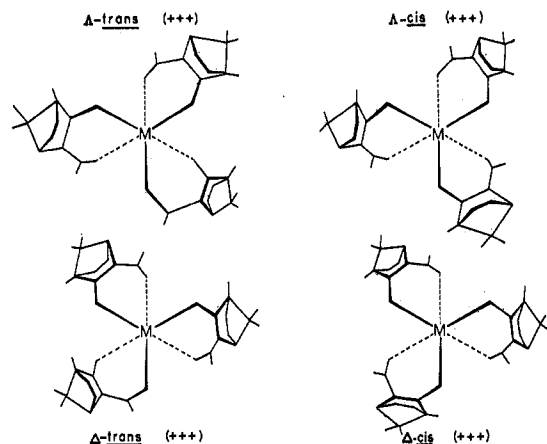

Figure 1.—The stereoisomers of an M((+)atc)$_3$ complex.

form of the ligand is used, each isomer bears a diastereomeric relationship with the others. The two cis isomers have C_3 symmetry while the two trans isomers have only C_1 symmetry. The three ligands in a cis complex are related to one another by the C_3 axis and are thus equivalent. Therefore, only one nmr signal is to be expected for each of the different protons in a ligand. For a cis isomer there should be one acetyl, one 8-, one 9-, and one 10-methyl resonance. For a trans isomer, in which the ligands are diastereotopic, there should be three acetyl, three 8-, three 9-, and three 10-methyl resonances. Thus, a mixture of all four isomers could show as many as 8 lines in the acetyl methyl region (−1.9 to −2.1 ppm) and 24 lines in the 8-, 9-, and 10-methyl region (−0.7 to −1.2 ppm). When an nmr spectrum of the benzene phase of the synthetic mixture is examined on an expanded scale, it is evident that more than one stereoisomer is present.

As the various fractions were collected from the alumina chromatographic column, their nmr spectra were examined in the acetyl and 8-, 9-, and 10-methyl regions on expanded scale. Figure 2 shows the spectra
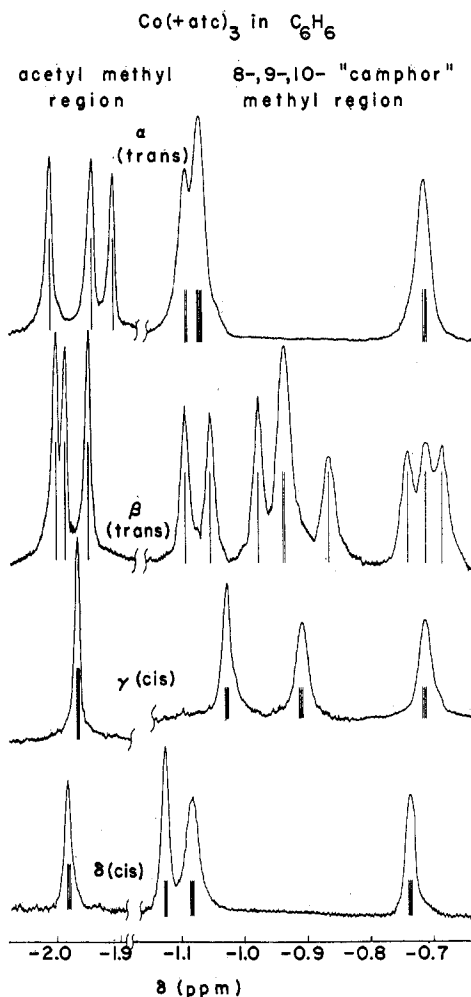

Figure 2.—The ^{1}H nmr spectra of the isomers of Co((+)atc)$_3$ in the acetyl and 8-, 9-, and 10-(camphor)methyl regions. The spectra were obtained in benzene at ambient temperature. The relative areas are represented by the number of vertical lines under the peaks (each line corresponds to one methyl group). The spectrum in the acetyl methyl region and that in the camphor methyl region are not necessarily shown with the same vertical scale for a given isomer.

of the four isomers, separated in this way, in these regions. Pertinent data are summarized in Table III. The acetyl methyl region clearly shows that the α and β isomers are trans since they each exhibit three peaks. The γ and δ isomers are therefore cis. The 8-, 9-, and 10-methyl resonances are well resolved in each of these latter isomers. All but two of these resonances are resolved in the β isomer. In the α isomer, there is a great

deal of accidental degeneracy in the 8-, 9-, and 10-methyl regions. It seems reasonable to suggest here that the cis isomers γ and δ are more strongly absorbed on the column because their molecular dipole moments are most likely greater than those of the trans isomers. This chromatographic behavior has been noted before in the separation of geometrical isomers of tris(β-keto enolato)cobalt(III) complexes.[25] Recently, however, Everett and Chen have reported the following order of elution on a silica gel thin layer plate of the isomers of the Co(III) tris complex of (−)-hydroxymethylenecarvone, a chiral β-keto enolate ligand: Λ-cis > Δ-trans > Λ-trans > Δ-cis (*i.e.*, Λ-cis is the least strongly absorbed).[26]

The electronic absorption spectra of the four isomers are almost identical. The energies and maximum extinction coefficients of peaks assigned to the $^1A_{1g} \rightarrow ^1T_{1g}$ (in idealized O_h symmetry) "d–d" transition are as follows: 16,200 cm^{-1} (145), 16,300 cm^{-1} (161), 16,200 cm^{-1} (137); 16,300 cm^{-1} (235). The $^1A_{1g} \rightarrow ^1T_{2g}$ transitions were not clearly resolved but the circular dichroism studies (*vide infra*) show them to be centered at about 22,500 cm^{-1}. The weak intensities of these "d–d" transitions indicate that octahedral selection rules are in effect to a good approximation. Peaks at ~340 nm which are shoulders on more intense absorptions in the uv spectrum have intensities similar to that of the Co(acac)$_3$ transition at 324 nm which recent SCF–MO calculations have indicated to be a metal $d\pi \rightarrow$ ligand π^* charge-transfer transition.[27] Their energies and intensities (ϵ_{max}) are as follows: α, 29,500 cm^{-1} (87 × 10^2); β, 29,300 cm^{-1} (87 × 10^2); γ, 29,200 cm^{-1} (70 × 10^2); δ, 29,200 cm^{-1} (70 × 10^2). These spectra are in agreement with that portion of the spectrum of the trans fraction of Co((+)atc)$_3$ shown by Chen and Everett.[15] The α and δ isomers have a distinctly brownish green color when compared to the deep green of the β and γ isomers. This is due to a shift of the minimum in the visible region from ~545 nm for the β and γ isomers to ~555 nm for the α and δ isomers. This explains the band shading noted during the chromatography of the isomers.

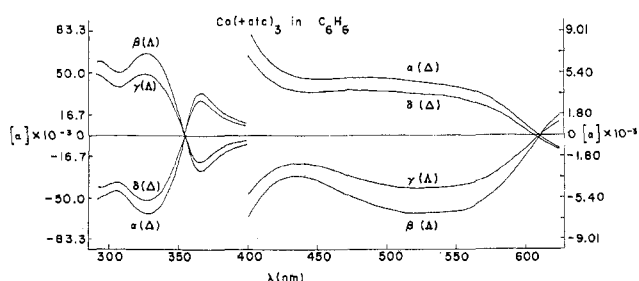The ORD curves for the four isomers are shown in Figure 3. The α and δ isomers are seen to be (+) iso-

Figure 3.—The optical rotatory dispersion curves for the four Co((+)atc)$_3$ isomers in benzene solution.

mers while the β and γ isomers are (−). More importantly, the bands at ~615 nm are seen to exhibit negative Cotton effects in the α and δ isomers and positive Cotton effects in the β and γ isomers. The Cotton

effects for the charge-transfer bands are exactly opposite those at ~615 nm for all the isomers. The signs of the Cotton effects of the bands at ~445 nm cannot be easily determined from the ORD curves (see, however, the CD spectra below).

The maximum specific rotation of the β isomer in the "d–d" spectral region (−6750 at 524 nm) is almost twice that shown for a chloroform solution of the fraction of Co((+)atc)$_3$ assigned the Λ-trans structure by Chen and Everett.[15] Since the change to a benzene solution is expected to increase the rotation by only *ca.* 6%,[14] this is a significant difference. It is clear that their fraction contained an appreciable amount of the α isomer which has a generally opposite ORD curve from that of the β isomer. In the synthetic mixture, the β isomer is present in greater amounts than the α isomer and has a stronger rotation (*vide infra*), and therefore Chen and Everett's chromatographic fraction had an ORD curve with the general shape of that of the β isomer. Likewise, their second fraction, assigned the Λ-cis structure, was actually a mixture of the γ and δ isomers with the γ isomer in excess (*vide infra*). It should be noted here that observations similar to these can almost certainly be made on all the reports in the literature concerning the magnitude of the optical activity measured for the Co(hmc)$_3$ complexes.[7a,b,11,13b,c,14,15,28,29] Incomplete separation of all the isomers has resulted in incorrect assignments and conclusions. Nuclear magnetic resonance has been an invaluable aid in ensuring the purity and structural assignments of the isomers in the present study.

The circular dichroism curves for the four isomers are shown in Figure 4. Some of the data are summarized
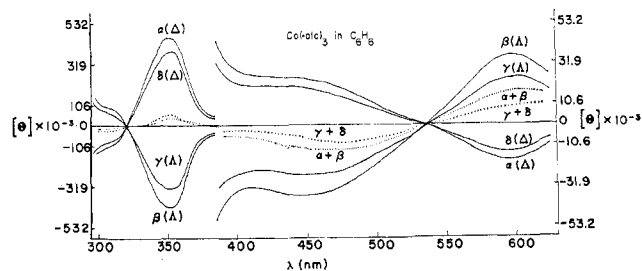
Figure 4.—The circular dichroism curves for the four Co((+)atc)$_3$ isomers in benzene solution.

TABLE IV
The Circular Dichroism Data for the Four Co((+)atc)$_3$ Isomers[a]

Isomer	$^1A_1 \rightarrow ^1E_a$		$^1A_1 \rightarrow (^1E_b, ^1A)$		Charge transfer	
	$\bar{\nu}$, cm^{-1}	$(\epsilon_l - \epsilon_r)_{max}$	$\bar{\nu}$, cm^{-1}	$(\epsilon_l - \epsilon_r)_{max}$	$\bar{\nu}$, cm^{-1}	$(\epsilon_l - \epsilon_r)_{max}$
α	16,800	−5.64	22,400	+7.36	28,400	+138
β	16,700	+10.8	22,400	−11.1	28,400	−129
γ	16,700	+7.39	22,100	−7.79	28,400	−100
δ	16,800	−4.33	22,600	+6.03	28,400	+116

[a] These data were obtained from benzene solutions.

in Table IV. Although the maximum symmetry possible for any of the isomers is C_3, the spectral assignments of the transitions responsible for the optical activity in Co((+)atc)$_3$ have been made with reference to idealized D_3 symmetry by Chen and Everett.[15] These are the same assignments made originally by Mason and

(25) R. A. Palmer, R. C. Fay, and T. S. Piper, *Inorg. Chem.*, **3**, 875 (1964).

(26) G. W. Everett and Y. T. Chen, *J. Amer. Chem. Soc.*, **92**, 508 (1970).

(27) I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, **50**, 265 (1969).

(28) J. H. Dunlop and R. D. Gillard, *Advan. Inorg. Chem. Radiochem.*, **9**, 211 (1966).

(29) R. D. Gillard in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Interscience, New York, N. Y., 1968, p 197.

coworkers for $Co((+)hmc)_3$[18,b,c] and are also used here. Thus, the degeneracy of the $^1T_{1g}$ state in octahedral symmetry is partially removed to give $^1A_2$ and ^1E (designated ^1E_a) states in D_3. Mason, *et al.*, reported transitions at 700 and 610 nm with weakly negative and strongly positive CD peaks, respectively, for $Co((+)-hmc)_3$.[18,b,c] They assign the peaks to the $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E_a$ excitations, respectively, on the basis of their experience that the E_a transition usually shows the greater rotational strength and in order to be consistent with the results of Piper, whose single-crystal polarized spectra of $Co(acac)_3$ indicate that in this compound the trigonal splitting constant, K, is positive (*i.e.*, the ^1E_a state lies at higher energy than the $^1A_2$ state).[30] The CD peaks here reported at 600 nm are similarly assigned. Instrumental limitations prevented us from observing the $^1A_1 \rightarrow {}^1A_2$ component.

The $^1T_{2g}$ state goes over into $^1A_1$ and $^1E({}^1E_b)$ states in D_3 symmetry. The $^1A_1 \rightarrow {}^1A_1$ transition is symmetry forbidden in D_3,[31] so Mason and coworkers tentatively assign the CD peak that they observe at 440 nm for $Co((+)hmc)_3$ to the $^1A_1 \rightarrow {}^1E_b$ transition.[18,b,c] Concern has been expressed that the sign of rotation of this band (negative) is opposite that of the lower energy transition assigned to $^1A_1 \rightarrow {}^1E_a$.[29] However, it is clear from the theoretical treatment of Karipides and Piper that when K is positive, the signs of the E_a and E_b transitions will be opposite.[32] Also, in the lower symmetry of these complexes, C_3 or C_1, the $^1A \rightarrow {}^1A$ transition would, of course, become allowed and could gain intensity through the action of a small component of the potential field serving to reduce the D_3 symmetry. Thus, the assignment given in Table IV for the bands at 445 nm is $^1A_1 \rightarrow ({}^1E_b, {}^1A)$. It is obvious that the sign of the Cotton effect of this band is opposite that of the $^1A_1 \rightarrow {}^1E_a$ transition for each isomer. The sign of the Cotton effect of the charge-transfer band at 352 nm is always the same as that of the $^1A \rightarrow ({}^1E_b, {}^1A)$ band.

Mason and coworkers have used the sign of the Cotton effect of the E_a band to assign the absolute configuration of $Co((+)hmc)_3$ by analogy to their work with diaminecobalt(III) complexes having five-membered chelate rings and N_6 donor systems.[13] Thus, a positive sign for this band was taken to indicate the Λ configuration. From similar considerations, Dunlop, Gillard, and Ugo[14] and Chen and Everett[15] have assigned the Λ configuration to all the fractions of $Co((+)hmc)_3$ or $Co((+)atc)_3$ which they have isolated and the Δ configuration to the fractions of the $Co((-)-hmc)_3$ complex (Chen and Everett). However, the extension of this analogy to these systems with six-membered chelate rings and oxygen donors is by no means unequivocal[26,32-34] and its use here will be strictly tentative. Thus we assign the α isomer the Δ-trans structure, β the Λ-trans structure, γ and δ the Λ-cis and Δ-cis configurations, respectively.[35] The

(30) T. S. Piper, *J. Chem. Phys.*, **35**, 1240 (1961).

(31) W. Moffitt, *ibid.*, **25**, 1189 (1956).

(32) A. G. Karipides and T. S. Piper, *ibid.*, **40**, 674 (1964), and references cited therein.

(33) G. R. Brubaker and L. E. Webb, *J. Amer. Chem. Soc.*, **91**, 7199 (1969).

(34) R. R. Judkins and D. J. Royer, *Inorg. Nucl. Chem. Lett.*, **6**, 305 (1970).

(35) These assignments have recently been confirmed by an X-ray crystallographic determination of the absolute configuration of Λ-*trans*-Cr-$((+)atc)_3$: W. D. Horrocks, D. L. Johnson, and D. MacInnes, *J. Amer. Chem. Soc.*, **92**, 7620 (1970). King and Everett have shown by X-ray powder photography that this complex is isomorphous with their B isomer (our β isomer).[17]

study of the circular dichroism of the exciton-coupled, long-axis-polarized $\pi \rightarrow \pi^*$ transition of the β-keto enolate ligand bids to yield fruitful results in the determination of the absolute configuration of tris(β-keto enolate) complexes.[36,37] Instrumental limitations have prevented us to date from investigating this transition which occurs at 229 nm in $Co(acac)_3$.[27] The energies of the π and π^* levels in the 3-acylated camphorato ligands would be expected to be altered somewhat by the strain in the camphor ring system.[16] The fact that the ligand itself is chiral would, of course, also have to be taken into account in a study of the CD of this $\pi \rightarrow \pi^*$ excitation.

In order to determine the equilibrium distribution of isomers, a solution of α-$Co((+)atc)_3$ in benzene was heated for 60 hr at 60° in a sealed nmr tube as described in the Experimental Section.[38] A reproduction of the spectrum obtained after such treatment is presented in Figure 5. In the spectrum shown, the acetyl methyl region was recorded at a slightly greater spectrum amplitude setting than the 8-, 9-, and 10-methyl region. However, in the spectra analyzed, both regions were recorded at the same settings. The resolutions shown in the figure were done by manual analysis. Those in the crowded regions of the spectrum (-2.0, -1.1, and -0.7 ppm) are only approximations. (Accurate resolutions in these regions were found to tax even an electronic curve resolver, such that inconsistent results were obtained.) Accurate results were obtained from the following well-resolved peaks: the α peak at -1.91 ppm, the γ peaks at -1.03 and -0.90 ppm, and the β peaks at -0.97, -0.93, and -0.86. Complete resolutions of these peaks were made with the aid of the line widths known from the spectra of the pure isomers. The relative amounts of the α, β, and γ isomers were obtained by weighting the areas of these peaks by the number of methyl groups they represent. The values for the β and γ isomers were obtained from the averages of their several peaks. There is no cleanly resolved peak for δ and its relative abundance was determined by difference from the highly degenerate transitions at -2.0, -1.1, and -0.7 ppm. The mole percentages of the isomers obtained by such treatment are as follows: α, $31.3 \pm 0.8\%$; β, $45.2 \pm 1.3\%$; γ, $16.4 \pm 1.0\%$; δ, $7.0 \pm 1.0\%$. These results were reproduced in separate experiments. Essentially identical results were obtained from similar analyses of the reaction mixture but the presence of impurity peaks limited the accuracy of the integrations of the isomer resonances.

Discussion

Since the four stereoisomers of tris[(+)-3-acetylcamphorato]cobalt(III) bear a diastereomeric relationship to one another, there is no necessity for their having the same stabilities. Consequently, all of the investigators who have studied such complexes over the years have commented on the strong stereoselectivity[7,11,13-15] or even total stereospecificity[28] which they exhibit. The results obtained for $Co((+)atc)_3$ in this investigation call all of the preceding studies into serious ques-

(36) E. Larsen, S. F. Mason, and G. H. Searle, *Acta Chem. Scand.*, **20**, 191 (1966).

(37) For a recent review of this approach see B. Bosnich, *Accounts Chem. Res.*, **2**, 266 (1969).

(38) The kinetics of this reaction and the analogous ones of the other isomers are under investigation: C. S. Springer, to be submitted for publication.
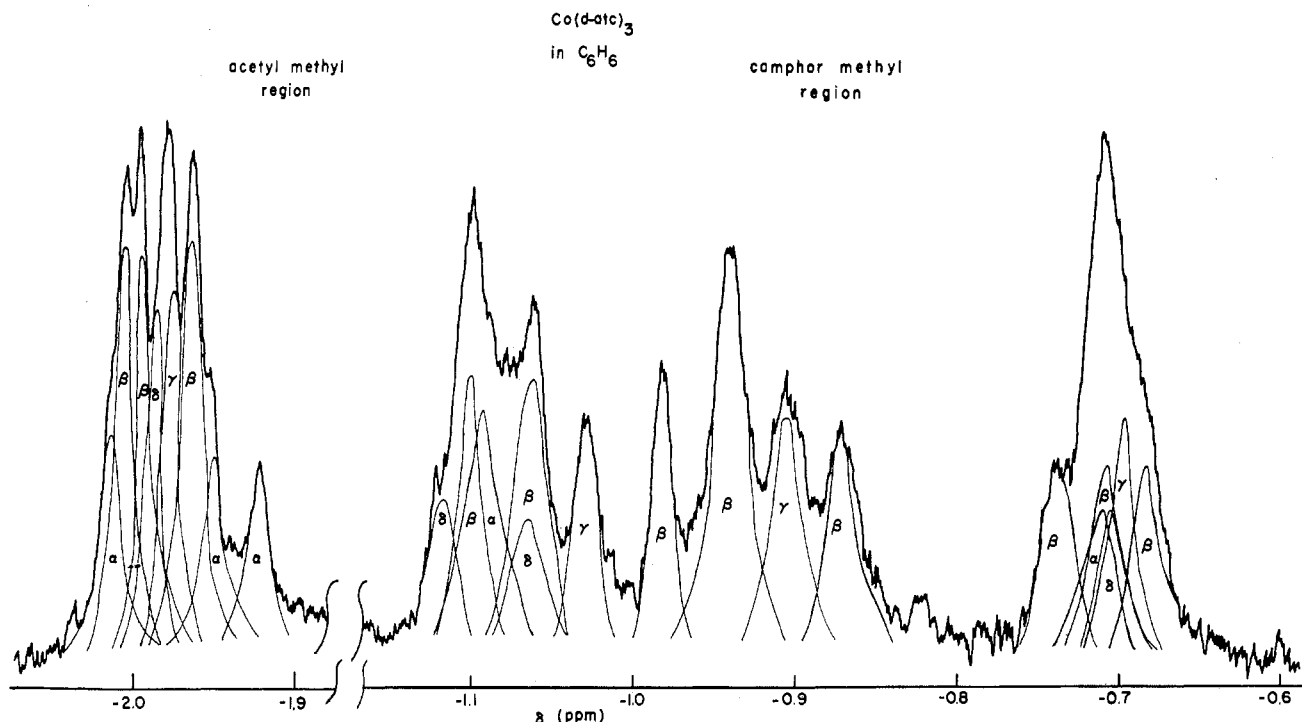
Figure 5.—The acetyl and 8-, 9-, and 10-(camphor)methyl regions of the ^{1}H nmr spectrum of an equilibrium mixture of the stereoisomers of Co((+)atc)$_3$ in benzene.   The two regions were recorded at slightly different spectrum amplitude settings.

tion.   After approximately 50 hr at 60°, a benzene solution of Δ-*trans*-Co((+)-atc)$_3$ was converted into an equilibrium mixture of the Δ-trans, Λ-trans, Λ-cis, and Δ-cis isomers.   Analysis of this mixture indicates that at 60° the equilibrium ratios of the concentration of the trans to the cis isomer for both the Λ (2.8 ± 0.3) and the Δ (4.5 ± 0.6) cobalt epimers are close to the statistically expected value of 3.   Thus, with regard to these two pairs, stereoselectivity is negligible.   For the two pairs whose members bear epimeric relationships about the chiral center at the cobalt, $K = \Lambda$-trans/Δ-trans $= 1.4 ± 0.1$ and $K = \Lambda$-cis/Δ-cis $= 2.3 ± 0.4$ at 60°.   These reflect $\Delta G°$ values of $-0.22 ± 0.07$ kcal/mol and $-0.55 ± 0.12$ kcal/mol, respectively, which indicate only a very slight stereoselectivity in favor of the Λ configuration.   In tris chelates of chiral bidentate ligands where the interligand interactions are dominated by the ring conformation (*i.e.*, the 1,2-diamine ligands) stereoselective effects are on the order of 1 kcal or greater.[28]   Thus in tris(β-keto enolate) complexes steric interactions of the ring substituents are reduced, possibly by the slight folding of the chelate rings about the O–O line.[35]   Inspection of molecular models reveals no extreme interactions between the various components of the Co((+)atc)$_3$ molecules and this is borne out by the experimental results.   A free energy difference of approximately 0.25 kcal was also found between the Λ-trans and Δ-trans isomers of the tris(L-leucinato)-cobalt(III) complex at 117°.[39]   This is to be expected since chelate rings in α-amino acid complexes are much less puckered than those in 1,2-diamino complexes.[28]

Although they reported no evidence for Δ-*cis*-V-((+)atc)$_3$, Chen and Everett found that the Λ-trans isomer was more stable than the Δ-trans isomer by approximately 0.7 kcal at 29°.[15]   The Λ-trans:Λ-cis ratio was also found to be statistical.   The Λ-trans:

(39) R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966).

Δ-trans ratio of V((+)hmc)$_3$ seemed to be about the same as that of V((+)atc)$_3$.   Estimates of the trans:cis ratio of the Λ and Δ epimers of V((+)hmc)$_3$ could not be made.

Everett and Chen have also recently studied the Co(III) and V(III) complexes of some novel chiral β-keto enolate ligands produced by the formylation of (+)- and (−)-carvone and (+)-pulegone.[26]   They also found that the stereoselectivity evidenced is slight (<0.5 kcal).   For example, based on nmr and tentative CD arguments similar to those used here, they made the following assignments of the equilibrium mixture of the tris[(−)-hydroxymethylenecarvonato]cobalt(III) complex, Co((−)hmcar)$_3$: Λ-trans, 48 mol %; Δ-trans, 26 mol %; Δ-cis, 18 mol %; Λ-cis, 8 mol %.   The CD spectra of the two cis isomers are somewhat unusual (particularly that assigned to the Λ-cis isomer).   It is interesting to speculate that if there were some unusual factor in the electronic structures of the cis isomers to cause a reversal of the Cotton effects from the pattern exhibited by the trans pair, so that the configurational assignments would be reversed, the trans:cis ratio in each epimeric form would be almost exactly the statistical value of 3.

It should be noted that the equilibrium mixture of diastereomers of Co((+)atc)$_3$ is also obtained in the mixture produced by the reaction of [Co(CO$_3$)$_3$]·3H$_2$O^{3-} with 40% exo-, 33% anti-, and 27% endo-H-((+)atc) in benzene at room temperature.   This indicates that the product ratio in the synthetic reaction is under thermodynamic control.

In most of the chiral chelates with chiral ligands studied in the past, the ligands have been 1,2-diamines or α-amino acids and in such complexes there are three possible contributions to the optical activity: (1) the configurational effect (due to the chiral arrangement of the ligand rings about the metal ion);   (2) the conforma-

TABLE V

THE CONFIGURATIONAL EFFECT IN THE CD SPECTRA OF TRIS(β-KETO ENOLATE)COBALT(III) COMPLEXES

	Configurational effects											
	Λ-Trans[b]		Λ-Cis[c]		Δ-Trans[d]		Δ-Cis[e]		Co(acac)$_3$[a]			
									(+)$_{546}$		(−)$_{546}$	
Transition	λ, nm	[θ]$_{max}$, deg	λ, nm	[θ]$_{max}$, deg	λ, nm	[θ]$_{max}$, deg	λ, nm	[θ]$_{max}$, deg	λ, nm	[θ]$_{max}$, deg	λ, nm	[θ]$_{max}$, deg
$^1A_1 \rightarrow {}^1E_a$	598	−27,000	596	−19,200	598	27,000	598	19,200	570	−27,000	570	19,710
$^1A_1 \rightarrow ({}^1E_b, {}^1A)$	446	30,800	446	22,400	446	−30,800	446	−22,400	427	15,000	425	−16,127

[a] Reference 41. The solvent used for these measurements was absolute alcohol. The values for the (−)$_{546}$ isomer are reported in the reference, while the values for the (+)$_{546}$ isomer were interpolated from the reported CD curves and are thus less accurate. [b] $\alpha - [(\alpha + \beta)/2]$. [c] $\delta - [(\gamma + \delta)/2]$. [d] $\beta - [(\alpha + \beta)/2]$. [e] $\gamma - [(\gamma + \delta)/2]$.

tional effect (due to the chirality of the ring conformations themselves); (3) the vicinal effect (due to the presence of chiral centers on the ligands). Douglas and his coworkers have shown that contribution (1) and the combination of (2) and (3) are reasonably additive in the metal "d–d" transition of chelates with 1,2-diamine or α-amino acid ligands.[40] However, contributions (2) and (3) have proven to be intimately dependent upon one another in these ligands because the asymmetric center on the ligand dictates the conformation which the chelate ring assumes. In the 3-acylcamphorato complexes the chelate rings show a slight fold in the solid state,[35] and, thus, there may be a slight conformational effect in this system also. Previous investigators have failed to detect any conformational or vicinal effect. In Figure 4, the CD curve of the Λ-trans isomer was added to that of the Δ-trans isomer, and the Λ-cis and Δ-cis curves were similarly combined. Assuming the above-mentioned additivity, the configurational effects are cancelled in the two resultant curves and significant vicinal effects are observed.

Some evidence for the, at least approximate, additivity of these effects is found in the following treatment. If half of the $\alpha + \beta$ curve (Figure 4) is subtracted from the α curve and half the $\gamma + \delta$ curve is subtracted from the δ curve, the resultant curves should represent the Δ configurational effect for the trans and cis isomers, respectively. Analogous treatment of the β and γ curves gives the Λ-trans and Λ-cis configurational effect curves. The magnitudes of the rotational strengths in these curves should approximate those in the CD spectra of the enantiomers of Co(acac)$_3$. Collman and Sun have succeeded in completely resolving Co(acac)$_3$ and have recorded the CD spectra of the enantiomers in absolute ethanol.[41] The maximum molar ellipticities for the two "d–d" bands of these two isomers and the calculated configurational effects are compared in Table V. The agreement for the $^1A_1 \rightarrow {}^1E_a$ transition peaks is certainly fortuitous, considering that the spectra were recorded in different solvents and that the transitions occur at different energies. For the $^1A_1 \rightarrow ({}^1E_b, {}^1A)$ transition, the calculated intensities are seen to be larger than those of the Co(acac)$_3$ enantiomers. Dunlop, *et al.*, have reported that benzene increases the optical activity of Co((+)hmc)$_3$ by *ca.* 30% over the value found in methanol in a spectral region dominated by this transition.[14] Thus, some of the observed differences may be attributed to solvent effects.

The two vicinal effect curves have the same character

as the configurational effect in the two metal "d–d" bands (*i.e.*, the rotational strengths of the $^1A_1 \rightarrow {}^1E_a$ and $^1A \rightarrow ({}^1E_b, {}^1A)$ transitions are of opposite signs). It has been suggested that vicinal effect CD curves for complexes are not "characteristic of particular optically active ligands" but are "determined primarily by the total molecular symmetry of the complex."[40e] However, the operative mechanism for the vicinal effect in metal complexes is still not well understood, and why the (+) form of the ligands in this complex should have the same effect on the activity of the metal electronic transitions as the Λ configuration is unknown. The parallel behavior of the signs of the vicinal and configurational effects is broken in the charge-transfer transition, where the vicinal effect mimics the Δ configuration.

Although the authors have not explicitly combined them, the CD curves shown by Everett and Chen for Λ-*trans*- and Δ-*trans*-Co((−)hmcar)$_3$ and -Co((+)-hmcar)$_3$ indicate that very similar vicinal effects are operative.[26] The curves are only shown in the region of the $^1A_1 \rightarrow {}^1E_a$ transition but from the tails of the $^1A_1 \rightarrow ({}^1E_b, {}^1A)$ transitions, one can surmise that the vicinal effect here also parallels the configurational effect in the two "d–d" bands. The (−)hmcar ligands mimic the Λ configuration while their (+) enantiomorphs mimic the Δ configuration. Everett and Chen note that the "absolute configurations of (+)-camphor and (−)-carvone are closely related."

Finally, it might be noted that the nmr spectra in Figure 3 indicate that there are some differences in solvation of the diastereomers by benzene. This is most evident in the 8-, 9-, and 10-methyl regions. Baker and Davis have shown that, of the three resonances due to these methyls in bornane derivatives, the 8- and 9-methyl peaks are always broader due to a small spin coupling between them.[24] During their rotational excursions, pairs of the protons in these two methyl groups will occasionally find themselves with a "W" configurational relationship.

Thus the δ (Δ-cis) peak at −1.12 ppm and the γ (Λ-cis) peak at −1.03 ppm can be clearly assigned to the protons of the sets of three equivalent 10-methyl groups of these two isomers. The assignments of the other two peaks for each isomer cannot be unambiguous. (If they follow the same pattern as that of camphor itself, the lower field member would be due to the 9-methyl groups.[42,43]) The three β (Λ-trans) peaks at −1.09, −1.05, and −0.97 ppm can be assigned to the three nonequivalent 10-methyls in this isomer. Although no other definite assignments can be made, the

(40) (a) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); (b) B. E. Douglas and S. Yamada, *ibid.*, **4**, 1561 (1965); (c) B. E. Douglas, *ibid.*, **4**, 1813 (1965); (d) S. K. Hall and B. E. Douglas, *ibid.*, **8**, 372 (1969); (e) C. Y. Lin and B. E. Douglas, *Inorg. Chim. Acta*, **4**, 3 (1970).

(41) J. P. Collman, personal communication; J.-Y. Sun, Ph.D. Thesis, University of North Carolina, 1967; *Diss. Abstr.*, **28**, 4482-B (1968).

(42) J. D. Connolly and R. McCrindle, *J. Chem. Soc. C*, 1613 (1966), and references cited therein.

(43) P. V. Demarco, D. Doddrell, and E. Wenkert, *Chem. Commun.*, 1418 (1969).

8-, 9-, and 10-methyl spectral regions show an interesting pattern. The three 10-methyl peaks in the β (Λ-trans) isomer are centered close to the position of the 10-methyl peak in the γ (Λ-cis) isomer which is shifted more than 0.1 ppm upfield from the position of the 10-methyl peak in the δ (Δ-cis) isomer. In fact, overall, the spectra of the β and γ isomers resemble one another in these regions as do the spectra of the α and δ isomers. Thus, if the two β peaks at -0.93 (doubly degenerate) and -0.86 ppm are given the same assignments as the γ peak at -0.90 ppm and if the three β peaks centered at -0.70 ppm are given the same assignments as the γ peak at -0.70 ppm, then the effect on the spectrum of going from γ (Λ-cis) to β (Λ-trans) is quite small. The lowering of the symmetry from C_3 to C_1 barely serves to remove the degeneracy of the transitions. Likewise, if the appropriate relative assignments are made, the change from δ (Δ-cis) to α (Δ-trans) is so small that none of the spectral degeneracy is removed. The biggest differences in the spectra occur in the Δ to Λ configurational inversion. Since most peaks are shifted upfield in going from Δ to Λ, it would seem that the Λ isomers are more strongly solvated. The small changes upon conversion from trans to cis could be due to intramolecular electronic effects on the chemical shifts.

Benzene is known preferentially to solvate the positive end of molecular electric dipoles[43] and Linck and Sievers have shown that this is observed for neutral tris(β-keto enolate) complexes.[44] In the cis isomers, the dipole moment lies along the C_3 axis, but which end

(44) R. G. Linck and R. E. Sievers, *Inorg. Chem.*, **5**, 806 (1966).

of this axis would be more positive in these complexes is not known with certainty. Around one end are arrayed the acetyl methyl groups whose degenerate resonance position is not much affected by the change from Δ to Λ although the Λ peak (γ) is shifted slightly upfield. About the other end, are clustered the 8- and 10-methyl groups in the Δ isomer. In the Λ molecule the 8-methyl groups become well shielded from the trigonal face at the end of the C_3 axis by the 10-methyl groups which are still arrayed about it. The fact that the 10-methyl resonance, as mentioned before, shifts significantly upfield upon conversion from Δ to Λ is consistent with increased solvation occurring at this face. The lesser number of methyl groups about this face in the Λ isomer might be the driving force for this increased solvation. It is interesting that the highest field methyl peak which (as also mentioned before) might be assigned to the 8-methyl group is hardly shifted at all upon conversion from Δ to Λ.

Substitution Reactions of Metallic Complexes of β,β',β''-Triaminotriethylamine. VI. Kinetics of Aquation of cis-Chloroaquo(β,β',β''-triaminotriethylamine)cobalt(III) Ion

By WARREN V. MILLER[1] AND STANLEY K. MADAN*

The kinetics of the acid hydrolysis of cis-Co(tren)H₂OCl²⁺ (tren = β,β',β''-triaminotriethylamine) have been investigated between 25 and 70°. The pseudo-first-order rate constant for the reaction at 65.0° was found to be 2.69×10^{-4} sec⁻¹ and was ionic strength independent in 1 M HClO₄. The acid hydrolysis reaction proved to be acid inhibited in the range of pH 1–2.3, presumably through an acid dissociation of the chloroaquo species to form the faster reacting chlorohydroxo species. The activation enthalpy for the reaction in 1 M HClO₄ was 21.6 kcal mol⁻¹, and the entropy of activation was found to be -11.0 cal mol⁻¹ deg⁻¹. A second isomer of the chloroaquo ion is believed to be present in solution during the initial stages of the reaction.

Introduction

Recently the kinetics of the acid hydrolysis of Co(tren)H₂OBr²⁺ (tren = β,β',β''-triaminotriethylamine) have been reported[2] and compared with those of the

reaction of Co(tren)Br₂⁺ [3a] and cis-Cr(en)₂H₂OBr²⁺ [3b] (en = ethylenediamine).

It was found that while the acid hydrolysis rate of Co(tren)Br₂⁺ is unaffected by pH changes in acid solution, the reaction of Co(tren)H₂OBr²⁺ is acid inhibited. This difference has been attributed to an acid–base equilibrium in the bromoaquo system, which results in

(3) (a) S. K. Madan and J. Peone, Jr., *ibid.*, **6**, 463 (1967); (b) L. P. Quinn and C. S. Garner, *ibid.*, **3**, 1348 (1964).