$$Fe(CN)_5SCN^{3-} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Fe(CN)_5NCS^{3-} \qquad (XIII)$$

$$Fe(CN)_5NCS^{3-} + OH^- \overset{(fast)}{\rightleftharpoons} Fe(CN)_5OH^{3-} + NCS^- \qquad (XIV)$$

If such a scheme applies, $k_5 = A = 0.0028 \text{ sec}^{-1}$. The value of k_{-5} can be determined as described in the literature,[4] for which we determined $k_{-5} = 0.036 \text{ sec}^{-1}$.[27] This would give for the linkage isomerization reaction

(27) Although they ascribed a N → S isomerization to the two-step reaction observed, Stasiw and Wilkins[4] did not carry out a study sufficient to characterize the system and did not cite a value for k_{-5}. The value given in the text was determined in the course of this study by repeating their measurements.

K_{XIII} the value of 0.08, which does not seem unreasonable considering the undoubtedly softer acidity of $Fe(CN)_5^{2-}$ compared to that of $Fe(H_2O)_5^{3+}$.

Further work on these complexes is planned, to study directly the immediate reactions of the complex $(Et_4N)_3Fe(CN)_5NCS$, known to be N bonded in the solid state,[5] when dissolved in aqueous solution, to attempt to provide further evidence for the generality of Schemes II and III by the study of other members of the $Fe(CN)_5X^{3-}$ series, and to study in considerably greater detail the novel two-step process by which the dimer $Fe_2(CN)_{10}^{4-}$ undergoes substitution and monomerization.

The Diastereomers of Tris[(+)-3-acetylcamphorato]ruthenium(III). Separation and Assignment of Absolute Configurations

By GROVER W. EVERETT, Jr.,* and RICHARD M. KING

Separation of the four diastereomers of tris[(+)-3-acetylcamphorato]ruthenium(III) was accomplished by thin-layer chromatography on silica gel. Proton and deuteron nuclear magnetic resonance spectra are used to distinguish the cis and trans diastereomers. Complete configurational assignments are based on the isomorphism of two of the diastereomers with two diastereomers of the analogous chromium(III) complex for which absolute configurations are known. The relative signs of Cotton effects in the circular dichroism spectra of the individual diastereomers are consistent with the configurational assignments.

The four diastereomers possible for tris complexes of chiral, bidentate ligands having inequivalent donor atoms may be designated Δ-cis, Δ-trans, Λ-cis, and Λ-trans. Here cis and trans refer to facial and meridional arrangements of like donor atoms in the octahedral coordination sphere, and Δ and Λ indicate right- and left-hand helicities about the C_3 or pseudo-C_3 axis of the complex.[1] These four diastereomers have been separated and characterized for a few α-amino acid and β-diketone complexes. Most work has involved cobalt(III) as the metal ion. For example, all twelve diastereomers of the Co(III) complexes of L-alanine, L-valine, and L-leucine have been isolated, and absolute configurations of the isomers have been assigned from CD and nmr data.[2] The configurational assignments are supported by an X-ray study of one diastereomer of the alanine complex.[3]

More recently the diastereomers of tris(β-diketonato)cobalt(III) complexes, where β-diketone = (+)- and (−)-hydroxymethylenecarvone ((+)- and (−)-Hhmcar),[4] (+)-hydroxymethylenepulegone ((+)-Hhmpul),[4] and (+)-3-acetylcamphor ((+)Hatc),[5,6]

have been separated chromatographically and investigated by ORD, CD, and nmr methods. The diastereomers of Cr((+)atc)₃ may also be separated by thin-layer chromatography (tlc) on silica gel, and X-ray powder diffraction data demonstrate the isomorphism of three of these diastereomers with three diastereomers of Co((+)atc)₃.[6] A single-crystal X-ray structural determination[7] of one of the diastereomers of Cr((+)-atc)₃ confirmed the configurational assignment made earlier and, combined with the X-ray powder diffraction studies, established absolute configurations of all eight diastereomers of Co((+)atc)₃ and Cr((+)atc)₃.[6] Paramagnetic vanadium(III) complexes of the above β-diketones show well-resolved, isotropically shifted pmr signals in solution.[4,8] The diastereomers present in a mixture can be identified by analysis of the pmr spectra in some cases, and signal integration provides a measure of the relative diastereomer abundances. For V((+)atc)₃ the relative proportions of diastereomers depend somewhat on the solvent used. However, all four isomers are clearly present in some solvents.[9]

The present work concerns the ruthenium(III) complex of (+)-3-acetylcamphor, Ru((+)atc)₃, I. This complex is unique in the series of acetylcamphor complexes studied thus far in that the diastereomers are sufficiently nonlabile to allow their separation and measurement of their individual CD spectra as was done for the Co(III) and Cr(III) complexes, yet the

(1) *Inorg. Chem.*, **9**, 1 (1970).

(2) (a) B. E. Douglas and S. Yamada, *ibid.*, **4**, 1561 (1965); (b) J. H. Dunlop and R. D. Gillard, *J. Chem. Soc.*, 6531 (1965); (c) E. Larsen and S. F. Mason, *J. Chem. Soc. A*, 313 (1966); (d) R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966); (e) R. D. Gillard and N. C. Payne, *J. Chem. Soc. A*, 1197 (1969).

(3) M. G. B. Drew, J. H. Dunlop, R. D. Gillard, and D. Rogers, *Chem. Commun.*, 42 (1966).

(4) G. W. Everett, Jr., and Y. T. Chen, *J. Amer. Chem. Soc.*, **92**, 508 (1970).
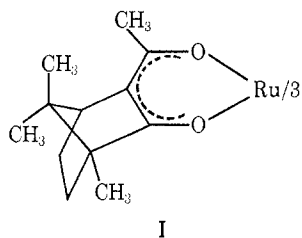
(5) C. S. Springer, Jr., R. E. Sievers, and B. Feibush, *Inorg. Chem.*, **10**, 1242 (1971).

(6) R. M. King and G. W. Everett, Jr., *ibid.*, **10**, 1237 (1971).

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

(8) Y. T. Chen and G. W. Everett, Jr., *ibid.*, **90**, 6660 (1968).

(9) R. M. King and G. W. Everett, Jr., *Inorg. Chim. Acta*, in press.

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isotropically shifted nmr signals of ligand nuclei are reasonably narrow, allowing nmr studies analogous to those carried out on the V(III) complex.

Few attempts to assign configurations to chiral Ru(III) complexes have been made. $(-)$-cis-RuCl$_2$-(en)$_2^+$ has been shown[10] to have the same configuration as $(+)$-cis-CoCl$_2$(en)$_2^+$, which in turn has the configuration of Λ-$(+)$-Co(en)$_3^{3+}$. Elsbernd and Beattie[11] resolved [Ru(en)$_3$]I$_3$ and assigned the Λ configuration to the $(-)_{350}$Ru(en)$_3^{3+}$ ion from a combination of crystallization and CD experiments.

Experimental Section

Syntheses.—$(+)$-3-Acetylcamphor was prepared from $(+)$-3-bromocamphor by Brühl's method.[12] This ligand was deuterated at the acetyl methyl position by the following procedure. Approximately 30 ml of $(+)$-3-acetylcamphor was allowed to reflux in a mixture of deuterium oxide (50 ml), ethanol (50 ml), and sodium carbonate (1 g). After 48 hr the solution was cooled and extracted (8 times) with ethyl ether. Ether was removed from the combined extracts under vacuum, fresh D$_2$O and base were added to the partially deuterated ligand, and refluxing was resumed for another 48 hr. After eight such cycles, the product was stripped of all solvent and vacuum distilled. Recovery of ligand was *ca.* 50%, 90–95% deuterated at the acetyl methyl position.

Ru$((+)$atc)$_3$ was prepared by a modification of the procedure outlined in Gmelin.[13] In a typical preparation, a mixture of 2.0 g of commercially available RuCl$_3 \cdot$1–3H$_2$O (Alpha-Ventron), 6.0 g of ligand, 50 ml of 1 M HCl, and 200 ml of toluene was refluxed under a nitrogen atmosphere for 12 hr. During this time the organic phase attained a deep blue-violet color. A deaerated solution of sodium carbonate (6.5 g) in water (100 ml) was added to the hot solution, and the mixture was then cooled to room temperature. The toluene layer containing the product was isolated, and upon removal of the solvent a dark blue oil remained. At this point it was no longer necessary to work in an inert atmosphere. The oil was dissolved in a minimum amount of ethanol and added dropwise to 250 ml of a vigorously stirred solution of 5% sodium carbonate. The precipitate which formed was filtered, washed well with water, dried *in vacuo*, and used without further purification for the isomer separation.

The complex containing deuterated ligand, designated hereafter as Ru$((+)$atc-d_3)$_3$, was prepared as outlined above, using D$_2$O and D$_2$SO$_4$ in place of H$_2$O and HCl in order to prevent loss of ligand deuterium by exchange.

Chromatography.—Separation of the four diastereomers of Ru$((+)$atc)$_3$ and Ru$((+)$atc-d_3)$_3$ was achieved by the thin-layer chromatographic technique previously described,[6] using precoated preparative tlc places (silica gel F-254). A 1:1 (by volume) *n*-heptane–ethyl ether solution was used to develop the plates. Good separation was accomplished by one development in most cases. Results of elemental analyses and R_f values are reported for each isomer in Table I.

Isomer Abundances.—The relative amounts of diastereomers present in the reaction mixture were determined spectrophotometrically, after separation, using the technique described earlier.[6] Results are given in Table I. In an effort to determine isomer abundances prior to separation, proton and deuteron nmr signal areas in the spectra of mixtures of all four diastereomers

(10) J. A. Broomhead and L. Kane-Maguire, *J. Amer. Chem. Soc.*, **91**, 3374 (1969).

(11) H. Elsbernd and J. K. Beattie, *Inorg. Chem.*, **8**, 893 (1969).

(12) J. W. Brühl, *Ber.*, **37**, 746 (1904).

(13) "Gmelins Handbuch der anorganischen Chemie," Vol. 8, Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 468.

TABLE I

CHARACTERIZATION OF
TRIS[$(+)$-3-ACETYLCAMPHORATO]RUTHENIUM(III)

Tlc band	$[\alpha]^{25}$D^a	Assigned configuration^b	—% calcd— C	H	—% found— C	H	$R_f{}^c$	Abundance, % of total^d
A	+2500	Δ-trans	63.51	7.55	63.38	7.78	0.65	33
B	−1700	Λ-trans	63.51	7.55	63.66	7.79	0.54	34
C	−2400	Λ-cis	63.51	7.55	63.34	7.74	0.38	20
D	+2200	Δ-cis	63.51	7.55	63.21	7.70	0.22	13

^{a} Obtained from ORD spectra. ^{b} See text for a discussion of these assignments. ^{c} Measured on preparative layer plates having a 2 mm thick layer of silica gel. Estimated accuracy ±0.02. ^{d} Determined from tlc.

were measured using a planimeter or a Du Pont Model 310 curve resolver.

Isomerization.—In order to assess the stability of Ru$((+)$atc)$_3$ toward isomerization, the following experiment was carried out. A solution of isomer C in Spectroquality carbon tetrachloride was degassed, sealed *in vacuo* in an nmr tube, and heated in a 60° bath for 5 days. Pmr spectra taken before heating and at regular intervals during the heating period were identical except that all signals became progressively weaker, indicating decomposition of the complex.

Physical Measurements.—Electronic absorption spectra of the diastereomers in cyclohexane solutions were recorded on a Cary Model 14 spectrophotometer. A Cary Model 60 spectropolarimeter was used to obtain ORD and CD spectra of 10^{-3}–10^{-4}M solutions of the diastereomers in cyclohexane. Proton and deuteron nmr spectra were obtained using a Varian Model HA-100 spectrometer operating at 100.0 MHz (^{1}H) and 15.35 MHz (^{2}H). The solvent used for all nmr spectra was CCl$_4$; internal references were tetramethylsilane (^{1}H) and $\sim$20% v/v benzene-d_6 (^{2}H). Spectra were calibrated by standard sidebanding techniques. Infrared spectra in the 800–4000-cm^{-1} range, recorded for carbon tetrachloride solutions on a Beckman Model IR8 spectrophotometer, were essentially identical for all four diastereomers. Absorbances occurred at the following frequencies (in cm^{-1}): 2955 (s), 2870 (m), 1585 (s), 1480 (s), 1380 (s), 1321 (m), 1286 (m), 1254 (m), 1219 (m), 1195 (m), 1175 (s), 1152 (vw), 1123 (w), 1103 (w), 1076 (m), 1004 (m), 926 (s), 876 (vw), 858 (vw), 835 (w) (abbreviations: s, strong; m, medium; w, weak; vw, very weak). The effective magnetic moment of isomer D was determined by the Faraday method to be 2.09 BM at 22°.

Results and Discussion

Separation and Relative Abundances of the Diastereomers.—Separation of the four diastereomers of Ru$((+)$atc)$_3$ on preparative layer plates of silica gel was achieved with far greater ease than for the Co(III) and Cr(III) complexes of the same ligand. The four well-separated chromatographic bands containing isomers A, B, C, and D in order of decreasing rate of elution were removed from the tlc plates using methods described previously.[6] R_f values are given in Table I. The individual diastereomers are microcrystalline solids varying from red-violet (A) to purple (B and C) and blue (D). Results of elemental analyses are shown in Table I.

As is the case for the Co(III) and Cr(III) analogs, the two isomers having highest R_f values, A and B, are the most abundant. These are the two trans isomers as shown by nmr (*vide infra*). The ratio of 0.97 for the abundances of these two isomers of Ru$((+)$-atc)$_3$ is much closer to the statistically expected value of 1.00 than is found for the corresponding isomers of Cr$((+)$atc)$_3$ and Co$((+)$atc)$_3$. However, the ratio (C + D)/(A + B) ($=0.49$), representing total cis isomer abundance relative to total trans isomer abundance, is appreciably larger than the statistical value of 0.33. An attempt was made to obtain an equilibrium

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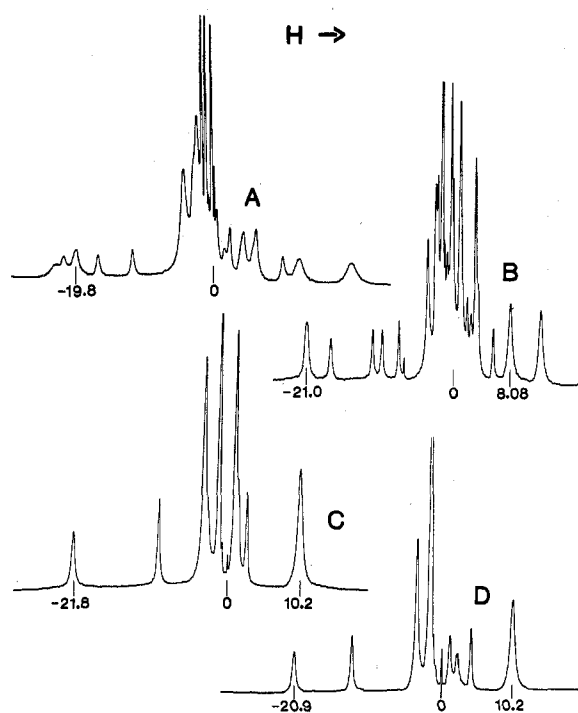
Figure 1.—Proton nmr spectra of the individual diastereomers A–D of Ru((+)atc)₃ in CCl₄ solutions at 32°. Numbers indicate the scale of chemical shifts in ppm relative to tetramethylsilane.

mixture of diastereomers by thermal isomerization, starting with isomer C (see Experimental Section). No equilibrium occurred, however, indicating the complex is kinetically inert. Thus the relative isomer abundances of Ru((+)atc)₃ are determined by their relative rates of formation during synthesis and not by their relative thermodynamic stabilities as is believed to hold true for the labile complex, V((+)atc)₃.[8]

Nuclear Magnetic Resonance.—The proton nuclear magnetic resonance (pmr) spectra of the four separated diastereomers of Ru((+)atc)₃ are shown in Figure 1. As a result of the paramagnetism of the complex (see Experimental Section) and accompanying isotropic shifts of the nuclear resonances, the pmr spectra cover a range of ~40 ppm at 32°. It is immediately apparent that the spectra of isomers C and D are simpler than those of A and B in that fewer signals are present. Cis isomers have a threefold symmetry axis relating corresponding nuclei on different ligands, and only one resonance signal for each kind of ligand nucleus is expected. On the other hand trans isomers have no symmetry, and up to three resonance signals for each kind of ligand nucleus may occur. Therefore it would appear from the pmr spectra that diastereomers C and D have the cis arrangement, whereas A and B are trans.

Resonance signals arising from the acetyl methyl protons were expected to occur upfield of the tetramethylsilane reference signal, since resonances in this region are found for chelate ring methyls of other tris-(β-diketonato)ruthenium(III) complexes.[14,15] However, these signals could not be unambiguously identified in the pmr spectra, particularly for diastereomers
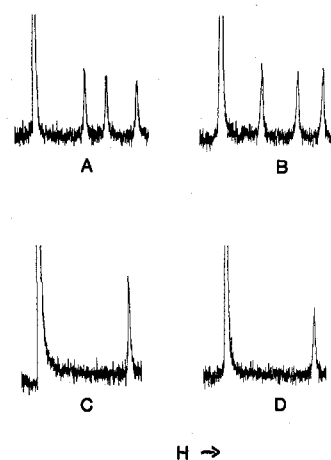
(14) D. R. Eaton, *J. Amer. Chem. Soc.*, **87**, 3097 (1965).
(15) (a) A. Johnson and G. W. Everett, Jr., *ibid.*, **94**, 1419 (1972); (b) G. W. Everett, Jr. and A. Johnson, *ibid.*, **94**, in press.

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Figure 2.—Deuteron nmr spectra of the individual diastereomers A–D of Ru((+)atc-d₃)₃ in CCl₄ solutions at 32°. The intense signal at low field in each spectrum is due to the benzene-d₆ reference. Chemical shifts are given in Table II. Spectra are not all recorded at the same scan rate.

A and B, due to overlap with other signals. Since the acetyl methyl protons of (+)-3-acetylcamphor may be replaced by deuterons (see Experimental Section), it was possible to prepare the partially deuterated complex, Ru((+)atc-d₃)₃. The four diastereomers of this complex were separated by chromatography using the same methods as for the fully protonated complex. Deuteron nuclear magnetic resonance (dmr) spectra were recorded for each isomer. These are shown in Figure 2. Three equally intense methyl signals are found in the dmr spectra of diastereomers A and B, proving that these are the trans isomers. A single CD₃ resonance occurs for isomer C and for isomer D, consistent with a cis arrangement of ligands. Since the acetyl methyl resonances are absent in the *pmr* spectra of Ru((+)atc-d₃)₃ diastereomers, these signals may be located in the pmr spectra of Ru((+)atc)₃ diastereomers by comparison. The assignments are supported by matching the isotropic shifts of the dmr signals with those of the pmr signals, since isotropic shifts on a part per million scale should be the same for pmr and dmr.[15a,16] Proton and deuteron isotropic shifts are compared in Table II. The difference in pmr and dmr isotropic shifts are attributed to isotope effects and to a solvent effect. Although CCl₄ was used as the solvent in each case, samples prepared for dmr contained ~20% v/v benzene-d₆ in order to provide a strong reference signal.

Previously it was demonstrated that the relative abundances of diastereomers present in solutions of V((+)atc)₃ and V((+)hmcar)₃ could be determined by integration of pmr signals.[4,8] These V(III) complexes readily isomerize, and the diastereomers could not be separated chromatographically. The nmr method works best when signals arising from a single kind of hydrogen are well isolated from other resonances and separated from each other in the spectrum of a solution containing a mixture of diastereomers. The pmr spectrum of Ru((+)atc)₃, recorded before separating

(16) Pmr and dmr *chemical* shifts (in ppm) should also match, provided they have a common reference signal. Isotropic shifts are compared here for simplicity since pmr signals are referenced to TMS, whereas benzene-d₆ was used as the reference in all dmr spectra.

TABLE II
NMR DATA (PPM) FOR
TRIS[(+)-3-ACETYLCAMPHORATO]RUTHENIUM(III)[a]

Isomer	Chemical shift[b]		Isotropic shift[c]	
	^{1}H	^{2}H	^{1}H	^{2}H
B	+0.92	+7.69	+3.17	+2.70
A	+6.02	+13.2	+8.27	+8.19
B	+8.08	+14.8	+10.3	+9.80
D	+10.2	+16.8	+12.4	+11.8
C	+10.2	+16.8	+12.4	+11.8
A	+12.4	+18.7	+14.6	+13.7
B	+12.4	+19.9	+14.6	+14.9
A	+19.8	+26.8	+22.0	+21.8

[a] From CCl$_4$ solutions at 32°. Data refer to the acetyl methyl signals only. [b] In ppm relative to TMS (proton) or benzene-d_6 (deuteron). Positive values indicate resonances occur at higher field than references. [c] In ppm relative to the free ligand signal. Positive values indicate resonances are upfield of the ligand signal.
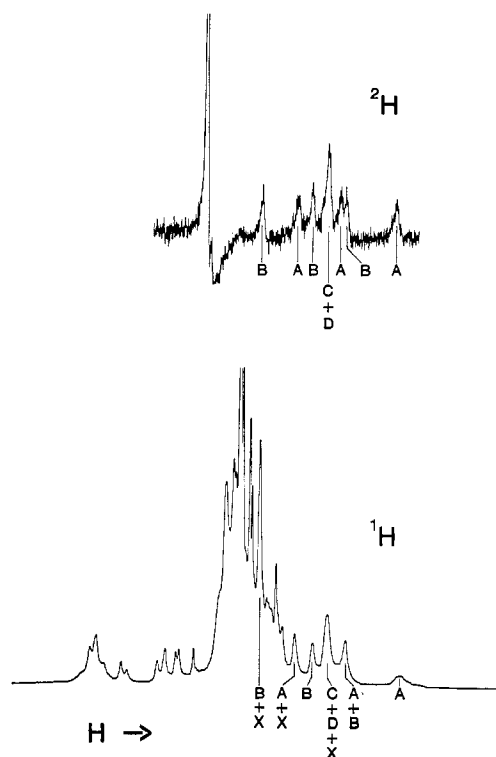

Figure 3.—Proton and deuteron nmr spectra recorded for CCl$_4$ solutions containing mixtures of all four diastereomers of Ru((+)atc)$_3$ and Ru((+)atc-d_3)$_3$, respectively. Assignments of the acetyl methyl resonances to diastereomers A–D are indicated. The letter X is used to signify the presence of a signal not arising from the acetyl methyl.

the individual diastereomers, is shown in Figure 3. Assignments for the acetyl methyl signals are made with the aid of the deuterated complex as described above. Area measurements are hampered by mutual overlap of these signals and by the presence of signals arising from other protons. However, the resonances from isomer A at 19.8 ppm and isomer B at 8.08 ppm may be integrated with the aid of a Du Pont curve resolver. The combined area of these two signals closely matches the area of the signal at 12.4 ppm, which is known to contain a resonance each from A and B. The ratio of isomer abundances A/B so obtained is 0.92, in reasonable agreement with the value obtained upon separating the diastereomers.

The dmr spectrum of the diastereomeric mixture of Ru((+)atc-d_3)$_3$ is also shown in Figure 3. Seven of the eight possible resonances are apparent; the resonances arising from the two cis isomers happen to coincide. The signal-to-noise ratio for the dmr spectrum prevents an accurate determination of the relative isomer abundances by signal integration. However, a rough estimate of the signal areas obtained by planimetry gives the following abundance ratios: A/B = 0.97; total cis (C + D)/total trans (A + B) = 0.40. The relative isomer abundances for Ru((+)atc-d_3)$_3$ are not necessarily expected to be the same as those found for Ru((+)atc)$_3$, since the complexes are kinetically inert, and relative isomer abundances may vary somewhat from one preparation to another. Note that as a result of the considerably smaller signal line widths and perhaps solvent effects for dmr, the pmr signal occurring at 12.4 ppm and containing resonances from isomers A and B is resolved into two signals in the dmr spectrum (cf. Figure 3). The advantages of using dmr rather than pmr for studies of paramagnetic complexes are discussed elsewhere.[15]

The isotropic nmr shifts observed for Ru((+)atc)$_3$ are used to advantage in that the spectra show increased resolution over those of diamagnetic complexes of (+)-3-acetylcamphor. A knowledge of the origin of the shifts, *i.e.*, whether they result from hyperfine contact or dipolar interactions or both, is not essential for these studies. Evidence has been presented[15b] to the effect that the dipolar interaction predominates in at least one tris complex of Ru(III), and this interaction could also be primarily responsible for the shifts observed for Ru((+)atc)$_3$.

Although no detailed assignments of all signals in the pmr spectrum of Ru((+)atc)$_3$ will be attempted here, the simplicity of the spectra for isomers C and D permits general assignments. The signal at highest field in each case arises from the acetyl methyl. The other three strong signals (two are coincident for D) must arise from the camphor methyls. The remaining signals of lower intensity are attributed to the five inequivalent protons on the camphor ring.

Circular Dichroism Spectra.—The nmr experiments described above are capable of distinguishing the cis and trans diastereomers of Ru((+)atc)$_3$; however, the helicity of the arrangement of chelate rings in each isomer must be known before absolute configurations can be assigned. A method widely used in determining the helicities of chiral, six-coordinate Co(III) complexes is to compare ORD or CD curves in the ligand field region for the complex with those of another Co(III) complex of closely related structure whose absolute configuration is unambiguously established. However, few ORD or CD spectra of chiral Ru(III) complexes have been reported, and the relationship between the helicity of the complex and the sign of the Cotton effect for a particular electronic transition is not well established.

CD spectra of the individual diastereomers of Ru((+)atc)$_3$ are shown in Figure 4 along with the absorption spectrum of isomer D. Absorption spectra of all four diastereomers are essentially identical. The two bands at higher energy may be assigned to $\pi \rightarrow \pi^*$ or charge-transfer transitions on the basis of their intensities; the absorption at ~18,000 cm^{-1} could be a d → d transition, but a more precise assignment is impossible at this point. It is readily apparent from

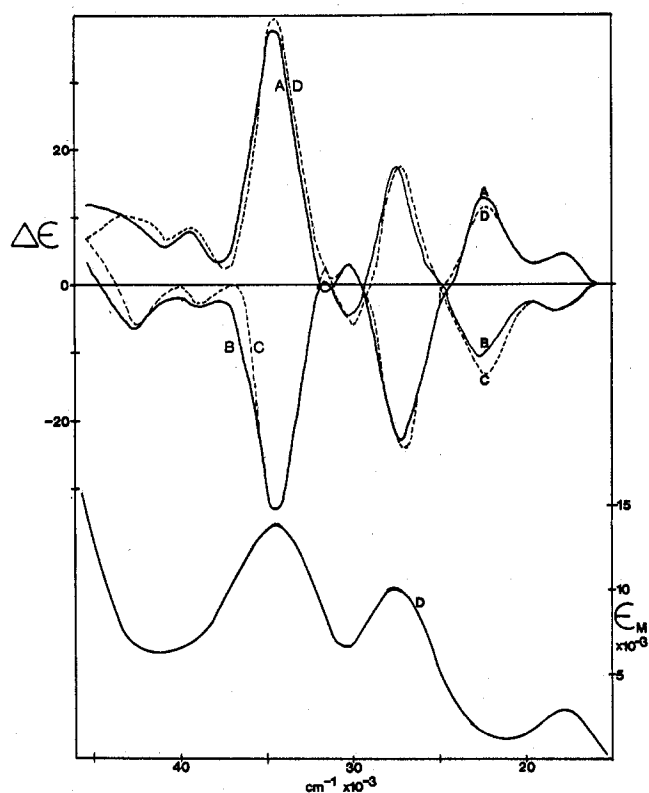Figure 4.—Absorption and circular dichroism spectra for diastereomers of Ru((+)atc)₃ in cyclohexane solutions at ~25°.

Tlc band	Interplanar spacings, Å
A	14.97 (w), 12.44 (s, b), 8.71 (m), 8.01 (m), 7.64 (ms), 7.04–6.56 (vs, vb), 5.80 (m), 5.09 (ms), 4.68 (ms), 4.44 (m, b), 4.25 (m, b)
B	12.90 (s), 10.75 (s), 10.10 (w), 8.87 (m), 7.17 (vs), 6.73 (s), 6.24 (vs), 5.99 (w), 5.42 (m, b), 5.10 (m), 4.75 (w), 4.26 (w), 4.11 (w), 3.91 (m), 3.75 (m), 3.56 (w)
C	12.94 (ms), 12.06 (s), 9.00 (m), 8.17 (ms), 7.08 (s), 6.72 (s, b), 6.10 (w, b), 5.63 (w), 5.44 (w), 5.01 (w), 4.81 (ms), 4.58 (w), 4.19 (w)
D	12.10 (m, b), 10.34 (s), 8.38 (vs), 7.48 (s), 6.26 (m, b), 5.83 (m), 5.59 (w), 5.45 (m), 5.29 (m), 5.05 (w, b), 4.59 (m)

configuration.[18] This is consistent with the opposing Cotton effects found in the CD spectra of these isomers throughout the visible and near-ultraviolet region. Another good match is found between the X-ray powder data for isomer D of Ru((+)atc)₃, known to have the cis configuration from nmr, and the powder data for isomers D of both Cr((+)atc)₃ and Co((+)-atc)₃ which were previously shown[6] to have the Δ-cis configuration. Therefore diastereomer D of Ru((+)-atc)₃ must be the Δ-cis isomer. It follows that the remaining cis isomer, C, of Ru((+)atc)₃ has the Λ-cis configuration.[18] Again the latter assignment is consistent with CD observations. The configurational assignments are summarized in Table I.

Summary

A combination of nmr, CD, and X-ray powder diffraction data has led to identification of the four diastereomers of Ru((+)atc)₃ which were separated by tlc on silica gel. The diastereomers labeled A, B, C, and D in order of decreasing R_f values are assigned the following absolute configurations: A = Δ-(+)-*trans*-Ru((+)atc)₃, B = Λ-(−)-*trans*-Ru((+)atc)₃, C = Λ-(−)-*cis*-Ru((+)atc)₃, and D = Δ-(+)-*cis*-Ru-((+)atc)₃. CD curves for these diastereomers may prove to be standards to which CD curves of other tris Ru(III) complexes of β-diketonate ligands can be compared in order to assign helical configurations. Deuteron nmr of the deuterium-labeled complex proved helpful in distinguishing cis and trans isomers and in estimating the relative abundances of diastereomers in a mixture.

A significant observation is that for the (+)-3-acetylcamphor complexes of Co(III), Cr(III), and Ru(III), diastereomers having the same absolute configuration have the same *relative* rates of elution on silica gel tlc plates. This is the case even though the eluting solvent is different for each complex.[19] Such behavior indicates that the overall polarity of a molecule of given absolute configuration relative to the polarities of its diastereomers is not significantly changed as a result of interchanging the ions Co³⁺, Cr³⁺, and Ru³⁺. This argument has been used to relate the absolute

the CD spectra that the two trans isomers, A and B, have opposite helicities as expected. The same is true of the cis isomers, C and D.[17] However, on the basis of the CD spectra alone, the absolute helicities cannot be determined at this time.

X-Ray Powder Diffraction.—The absolute configurations of all four diastereomers of Ru((+)atc)₃ may be assigned with certainty after comparing their X-ray powder diffraction patterns with those reported earlier for the diastereomers of Co((+)atc)₃ and Cr((+)atc)₃ whose absolute configurations are known.[6] The four diastereomers of each of these latter two complexes were also labeled A, B, C, and D in decreasing order of elution from tlc plates. On the basis of nmr, X-ray powder diffraction, and CD data, absolute configurations assigned to these diastereomers for both Co((+)-atc)₃ and Cr((+)atc)₃ were as follows: A = Δ-trans, B = Λ-trans, C = Λ-cis, and D = Δ-cis. These assignments were subsequently confirmed when Horrocks, *et al.*, found the Λ-trans configuration for isomer B of Cr((+)atc)₃ by single-crystal X-ray diffraction.[7]

X-Ray powder diffraction data for the diastereomers of Ru((+)atc)₃ are set out in Table III. The interplanar spacings and intensities for diastereomer B, shown above by nmr to have the trans configuration, closely match those found previously[6] for diastereomer B of Cr((+)atc)₃. Thus isomer B of Ru((+)atc)₃ is assigned the Λ-trans configuration, and the other trans diastereomer, A, of Ru((+)atc)₃ must have the Δ-trans

(17) Although diastereomers C and D (and A and B) have opposite helicities with respect to the C₃ (or pseudo-C₃) axis, their CD spectra do not bear an exact mirror-image relationship. This is because the ligand chirality is the same for both isomers; *i.e.*, C and D are diastereomers rather than enantiomers.

(18) X-Ray powder data for isomers A and C of Ru((+)atc)₃ do not match the powder data of isomers A and C of either Co((+)atc)₃ or Cr((+)atc)₃. However, assignments of absolute configuration for these diastereomers of Ru((+)atc)₃ follow logically from nmr and CD results and from process of elimination.

(19) A common solvent may be employed to elute all three complexes, and the order of elution of the diastereomers of each complex remains unchanged. However, this procedure generally results in a poorer overall separation of diastereomers.

configurations of diastereomers of tris(N-(R)-5-nitro-salicylaldiminato)cobalt(III) and those diastereomers of tris(N-(R)-5-nitrosalicylaldiminato)chromium(III) having the same relative rates of elution from tlc plates.[20] A somewhat related phenomenon was recently reported by Palamareva, *et al.*,[21] who compared the tlc behavior of 37 pairs of diastereomers of the type

(20) (a) J. E. Gray and G. W. Everett, Jr., *Inorg. Chem.*, **10**, 2087 (1971); (b) K. S. Finney and G. W. Everett, Jr., unpublished observations.

(21) M. Palamareva, M. Haimova, J. Stefanovsky, L. Viteva, and B. Kurtev, *J. Chromatogr.*, **54**, 383 (1971).

Ar–CH(X)–CH(Y)–Ar. In all cases the erythro isomers had higher R_f values on silica gel than the corresponding threo isomers, regardless of the polarity of the developing solvents.

Mechanism and Steric Course of Octahedral Aquation. XVI.[1] The Acid-, Base-, and Mercury(II)-Catalyzed Hydrolysis of *trans*-Chloroacetato- and *trans*-Chlorobenzoatobis(ethylenediamine)cobalt(III) Perchlorates

By T. P. DASGUPTA, W. FITZGERALD, and M. L. TOBE*

The preparation and properties of *trans*-[Co(en)$_2$RCOOCl]ClO$_4$ (R = CH$_3$, C$_6$H$_5$) are reported. The kinetics and steric course of the replacement of Cl by H$_2$O have been examined; $k_{25°}$ = 3.1 × 10^{-6} sec^{-1}, $\Delta H^{\ddagger}$ = 26.8 ± 0.3 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 6.7 ± 0.8 cal deg mol^{-1} for R = CH$_3$ and 1.2 × 10^{-6} sec^{-1}, 29.3 ± 0.7 kcal mol^{-1}, and 13.2 ± 2.2 cal deg^{-1} mol^{-1} for R = C$_6$H$_5$. The rate is independent of acid concentration and the immediate product of aquation (R = CH$_3$) is 80 ± 10% *cis*- and 20 ± 10% *trans*-[Co(en)$_2$CH$_3$COOH$_2$O]$^{2+}$ and the steric course of aquation of the benzoato complex is probably similar. The Hg^{2+}-catalyzed aquation (k_{Hg} = 0.40 M^{-1} sec^{-1} at 39.0°, μ = 0.10) produces 75 ± 2% *cis*- and 25 ± 2% *trans*-aquoacetato product. Base hydrolysis of the chloroacetato complex (k_{OH} = 10.8 M^{-1} sec^{-1} at 25.0°, μ = 0.1, $\Delta H^{\ddagger}$ = 22.6 ± 0.5 kcal mol^{-1}, $\Delta S^{\ddagger}$ = +22 ± 2 cal deg^{-1} mol^{-1}) yields 20% *cis*- and 80% *trans*-[Co(en)$_2$CH$_3$COOOH]$^{2+}$.

Introduction

In part XV,[1] the kinetics and steric course of the acid-catalyzed hydrolysis of *cis*- and *trans*-[Co(en)$_2$(OAc)$_2$]$^+$ were reported, and it was shown clearly that, in the trans complex, acetate served as a ligand that promotes substitution with stereochemical change. In order to separate the role played by acetate as "nonparticipating ligand" from that as leaving group, we have prepared and examined the *trans*-[Co(en)$_2$(CH$_3$COO)Cl]$^+$ complex, where the relatively labile chloride serves as leaving group. Although we have long been interested in assessing the role of –OCOR as a nonparticipating ligand in the acid and base hydrolysis of complexes of the type [CoL$_4$AX]$^{n+}$ (L$_4$ is a ligand or combination of ligands that provide four amine nitrogen donors; X is the leaving group) our attempts to prepare complexes with A = RCOO and X = Cl or Br were, until recently, without success. The method of Jackman, Scott, and Portman,[2] which involves the acetylation of the coordinated hydroxide, has been applied successfully to the preparation of *trans*-[Co(en)$_2$RCOOCl]$^+$ClO$_4^-$ (R = CH$_3$, C$_6$H$_5$), and the kinetics and steric course of acid and base hydrolyses of these complexes are reported in this paper.

(1) Part XV: T. P. Dasgupta and M. L. Tobe, *Inorg. Chem.*, **11**, 1011 (1972).

(2) L. M. Jackman, R. M. Scott, and R. H. Portman, *Chem. Commun.*, 1338 (1968).

Experimental Section

trans-Chlorohydroxobis(ethylenediamine)cobalt(III) chloride was prepared and purified by the method of Baldwin, *et al.*,[3] and converted to the perchlorate by adding a saturated aqueous solution of sodium perchlorate to a cold saturated aqueous solution of the chloride. The spectrum of a freshly prepared aqueous acid solution was identical with that in the literature.

trans-Chloroacetatobis(ethylenediamine)cobalt(III) Perchlorate.—*trans*-[Co(en)$_2$OHCl]ClO$_4$ (1.4 g) was added to a solution of acetic anhydride (0.22 ml) and N,N-dimethylbenzylamine (1.2 ml) in dimethylformamide (15 ml). The mixture was heated on a water bath at 60–70° for 20–25 min and then cooled. (If the starting material is pure, no precipitate should form at this stage.) Ethanol (30 ml) was then added, followed by diethyl ether (200 ml) which was added slowly, with constant stirring. The mixture was allowed to stand for 30 min and the supernatant liquid was decanted from the oil which was dissolved in water (3 ml) and filtered from the green insoluble *trans*-[Co(en)$_2$Cl$_2$]ClO$_4$. The filtrate was saturated with solid sodium perchlorate and cooled in ice. The red-purple crystals were filtered off and recrystallized from water; yield 0.29 g. *Anal.* Calcd for C$_6$H$_{19}$O$_6$N$_4$Cl$_2$Co: C, 19.3; H, 5.1; N, 15.0; Cl, 19.1. Found: C, 19.3; H, 4.9; N, 15.1; Cl, 19.3.

trans-Chlorobenzoatobis(ethylenediamine)cobalt(III) Perchlorate.—*trans*-[Co(en)$_2$OHCl]ClO$_4$ (1.96 g) was added to a solution of benzoic anhydride (0.665 g) and N,N'-dimethylbenzylamine (1.7 ml) in dimethylformamide (15 ml) and the mixture heated at 50–60° for 5 min and then cooled. An orange precipitate was filtered off and discarded. The filtrate was worked up and the complex recrystallized in the same way as was reported for the chloroacetato complex. *Anal.* Calcd for C$_{11}$H$_{21}$O$_6$N$_4$Cl$_2$Co:

(3) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).