than it reduces Co(NH$_3$)$_5$py^{3+}. It appears that an outer-sphere process may account for all or a substantial portion of the k_0 path for I and II.

It is apparent that especially at low acid concentrations a substantial part of the reaction proceeds through an inner-sphere activated complex. It is of interest to compare these inner-sphere processes for V^{2+} to other inner-sphere reactions in which 3- and 4-substituted pyridines act as bridging ligands.

The reductions of the N-coordinated pyridinecarboxylic acid complexes by Cr^{2+} proceed in part by paths with inverse dependence upon (H$^+$). The paths make a contribution to the observed rate equal to 0.015(H$^+$)$^{-1}$ M^{-1} sec^{-1} and $\leq$0.03(H$^+$)$^{-1}$ M^{-1} sec^{-1} for the reaction of Cr^{2+} with I and II, respectively.[7] These may be compared with 0.25(H$^+$)$^{-1}$ M^{-1} sec^{-1} and 0.97(H$^+$)$^{-1}$ M^{-1} sec^{-1} for the corresponding reductions by V^{2+}. The latter values are equal to k_3k_4/k_{-3} which would be the specific rates if substitution on V^{2+} were rapid.

It has been proposed[2] that the Cr^{2+} reduction of isonicotinamidepentaammineruthenium(III) proceeds by a resonance-transfer mechanism[8] in which the electron is transferred directly to the ruthenium(III) acceptor orbital. Ru(III) complexes are reduced much more rapidly by Cr^{2+} than the corresponding Co(III) complexes. Presumably this is due to symmetry matching of Ru(III) (a π acceptor) but not Co(III) (a σ acceptor) with the π-bridging ligand. Other studies[1] indicate that the isonicotinamidepentaamminecobalt(III) ion reacts with Cr^{2+} by a stepwise mechanism.[2]

A resonance-transfer mechanism is indicated for the V^{2+} reactions of this study because the effect of symmetry matching of the donor with the π-bridging ligand is evident. Thus V^{2+}, a weaker reductant but a π donor, reacts more rapidly than Cr^{2+} (a σ donor) with both of the Co(III) complexes.[9–11] Similar conclusions have been reached for the V^{2+} reductions of CrOAc^{2+} [12] and Co(NH$_3$)$_5$ox^{2+}.[10]

It is of interest to note that the rate of V^{2+} reduction (by the inverse acid path) of the isonicotinate complex is only about 4 times greater than that of the nicotinate complex. Because resonance effects are transmitted between para positions much more effectively than between meta positions, a larger factor would be expected. Thus the effectiveness of the bridging ligands in this study is not strongly dependent upon the π interaction they provide between the metal ions. Apparently the interaction between the donor and acceptor orbitals is great enough so that the probability of transfer during the lifetime of the energy-matched intermediate is near unity; *i.e.*, the process is adiabatic.

Acknowledgment.—This research was supported in part by the Petroleum Research Fund, administered by the American Chemical Society, and by the Center for Naval Analyses of the University of Rochester. Such support does not imply endorsement of the content by the U. S. Navy. A Uniroyal fellowship held in 1969–1970 by C. Norris is also gratefully acknowledged.

---

(7) F. R. Nordmeyer, work in progress.

(8) J. Halpern and L. E. Orgel, *Discuss. Faraday Soc.*, **29**, 32 (1960).

(9) A greater rate for V^{2+} would not be inconsistent with a stepwise process if electron transfer to the ligand were rate determining. However, this seems unlikely to us for two reasons: (1) electron transfer to the 3-substituted pyridine should be many times slower than to the more easily reduced 4-substituted system, whereas the corresponding complexes are reduced at similar rates (within a factor of 4); (2) Cr^{2+} is generally more reactive than V^{2+} in reducing unsaturated organic carboxylic acids.[10,11] This suggests that electron transfer to unsaturated systems is faster for Cr^{2+} than V^{2+}, but since the mechanisms of the organic reductions are unknown, this conclusion is uncertain.

(10) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

(11) E. Vrachnou-Astra and D. Katakis, *J. Amer. Chem. Soc.*, **89**, 6772 (1967); A. Malliaris and K. Katakis, *ibid.*, **87**, 3077 (1965).

(12) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF KANSAS, LAWRENCE, KANSAS 66044

Stereoselectivity in Octahedral Complexes. IV.[1] Separation and Identification of the Diastereomers of Tris[(+)-3-acetylcamphorato]cobalt(III) and -chromium(III)

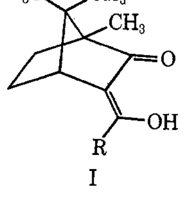
BY RICHARD M. KING AND G. W. EVERETT, JR.*

Received August 10, 1970

The four possible diastereomers of tris[(+)-3-acetylcamphorato]cobalt(III) and of tris[(+)-3-acetylcamphorato]chromium(III) have been separated by preparative thin layer chromatography on silica gel. Absolute configurations are assigned to the individual isomers of the Co(III) complex based on CD and pmr spectra. Certain of the Cr(III) and Co(III) diastereomers are shown to be isomorphous using X-ray powder diffraction data. Assuming the isomorphous isomers have the same absolute configurations, configurations are assigned to the individual Cr(III) diastereomers. CD spectra of Cr(III) and Co(III) diastereomers assigned the same configuration are qualitatively very similar. Relative isomer abundances for each complex are qualitatively the same; the Λ-trans isomer is most abundant for both metals. Kinetic control of stereoselectivity is maintained for the Cr(III) complex and apparently to some extent for the Co(III) complex.

Introduction

Camphor is readily available in high optical purity and is easily converted into bidentate β-keto enolate ligands such as hydroxymethylenecamphor, hmcH (I, R = H), or acetylcamphor, atcH (I, R = CH$_3$). The

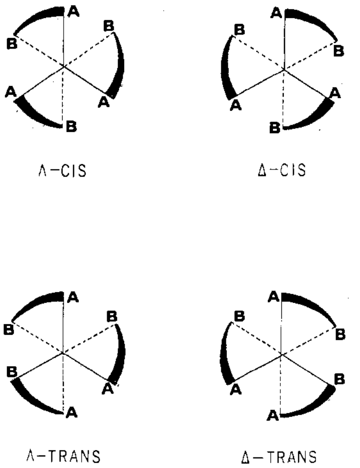


I

---

(1) Part III: K. S. Finney and G. W. Everett, Jr., *Inorg. Chem.*, **9**, 2540 (1970).

presence of a sterically stringent bicyclic ring along with the chiral nature of these ligands has interested inorganic chemists for many years.[2] Four diastereomers may exist for tris complexes of I since the ligands are chiral, and the donor oxygens are not equivalent. These diastereomers are designated Δ-trans, Λ-trans, Δ-cis, and Λ-cis, where Δ and Λ imply right- and left-hand helicity about the C_3 or pseudo-C_3 axis,[3] and cis and trans refer to the arrangement of donor atoms. Cis diasteromers belong to the C_3 point group; trans diastereomers have no symmetry (C_1 point group). Schematic drawings of the four isomers are shown in Figure 1.



Λ-CIS Δ-CIS

Λ-TRANS Δ-TRANS

Figure 1.—Diagrammatic representations of the four diastereomers of a six-coordinate complex having three bidentate, chiral ligands in which the donor atoms are inequivalent.

Our interest in tris complexes of hmcH and atcH lies in the feasibility of separating or otherwise detecting the diastereomers, assigning absolute configurations to them, and investigating the occurrence of stereoselectivity. In 1966, Dunlop, *et al.*,[4] reported the separation of Co((+)hmc)$_3$ into cis and trans forms using alumina columns. Both isomers were assigned the Λ configuration based on their ORD curves. Only one isomer (Λ-trans) was obtained for Cr((+)hmc)$_3$. In an earlier paper of the present series,[5] results were presented which confirmed the observations of Dunlop, *et al.*, and extended the investigation to complexes of Co((−)hmc)$_3$ and Co((+)atc)$_3$. Cis and trans forms of these latter complexes were separated by column chromatography and identified by nmr. ORD spectra indicated that both isolated forms of Co((+)atc)$_3$ have the Λ configuration, as was the case for Co((+)hmc)$_3$, but both forms of Co((−)hmc)$_3$ appeared to have the Δ configuration. The assignments of Δ and Λ configurations were based on the spectral assignments of McCaffery *et al.*[6]

Analysis of the isotropic pmr shifts of V((+)hmc)$_3$ and V((+)atc)$_3$ demonstrated that at least three of the four possible diastereomers exist in equilibrium in solution for both complexes,[5] and it was suggested that all four diastereomers of the corresponding Co(III) complexes may exist. The chromatographic technique employed at that time did not effect separation of Co(III) diastereomers differing only in helicity. The ORD spectra of cis and trans forms of the Co(III) complexes may be explained by assuming one helical configuration predominates, *e.g.*, Λ for cis- and trans-Co((+)atc)$_3$. Subsequently, other investigators reported separating all four diastereomers of Co((+)atc)$_3$ by column chromatography.[7] Recently it has been shown that the four diastereomers of tris[(+)- or (−)-hydroxymethylenecarvonato]cobalt(III) may be separated readily by thin layer chromatography, tlc, on silica gel.[8] In view of the superior resolving power of tlc over column methods, we have reinvestigated the complexes Co((+)atc)$_3$ and Cr((+)atc)$_3$ utilizing tlc. In this paper are presented the results of our study, including the successful separation of all four diastereomers for each complex, measurement of the relative abundances of the isomers, and assignments of absolute configuration. This work is part of a general investigation of diastereoisomerism in complexes of chiral ligands having planar, conjugated chelate rings.

Experimental Section

Syntheses.—(+)-3-Acetylcamphor was prepared from (+)-3-bromocamphor using the procedure described by Brühl.[9]

Co((+)atc)$_3$ was prepared by a modification of the method of Dunlop, *et al.*,[4] for synthesis of Co((+)hmc)$_3$. In a typical preparation, 2.00 g of ligand and 1.24 g of $Na_3Co(CO_3)_3 \cdot 3H_2O$[10] were vigorously stirred for 12 hr in 100 ml of a 1:1 mixture of benzene and water. The benzene layer containing the product was isolated, and upon removal of solvent a dark green oil remained. This oil was dissolved in ethanol and added dropwise to a vigorously stirred aqueous sodium carbonate solution. The precipitate which formed was filtered from the solution, washed well with water, dried *in vacuo* over P_2O_5, and then extracted with chloroform. The chloroform solution was evaporated under reduced pressure, leaving a glassy solid which was used without further purification for the diastereomer separation.

Cr((+)atc)$_3$ was prepared by adding a solution of 1.75 g of the ligand in 30 ml of methanol to a solution of 1.50 g of chromium alum, $K_2Cr_2(SO_4)_4 \cdot 24H_2O$, and 1.50 g of sodium acetate in 10 ml of water. This mixture was heated on a steam bath for *ca.* 1 hr or until most of the methanol had boiled away; more water was then added, and the product was extracted into benzene. Evaporation of the benzene solution gave a green glasslike material which was dissolved in ethanol and treated with aqueous sodium carbonate as above.

Separation of Diastereomers.—Separation was achieved by thin layer chromatography with silica gel as the sorbent. Precoated preparative tlc plates with a 2-mm layer of silica gel F-254 were purchased from Brinkmann Instruments, Inc. The multiple-development, ascending technique was employed using a 4:1 (by volume) *n*-pentane–diethyl ether solvent mixture for the Co(III) isomers and a 95:5 (by volume) chloroform–acetone

---

[2] (a) A. W. Bishop, L. Claisen, and W. Sinclair, *Ann. Chem.*, **281**, 314 (1894); (b) I. Lifschitz, *Recl. Trav. Chim. Pays-Bas*, **41**, 627 (1922); (c) I. Lifschitz, *Z. Phys. Chem.*, **105**, 27 (1923); (d) I. Lifschitz, *Recl. Trav. Chim. Pays-Bas*, **69**, 1495 (1950); (e) S. F. Mason, *Quart. Rev., Chem. Soc.*, **17**, 20 (1963).

[3] These symbols have been recommended by the IUPAC: *Inorg. Chem.*, **9**, 1 (1970).

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

[5] Y. T. Chen and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **90**, 6660 (1968).

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

[7] (a) C. S. Springer, Jr., R. E. Sievers, and B. Feibush, *Inorg. Chem.*, **10**, 1242 (1971). (b) The work by Springer, Sievers, and Feibush on Co((+)atc)$_3$ was submitted for publication about the same time as this paper (C. S. Springer, private communication). The two independent sets of results are in good agreement with regard to assignments of configuration and relative isomer abundances. CD spectra of the isomers are qualitatively the same but differ slightly in Δε values because different solvents were employed. Springer, *et al.*, were able to equilibrate the diastereomers of Co((+)atc)$_3$ *without decomposition* in degassed benzene solutions at 60° in sealed nmr tubes. Relative isomer abundances in the equilibrated mixture were found to be the same as in the mixture produced during synthesis.

[8] G. W. Everett, Jr., and Y. T. Chen, *J. Amer. Chem. Soc.*, **92**, 508 (1970).

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

[10] H. F. Bauer and W. C. Drinkard, *Inorg. Syn.*, **8**, 202 (1966).

TABLE I

CHARACTERIZATION OF TRIS[(+)-ACETYLCAMPHORATO]COBALT(III) AND -CHROMIUM(III) COMPLEXES

Tlc band[a]	Assigned confign[b]	% calcd C	% calcd H	% found C	% found H	Abundance, % of total	CD max, cm^{-1} ($\Delta\epsilon$)[c]
A	Δ-*trans*-Co((+)atc)$_3$	67.69	8.04	66.77	8.05	29.5	14,814 (1.99), 16,863 (−3.68)
B	Λ-*trans*-Co((+)atc)$_3$			68.00	8.32	48.2	14,556 (−2.15), 16,835 (6.22), 22,472 (−7.01)
C	Λ-*cis*-Co((+)atc)$_3$			66.76	8.57	12.9	14,640 (−1.54), 16,835 (5.68), 22,472 (−7.12)
D	Δ-*cis*-Co((+)atc)$_3$			66.57	8.61	9.4	14,814 (1.88), 16,950 (−2.74), 23,420 (4.50)
A	Δ-*trans*-Cr((+)atc)$_3$	68.44	8.14	68.22	8.16	28.8	16,393 (1.89), 18,519 (−2.89)
B	Λ-*trans*-Cr((+)atc)$_3$			68.46	8.20	36.3	16,393 (−1.71), 18,519 (3.63)
C	Λ-*cis*-Cr((+)atc)$_3$			68.85	8.22	19.4	16,313 (−1.85), 18,416 (3.07)
D	Δ-*cis*-Cr((+)atc)$_3$			68.51	8.14	15.5	16,313 (1.63), 18,416 (−2.71)

[a] Isomers A–D are in decreasing order of elution on the tlc plates. [b] See text for a discussion of these assignments. [c] Data refer to the visible region only.

mixture for the Cr(III) isomers. About 250 mg of mixed diastereomer sample could be chromatographed on each 20 × 20 cm plate; the separation required about 16 hr total development time. After separation, the four bands were removed from the plate, and the samples were extracted from the sorbent with acetone or methanol. The solvent was removed using a rotary evaporator at room temperature, and the samples were dried *in vacuo* over P_2O_5. The samples were then dissolved in carbon tetrachloride; the solutions were filtered to remove any remaining silica gel, and the solid diastereomers were recovered by evaporation of the solvent. Elemental analyses were carried out on all the separated diastereomers (see Table I). The diastereomers of Cr((+)atc)$_3$ were readily obtained in good microcrystalline form, whereas those of the corresponding Co(III) complex formed glasslike solids. Analyses for the Cr(III) isomers were generally better than those of the Co(III) isomers. The Co(III) isomers showed noticeable decomposition within 2 days in the solid state or in solution, forming a tan solid which was insoluble in carbon tetrachloride, chloroform, or cyclohexane. The individual diastereomers of the Co(III) complex are all green, whereas for the Cr(III) complex, isomers B and C are green and isomers A and D are brown. Infrared spectra in the 900–4000-cm^{-1} range are essentially identical for all eight diastereomers of Co((+)atc)$_3$ and Cr((+atc)$_3$. Absorbances occurred at the following frequencies (in cm^{-1}): 2960 (s), 2880 (w), 1760 (w, b), 1710 (w, b), 1605 (s), 1490 (s), 1400 (m), 1390 (m), 1380 (m), 1335 (mw), 1290 (w), 1265 (w), 1230 (m), 1205 (m), 1190 (mw), 1160 (w), 1130 (w), 1110 (w), 1080 (w), 1045 (w), 1010 (w, b), 930 (m) (abbreviations: s, strong; m, medium; w, weak; b, broad).

Measurement of Stereoselectivity.—In order to determine the relative amounts of diastereomers present, an effort was made to remove each band quantitatively from the tlc plates. The samples were isolated as described above and dissolved in accurately known volumes of chloroform or cyclohexane. Visible absorption spectra were recorded for each solution. From the absorbances of these solutions and the ϵ_M values obtained from solutions of the purified isomers, the relative abundances of diastereomers from the preparative reaction could be obtained. The results are given in Table I.

Physical Measurements.—Electronic absorption spectra of the individual diastereomers in chloroform or cyclohexane solution were recorded on a Cary Model 14 spectrophotometer. A Cary Model 60 spectropolarimeter was used in obtaining CD spectra of chloroform or cyclohexane solutions of the diastereomers at room temperature. Vibrational absorption spectra were recorded for carbon tetrachloride solutions on a Beckman Model IR8 spectrophotometer. Pmr spectra of the Co(III) isomers were obtained using a Varian Model HA100 spectrometer with carbon tetrachloride or benzene as the solvent. X-Ray powder patterns were made by the Debye–Scherrer technique using Ni-filtered Cu Kα radiation. Elemental analyses were carried out using an F & M Model 185 C, H, and N analyzer.

Results and Discussion

Cobalt(III) Complexes.—Thin layer chromatography of the mixture of diastereomers results in four green bands, designated hereafter as A, B, C, and D in decreasing order of elution. The separated diastereomers were isolated from the sorbent as described in the Experimental Section; elemental analyses of the separated isomers are given in Table I. Electronic absorption spectra of all four diastereomers are essentially the same. From the CD curves (Figure 2) it is immediately apparent that isomers A and D have the same helical configuration which is opposite to that of isomers B and C. The 100-MHz pmr spectrum of isomer A in benzene solution shows splitting of the acetyl methyl resonance; this resonance is clearly split for isomer B in CCl_4 solution. No splitting of this signal in either solvent is found for isomers C and D. This establishes the trans configuration (C_1) for A and B; isomers C and D must have the cis configuration (C_3), where all three methyl groups are related by symmetry. These assignments are consistent with previous work on Co((+)hmc)$_3$ and Co((+)atc)$_3$ using column chromatography; *i.e.*, the faster moving samples were assigned the trans configuration on the basis of their pmr spectra.[4,5,7]

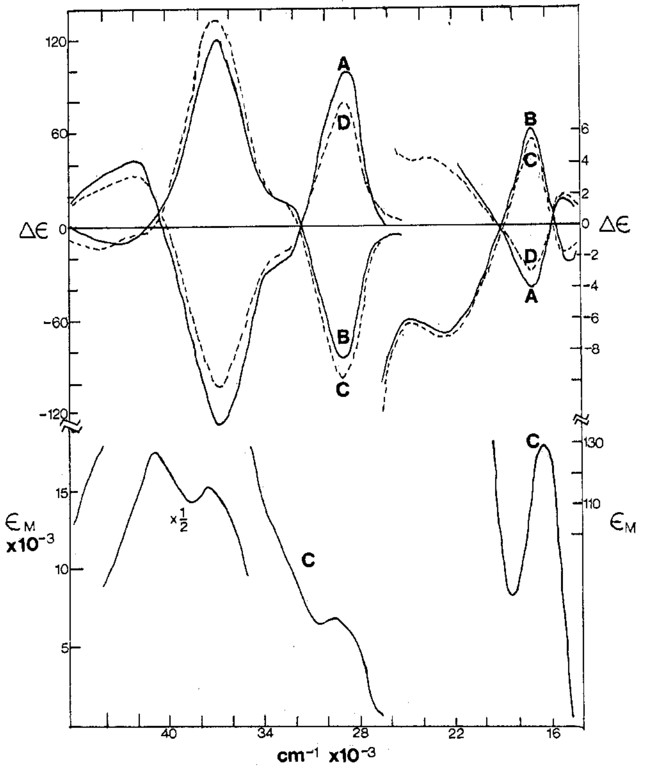


Figure 2.—Absorption and CD spectra of Co((+)atc)$_3$ diastereomers in cyclohexane solutions. Letters in the figure correspond to those in Table I.

The uncertainties involved in assigning Δ and Λ configurations to tris-β-diketone complexes have been discussed earlier.[8] Assuming effective D_3 symmetry in these complexes, the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ (O_h) transition is split into transitions of A_2 and E symmetry which should have CD's of opposite sign. If these transitions can be identified, an empirical rule, which seems to be valid for a number of trigonal complexes of d^3 and low-spin d^6 electron configurations, may be used to assign the absolute configuration. According to the rule, if a positive CD is found for the transition of E symmetry, the complex has the Λ configuration.[6] It is also observed that for most trigonal complexes of d^3 or low-spin d^6 electron configuration, the stronger CD band in the visible region arises from the transition of E symmetry.[6]

In the visible region all four diastereomers of $Co((+)\text{-}atc)_3$ show a well-defined CD band at ~16,800 cm^{-1} and another weaker band of opposite sign at ~14,700 cm^{-1}. Piper[11] analyzed the single-crystal polarized spectrum of tris(acetylacetonato)cobalt(III) and assigned the higher energy component (17,000 cm^{-1}) to the ^1E transition; the transition of A_2 symmetry occurs at 16,200 cm^{-1}. Since the relative order of energy levels for $Co((+)hmc)_3$ is not expected to differ from that of the acetylacetone complex, McCaffery, *et al.*,[6] and Dunlop, *et al.*,[4] assigned the higher energy (16,400 cm^{-1}) and lower energy (14,300 cm^{-1}) components to transitions of ^1E and $^1A_2$ symmetry, respectively. Assuming these assignments are valid also for $Co((+)atc)_3$ and applying the rule mentioned above, absolute configurations may be assigned to the diastereomers of $Co((+)atc)_3$ as follows: A, Δ-trans; B, Λ-trans; C, Λ-cis; D, Δ-cis. These assignments must be considered tentative, however, until the absolute configuration of at least one trigonal d^3 or d^6 β-diketone complex has been established by X-ray methods.[12] The rule relating the sign of the CD of the E transition to the absolute configuration has recently been shown to be inapplicable[13] for the Δ-(+)-tris(1,3-diaminopropane)cobalt(III) cation, where the N–Co–N angle exceeds 90°. The O–M–O angles in $Co(atc)_3$ and $Cr(atc)_3$ are expected to be close to 90°, since values in this range are found for other tris-β-diketone complexes.[14] In principle, CD spectra in the uv region could be used to assign absolute configurations to tris-β-diketone complexes of transition metals as has been done for the tris(acetylacetonato)silicon(IV) ion using the exciton theory.[15] However, for $Co((+)atc)_3$ and $Cr((+)atc)_3$ the absorption of the ligand anion, which occurs at ~33,000 cm^{-1}, cannot clearly be distinguished in the spectra of the complexes. Furthermore, other criteria for application of exciton theory[16] appear not to be satisfied in these complexes; thus no attempt to analyze the CD spectra in the uv region is made in this paper.

The relative abundances of diastereomers A–D of $Co((+)atc)_3$ are given in Table I. The trans diastereomers are most abundant, as expected, since the probability of forming a trans isomer is 3 times that of forming a cis isomer. In fact, the sum of abundances of C and D divided by the sum of abundances of A and B is close (0.29) to the statistical value of 0.33. Considering either the cis or the trans isomers, the one assigned the Λ configuration is most abundant and also has the largest $|\Delta\epsilon|$ at ~16,800 cm^{-1}. This explains the net positive Cotton effect at this frequency found for both cis and trans forms in previous work where Δ and Λ diastereomers were not separated.[5] The ratio of abundances of Δ-trans to Λ-trans diastereomers is 0.61. This is close to the ratio found for the corresponding diastereomers of tris[(−)-hydroxymethylenecarvonato]cobalt(III)[8] and may be a consequence of the related absolute configurations of the two ligands. Comparison of the V(III) complexes of these two ligands, where stereoselectivity must be thermodynamically controlled, reveals a much higher degree of stereoselectivity for the acetylcamphor complex.[5,8] Since the Δ-trans/Λ-trans ratio is not appreciably different for the corresponding Co(III) complexes, it must be concluded that some kinetic control of stereoselectivity occurs for the Co(III) complexes. Unfortunately the ease with which the individual diastereomers of $Co((+)atc)_3$ decompose precludes isomerization experiments designed to assess isomer abundances under conditions of thermodynamic equilibrium.[7b]

Chromium(III) Complexes.—The four diastereomers of $Cr((+)atc)_3$, labeled A–D in decreasing order of elution, are readily separated by tlc. Table I contains the results of elemental analyses along with CD data and relative isomer abundances. CD spectra in the visible and uv regions are shown in Figure 3. It is apparent from the CD spectra that diastereomers A and D have the same helicity but opposite to that of diastereomers B and C, as was found for the corresponding Co(III) isomers. Since nmr could not be used to distinguish cis and trans isomers for the paramagnetic Cr(III) complexes, efforts were made to relate the configurations of these diastereomers to those of $Co((+)atc)_3$. It should be emphasized here that isomers A–D for a given complex are *diastereomers* and, as such, are chemically and physically different. Diastereomers may, for example, have different crystalline structures.

X-Ray powder diffraction data for the individual diastereomers of $Cr((+)atc)_3$ and $Co((+)atc)_3$ are presented in Table II. It is apparent that the diastereo-

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR TRIS[(+)-ACETYLCAMPHORATO]COBALT(III) AND -CHROMIUM(III) COMPLEXES

Complex	Tlc band	Interplanar spacings Å
$Co((+)atc)_3$	A	12.36 s, 9.33 m, 8.14 m, 6.82 s, 6.62 s, 6.41 s, 5.84 s, 5.00 m
$Cr((+)atc)_3$	A	12.54 s, 9.43 m, 8.25 m, 6.86 s, 6.62 s, 6.46 s, 5.86 s, 5.07 m
$Co((+)atc)_3$	B	10.88 s, 10.02 vs, 8.80 m, 6.84 vs, 6.57 m, 6.08 s, 5.62 m, 5.46 w, 4.36 m
$Cr((+)atc)_3$	B	12.81 s, 10.68 s, 10.11 w, 8.76 w, 7.15 vs, 6.68 m, 6.17 vs, 5.38 m, 5.07 m, 4.74 w
$Co((+)atc)_3$	C	13.39 m, 11.33 w, 9.51 vs, 8.89 m, 8.08 m, 7.36 m, 7.01 s, 6.73 s, 6.55 m, 5.98 s, 5.80 m, 5.70 s, 4.41 m
$Cr((+)atc)_3$	C	13.34 s, 12.03 w, 11.30 w, 9.46 vs, 8.85 m, 8.13 m, 7.41 m, 6.75 s, 5.95 vs, 5.57 s, 4.42 m
$Co((+)atc)_3$	D	12.11 s, 10.25 s, 8.41 s, 7.50 vs, 6.31 w, 5.85 m, 5.57 m, 5.40 mw, 5.26 w, 4.60 w
$Cr((+)atc)_3$	D	12.11 s, 10.25 s, 8.41 s, 7.50 s, 6.31 m, 6.10 w, 5.85 s, 5.57 m, 5.40 ms, 5.26 m, 4.60 m

---

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

(12) W. D. Horrocks, Jr., D. L. Johnston, and D. MacInnes, *J. Amer. Chem. Soc.*, **92**, 7620 (1970).

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

(14) (a) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966); (b) B. Morosin, *Acta Crystallogr.*, **19**, 131 (1965).

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

(16) S. F. Mason, *Inorg. Chim. Acta Rev.*, **2**, 89 (1968).

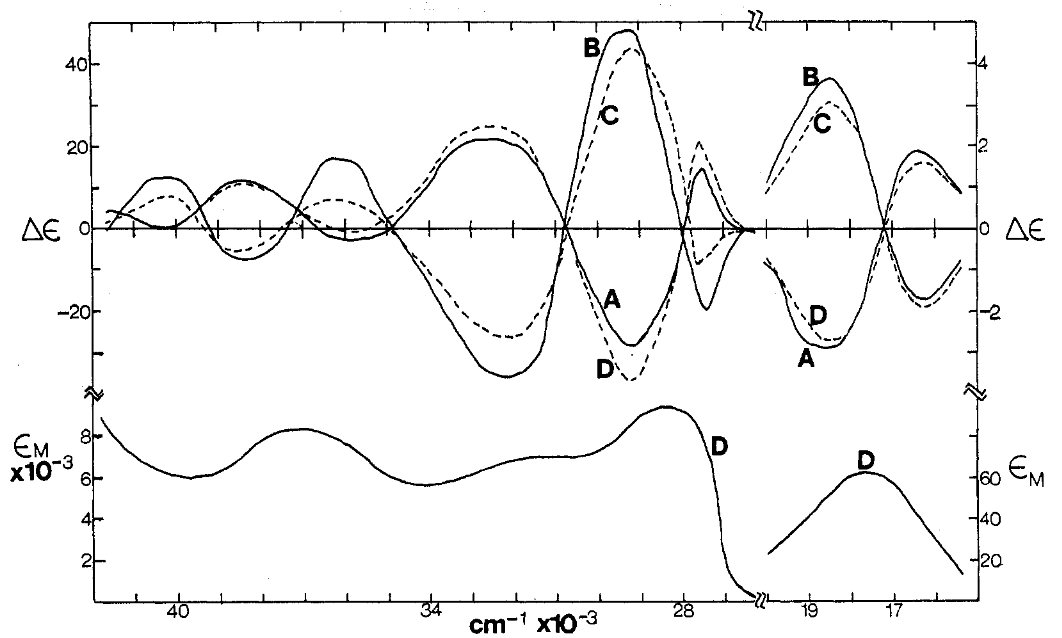


Figure 3.—Absorption and CD spectra of Cr((+)atc)$_3$ diastereomers in chloroform (visible region) and cyclohexane (uv region) solutions. Letters in the figure correspond to those in Table I.

mers A–D of a given complex have different crystalline structures. Of greater interest and significance is the close match between the interplanar spacings of isomers A, C, and D of Cr((+)atc)$_3$ and those of isomers A, C, and D, respectively, of Co((+)atc)$_3$. We interpret these results in the following way. Diastereomers A of Co((+)atc)$_3$ and Cr((+)atc)$_3$ are isomorphous and have the same molecular configuration; the same is true of diastereomers C and D. By process of elimination, the B diastereomers of Co((+)atc)$_3$ and Cr((+)-atc)$_3$ must have the same configuration. Thus the four diastereomers of Cr((+)atc)$_3$ may tentatively be assigned the following absolute configurations: A, Δ-trans; B, Λ-trans; C, Λ-cis; Δ-cis.[17] These assignments are consistent with the tlc observations. Since the polarities of Co(III) and Cr(III) diastereomers of the same configuration are expected to be very similar, the order of elution for the Cr(III) diastereomers should be the same as for the Co(III) diastereomers.

In the D_3 point group the first spin-allowed transitions for a d^3 electron configuration have the same symmetries as for a d^6 configuration, *i.e.*, A$_2$ and E. Although the relative energies of these transitions are sometimes reversed on going from a Co(III) complex to the corresponding Cr(III) complex, the rule (*vide supra*) relating the helicity to the sign of the Cotton effect of the E transition is valid in a number of cases.[6,18] Components of the first spin-allowed transition of Cr((+)atc)$_3$ may be seen in the visible region of the CD spectra in Figure 3. Both transitions occur at higher energy than those of Co((+)atc)$_3$, but the overall pattern is the same, *i.e.*, a weak CD followed by a stronger CD of opposite sign at higher energy. The Cotton effects of the two transitions of a given diastereomer of Cr((+)atc)$_3$ parallel those of the diastereomer of Co((+)atc)$_3$ having the same configuration. The component at high energy (18,350 cm^{-1}) in Cr((+)hmc)$_3$ has been assigned to the E transition,[6] and presumably this assignment is valid for the diastereomers of Cr((+)atc)$_3$. Thus diastereomers B and C, which are assigned the Λ configuration on the basis of their isomorphism with the Co(III) complexes having the Λ configuration, show positive Cotton effects for the E transition at ~18,500 cm^{-1}, and the empirical rule appears to be valid.

The relative abundances of diastereomers A–D of Cr((+)atc)$_3$ (Table I) qualitatively parallel those of the Co(III) complexes. The Λ-trans isomer is most abundant; however the ratio of the combined abundances of cis isomers to the combined abundances of trans isomers (0.54) deviates appreciably from the statistical value of 0.33. These Cr(III) diastereomers are kinetically inert as demonstrated by the fact that refluxing for 12 hr in chloroform, methanol, or methanol–water in the presence of activated charcoal does not result in isomerization detectable by tlc. It is concluded that stereoselectivity is kinetically controlled in these Cr(III) complexes, and the relative isomer abundances reflect their relative rates of formation.

Acknowledgment.—This work was supported by the National Science Foundation under Grant GP-8871 and by the General Research Fund of the University of Kansas. We are indebted to Professor Gilles of this department for use of his X-ray equipment.

---

[17] The absolute configuration of diastereomer B of Cr((+)atc)$_3$ has recently been determined by single-crystal X-ray diffraction.[12] The complex has the Λ-trans configuration, in agreement with our assignment. This structural determination, in combination with the powder data in Table II, confirms our configurational assignments for all eight diastereomers of Co((+)atc)$_3$ and Cr((+)atc)$_3$.

[18] An apparent exception to this rule has recently been reported for tris(biguanide)chromium(III): G. R. Brubaker and L. E. Webb, *J. Amer. Chem. Soc.*, **91**, 7199 (1969).