Contribution from the Departments of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A. and La Trobe University, Bundoora, Victoria, 3083, Australia

Stereochemistry and Rearrangement Rates of Some Tris(β-Diketonato)- and Tris-(β-Thioketonato)Metal(III) Complexes

J.G. Gordon, II,[1,2] M.J. O'Connor,[3] and R.H. Holm[2]

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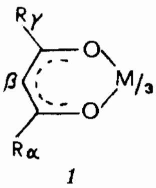
Series of tris(β-diketonato) - (1, M = V, Mn, Fe, Ru, Co, $R_\alpha \neq R_\gamma$) and tris(β-thioketonato)metal(III) complexes (2, M = V, Co) have been investigated in order to establish cis-trans *isomer distributions and relative rates of isomerization. Preparation of all new compounds and separation of the geometrical isomers of tris(trifluoroacetylacetonato)- and tris(benzoylacetonato)ruthenium(III) are described. In weakly polar media the* trans *isomer of trifluoroacetylacetonate complexes, M(tfac)$_3$, is more stable whereas the isomer distribution of similar complexes with R_α, R_γ =alkyl, Ph is statistical or slightly favours the* cis *form. On the basis of the present results and data reported earlier the dependence of isomerization rates on metal ions in the M(tfac)$_3$ series is Fe, In>Mn>Ga>Al>V>Co>Ru>Rh. Rate constants and activation parameters for the isomerization reactions of Ru(tfac)$_3$ in* sym-*tetrachloroethane have been determined. Pmr studies of tris(β–thioketonato)vanadium(III) and cobalt(III) complexes have shown that, in contrast to their β–diketonate analogs, these species populate only the* cis *isomer in solution. Pmr data in deuteriochloroform at ~29° are reported for complexes of type* 1 *and* 5.

Introduction

Octahedral trischelate complexes containing identical unsymmetrical bidentate ligands can exist as enantiomeric *cis* and *trans* isomers. Recent investigations[4-6] of such trischelates in these laboratories have been directed toward an elucidation of the relative stabilities of geometrical isomers and the mechanisms of intramolecular rearrangements which, for complexes of the M(A–B)$_3$ type such as *1* ($R_\alpha \neq R_\gamma$), effect isomerization and inversion of the overall molecular configuration. In these studies as well as in the present one and others cited below, the nmr method is particularly useful in that it allows ready distinction between *cis*– and *trans*–M(A–B)$_3$ species, which possess C_3 and C_1 symmetry, respectively.

The presently available body of information on relative isomeric stabilities, which deals principally with neutral vanadium(III) and cobalt(III) trischelates under ambient conditions in weakly polar solvents, indicates that equilibrium *trans*:*cis* distributions are subject to steric control. Complexes of N–substituted salicylaldimines and their variants (*2*, R'=H[7], alkyl[8]), β–ketoamines[9] (*3*), pyrrole–2–aldimines,[7a,9] and cobalt(III) arylazooximes[10] and 2–arylazophenols[11] exist exclusively as the *trans* isomer. The crowding which results from placing the nitrogen substituents of all these ligands around the same triangular face of the coordination octahedron is severe enough to destabilize completely the *cis* isomers at ordinary temperature. On the other hand, tris(β–diketonate) complexes



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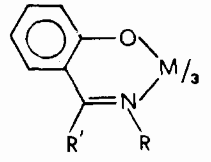

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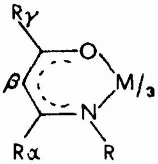

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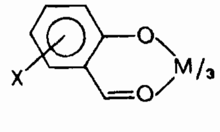

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(*1*, R=H, aryl, alkyl) of vanadium(III),[12] cobalt(III),[4,13] aluminium(III),[5] and gallium(III),[5] which lack significant steric interaction, exhibit nearly statistical (1:3, *cis*:*trans*) isomer ratios at equilibrium. Equilibrium mixtures of tris(trifluoroacetylacetonato)-M^{III} complexes (M=Co, Al, Ga,[14] and V[12]) contain

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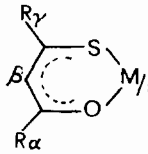
(1) National Science Foundation Predoctoral Fellow, 1967-1970.
(2) Massachusetts Institute of Technology.
(3) La Trobe University.
(4) J.G. Gordon, II, and R.H. Holm, *J. Amer. Chem. Soc.*, *92*, 5319 (1970).
(5) J.R. Hutchison, J.G. Gordon, II, and R.H. Holm, *Inorg. Chem.*, *10*, 1004 (1971).
(6) L.H. Pignolet, R.A. Lewis, and R.H. Holm, *J. Amer. Chem. Soc.*, 93, 360 (1971).
(7) (a) A. Chakravorty and R.H. Holm, *Inorg. Chem.*, *3*, 1521 (1964); (b) F. Röhrscheid, R.E. Ernst, and R.H. Holm, *J. Amer. Chem. Soc.*, *89*, 6472 (1967); (c) K.S. Finney and G.W. Everett, Jr., *Inorg. Chem.*, *9*, 2540 (1970).
(8) A. Chakravorty and K.C. Kalia, *ibid.*, *6*, 690 (1967); A. Chakravorty and B. Behera, *ibid.*, *6*, 1812 (1967).
(9) F. Röhrscheid, R.E. Ernst, and R.H. Holm, *ibid.*, *6*, 1607 (1967).
(10) (a) K.C. Kalia and A. Chakravorty, *ibid.*, *7*, 2016 (1968); (b) K.C. Kalia and A. Chakravorty, *ibid.*, *8*, 2586 (1969); (c) K.C. Kalia and A. Chakravorty, *J. Inorg. Nucl. Chem.*, *31*, 1791 (1969); (d) A. Chakravorty, B. Behera, and P.S. Zacharias, *Inorg. Chim. Acta*, *2*, 85 (1968).
(11) K.C. Kalia and A. Chakravorty, *ibid.*, *2*, 154 (1968).
(12) F. Röhrscheid, R.E. Ernst, and R.H. Holm, *Inorg. Chem.*, *6*, 1315 (1967).
(13) A.Y. Girgis and R.C. Fay, *J. Amer. Chem. Soc.*, *92*, 7061 (1970).
(14) R.C. Fay and T.S. Piper, *ibid.* *85*, 500 (1963).

considerably less *cis* form than the statistical value of 25%, and several ring substituted tris(salicylaldehydato)V^{III} complexes (*4*, X=Me) are exclusively *trans*.[7b] Inasmuch as steric effects do not appear to be significant in these cases, the results suggest that electronic and other factors are responsible for the deviations from statistical distribution.[15]

The present investigation has been undertaken in order to assess the effects of certain electronic and structural variations on isomer distribution and isomerization rates. The structural changes of interest are variation of ring substituents in *1* from alkyl to CF_3, and replacement of oxygen by sulfur donor atoms in passing from the complexes *1* to the tris(β–thioketonato)metal(III) species *5*.[16] Recent evidence clearly shows that sulfur donors can have significant stereochemical consequences, as in the stabilization of trigonal prismatic geometry[17] and destabilization of tetrahedral relative to planar isomers.[18] The effect of changing the metal has been examined in a series of $M(tfac)_3$ complexes. This report describes structural and kinetic studies carried out mainly by pmr, preparation of new chelates of types *1* and *5*, and separation of *cis* and *trans* isomers of several ruthenium(III) chelates. Results concerning the comparative stereochemistry of cobalt(III) and vanadium(III) complexes *1* and *5* summarized earlier[19] are presented in full here.



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Experimental Section

Preparation of Compounds. (a) *Ligands.* 5–Methylhexane–2,4–dione was prepared by the method described elsewhere.[4] 5,5–Dimethylhexane–2,4–dione was obtained by the same method and was purified by distillation at 72°/21 mm (lit.,[20] 70-71°/20 mm). All other β–diketones were commercial samples. The following β–thioketones were prepared by published procedures based on the reaction of hydrogen sulfide with the appropriate β–diketone in the presence of hydrogen chloride or morpholine: 4–mercaptopent–3-en-2-one,[21] 3-mercapto-1-phenylbut-2-en-1-one,[22] 1,1,1-trifluoro-4-mercaptopent-3-en-2-one.[23] In our hands this general procedure proved to be quite sensitive to reaction conditions and gave highly variable yields. 5,5-Dimethyl-4-mercaptohex-3-en-2-one, 5-methyl-4–mercapto-hex-3-en-2-one and 4-mercapto-4-phenylbut-3-en-2-one were synthesized by condensation of the methyl ester of the appropriate thionacid with acetone in the presence of sodium hydride[24] using a mole ratio of ester: acetone: hydride of 1:2:2. The esters were prepared from the corresponding nitriles following the method of Renson and Bidaine.[25] All of the starting nitriles were commercially available except for pivalonitrile, which was prepared from pivalic acid following the published procedure for the synthesis of isobutyronitrile.[26]

(b) *Tris*(β–*diketonato*)*metal*(*III*) *Complexes.* (1) *trifluoracetylacetonates.* $V(tfac)_3$[12] and $Fe(tfac)_3$[14] were prepared by the published methods. *Mn*(*tfac*)$_3$.—The following procedure is simpler and less wasteful of ligand than that reported by Fay and Piper;[14] it also eliminates contamination by $Mn(tfac)_2$. Manganese-(III) acetate dihydrate[27] (1.3 g, 4.9 mmol) and trifluoroacetylacetone (3.1 g, 20 mmol) were stirred together in 15 ml of absolute ethanol at room temperature for 5 min. The mixture was then warmed on a steam bath for 5 min to give a deep greenish-brown solution, which was quickly filtered. Upon cooling the filtrate 1.5 g (60%) of deep green crystals were obtained, which were washed with *n*–pentane and dried *in vacuo;* m.p. 115-116°, lit.,[14] 113-14°.

Ru(*tfac*)$_3$. Hydrated ruthenium trichloride (10 g, ~40 mg - atom Ru), 5 g (50 mmol) of potassium bicarbonate and 20 ml (*ca.* 150 mmol) of trifluoroacetylacetone were refluxed overnight. An additional 10 g of potassium bicarbonate was added and refluxing was continued for 24 hr. Excess trifluoroacetylacetone and water were removed under reduced pressure and the solid residue was extracted with dichloromethane until the extracts were colorless. The solvent was removed from the combined extracts and the red granular solid was dried overnight *in vacuo* to give 22.9 g of crude product. A considerably lower yield was obtained with anhydrous ruthenium trichloride as starting material. Crude $Ru(tfac)_3$ was purified by rapid chromatography on alumina (Merck, acid-washed, 50 g/g complex) with benzene as the eluant. Black and brown bands remained at the top of the column. To minimize decomposition residence times on the column were held to less than 30 min. The bright red powder left after removal of the benzene was dried in vacoom. This mixture of isomers melted at 155-160°. Recrystallization from ether/*n*–pentane raised the melting point to 171-172°, probably because

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(15) Possible exceptions to steric control of relative isomer stabilities are several tris(arylazooximato)Rh^{III} complexes, for which as much as 50% *cis* form has been obtained in some preparations.[10h] However, it has not been established that the isomer ratios are thermodynamically and not kinetically controlled.

(16) The following abbreviations of β-diketonate and β-thioketonate anions are used throughout: acac, MeCOCHCOMe; Sacac, MeCSCHCOMe; tfac, $CF_3COCHCOMe$; tfSac, $CF_3COCHCSMe$; bzac, PhCOCHCOMe; Sbzac, PhCSCHCOMe; bzSac, PhCOCHCSMe; mhd, $Me_2CHCOCHCOMe$; Smhd, $Me_2CHCSCHCOMe$; dhd, $Me_3CCOCHCOMe$; Sdhd, $Me_3CCSCHCOMe$; pmhd, $Me_2CHCOCHCOCH_2Ph$; SacSac, MeCSCHCSMe.

(17) J.A. McCleverty, *Progr. Inorg. Chem.*, *10*, 49 (1968); R. Eisenberg, *ibid.*, *12*, 295 (1970).

(18) (a) D.H. Gerlach and R.H. Holm, *J. Amer. Chem. Soc.*, *91*, 3457 (1969); (b) D.H. Gerlach and R.H. Holm, *Inorg. Chem.*, *8*, 2292 (1969).

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(21) R. Mayer, G. Hiller, M. Nitzsche, and J. Jentzsch, *Angew. Chem.*, *Int. Ed.*, *2*, 370 (1963).

(22) S.H.H. Chaston, S.E. Livingstone, T.N. Lockyer, V.A. Pickles, and J.S. Shannon, *Australian J. Chem.*, *18*, 673 (1965).

(23) R.K.Y. Ho, S.E. Livingstone, and T.N. Lockyer, *ibid.*, *19*, 1179 (1966).

(24) F. Uhlemann and Ph. Thomas, *J. Prakt. Chem.*, *34*, 180 (1966).

(25) M. Renson and J.B. Bidaine, *Bull. Soc. Chim. Belges*, *70*, 519 (1961).

(26) R.E. Kent and S.M. McElvain, *Org. Syn. Coll.*, *Vol. 3*, 493 (1955).

(27) O.T. Christensen, *Z. Anorg. Chem.*, *27*, 321 (1901).

the proportion of the higher melting *trans*-isomer was increased.

Anal. Calcd for $C_{15}H_{12}F_9O_6Ru$: C, 32.15; H, 2.16. Found: C, 32.59; H, 2.18.

A less detailed preparation of this complex has been reported;[28] the m.p. (164-166°) of product indicates that it is a *cis-trans* mixture.

Separation of cis– *and* trans–*Ru(tfac)$_3$*. The less soluble *trans*-isomer can be readily obtained by fractional crystallization from ethanol, benzene/hexane, or *sym*-tetrachloroethane. The mother liquors are enriched in the *cis* isomer, which can be quantitatively separated by chromatography on unactivated silica gel. *Ca.* 1 g of Ru(tfac)$_3$ dissolved in the minimum volume of benzene was applied to the top of a column 3.0 cm in diameter packed to a height of 27 cm with 95 g of PF-254 silica gel (Brinkmann Instruments). Elution with 1:1 benzene/hexane at a flow rate of ~2 ml/min (nitrogen pressure was required) produced two clearly separated bands in about 5 hr. Breakthrough of the faster moving *trans* band occurred after ~6 hr. The flow rate was then increased (nitrogen pressure) to hasten elution of the *cis* band. About 12 hr were required for the complete operation. The *cis*– and *trans*–isomers, recrystallized from *sym*–tetrachloroethane and identified by pmr (*cf.* Table II), melted at 132-133° (*cis*) and 172.5-173.5° (*trans*). The faster elution of the *trans*–isomer and the lower melting point of the *cis*–isomer are also found for other tris(β–diketonato)metal(III) complexes.[4,14,20,29] Attempted resolution of the enantiomers of the *cis* and *trans* forms by chromatography on lactose or cellulose were not successful.

Triphenylmethylarsonium tris(trifluoroacetylacetonato)ruthenate(II), (Ph_3AsCH_3)[Ru(tfac)$_3$]. Polarography in DMF (rotating platinum electrode) revealed that Ru(tfac)$_3$ underwent a reversible one-electron reduction at a half-wave potential of –0.04V *vs.* SCE. The anion was produced chemically and isolated with the expectation that resolution of its optical antipodes could be accomplished by fractional crystallization of diastereomers formed from a suitable optically active cation. All operations were carried out with rigorous exclusion of air.

Trans–Ru(tfac)$_3$ (1.00 g, 1.78 mmol) was dissolved in 300 ml of absolute ethanol and 82 mg (3.56 mg - atoms) of sodium metal, cut into small pieces, was added all at once. The bright red color gradually changed to intense purple. After all of the sodium had dissolved (~15 min), the volume was reduced to 100 ml, the solution filtered, and the nearly opaque filtrate added to a solution of 1.00 g (1.93 mmol) of triphenylmethylarsonium iodide and 0.1 g of acetic acid in 20 ml of 50% aqueous ethanol. Addition of 50 ml of water and reduction of the volume to ~100 ml produced a deep purple, nearly black, solid which was collected by filtration and washed with water (10 ml). The solid was dissolved in 15 ml of absolute ethanol and precipitated by the addition of 125 ml of water and cooling in ice. The precipitate was collected, washed with 100 ml of water and dried in vacuum, yielding 1.22 g (78%) of a purple powder which melted indistinctly at about 156°.

Anal. Calcd for $C_{34}H_{30}AsF_6O_6Ru$: C, 46.29; H, 3.43; F, 19.38. Found: C, 46.39; H, 3.65; F, 19.24.

The pmr spectrum of the salt in $CDCl_3$ solution showed four methyl signals of equal intensity at –2.90, –1.67, –0.25 and 0.00 ppm relative to TMS. These are assigned to the methyl protons of the triphenylmethylarsonium cation and the three inequivalent methyls of [Ru(tfac)$_3$]$^-$, revealing that rearrangement does not occur during reduction and that the ruthenium(II) complex is configurationally stable at room temperature. The rather large chemical shift spread of the three *trans* resonances is believed to be due to the presence of a small amount of the paramagnetic ruthenium(III) complex, with rapid electron exchange between the ruthenium(II) and ruthenium(III) species producing averaged signals. [Ru(tfac)$_3$]$^-$ is readily oxidized by iodine or oxygen. Thin layer chromatography (silica gel, dichloromethane eluant) reveals that the oxidation product consists of only one component which was identified as *trans*–tris(trifluoroacetylacetonato)ruthenium(III) by pmr. Thus the *geometrical* configuration is preserved during oxidation.

Attempts to resolve the enantiomers of the anionic *trans* complex through fractional crystallization of diastereomeric salts formed from various alkaloids (e.g. strychnine, brucine) or by chromatography on potato starch, cellulose, or cellulose based ion exchange resins were unsuccessful. Only Na[Ru(tfac)$_3$] could be precipitated from solutions containing *d*–*cis*–dinitrobis(ethylenediamine)cobalt(III) bromide and the recovered cobalt complex was racemic. Electron exchange between the ruthenium(II) and cobalt(III) complexes producing a labile cobalt(II) species was probably responsible for this racemization.

(2) *Benzoylacetonates.* M(bzac)$_3$ complexes with M=Co, Fe, and Mn were prepared by the procedure of Fay and Piper.[29]

V(bzac)$_3$. Potassium (1.2 g, 31 mg - atoms) was dissolved in 200 ml of dry *t*–butanol, 5.0 g (31 mmol) of benzoylacetone added, and the mixture stirred at room temperature for 10 min. All subsequent operations were carried out in the absence of air. Tetraethylammonium trichlorobromovanadate(III) (3.8 g, 10 mmol, prepared from vanadium trichloride and tetraethylammonium bromide in acetonitrile) was added and the resultant brown solution stirred at 70° for 7 hr. The solvent was removed under reduced pressure and the solid residue extracted with 250 ml of 3:1 *n*-heptane/toluene and then with 300 ml of toluene. An initial crop of product was obtained by cooling the first extract to *ca.* –10°. The volume of the second extract was reduced to about 100 ml and the filtrate from the first extract was added. Cooling of this solution *ca.* –10° afforded a second crop. The combined solids were sublimed *very slowly* at diffusion pump pressure. Sublimation at 190° yielded a brown crystalline fraction (A) m.p. 112-115° (sealed tube). Sublimation at or above 200° gave a second fraction (B) of similar appearance, m.p. 230-

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(28) H. Veening, W.E. Bachman, and D.M. Wilkinson, *J. Gas Chromatog.*, 5, 248 (1967).

(29) R.C. Fay and T.S. Piper, *J. Amer. Chem. Soc.*, 84, 2303 (1962).

232° (sealed tube). Both fractions gave identical pmr spectra in $CDCl_3$.

Anal. Calcd for $C_{30}H_{27}O_6V$: C, 67.41; H, 5.09. Found: (A) C, 67.56; H, 5.19; (B) C, 67.45; H, 5.49.

This complex has been prepared previously by a different method[30] and presumably was obtained as a mixture of the two forms found here, inasmuch as it was not purified by recrystallization or sublimation. Because the *cis* isomer of other $M(bzac)_3$ complexes (M = Cr, Co, Rh) melts at a lower temperature than the *trans* isomer,[29] the forms of $V(bzac)_3$ obtained are probably the *cis* (A) and *trans* (B) isomer.

Ru(bzac)₃. The previously reported method of synthesis[31] could not be satisfactorily reproduced. Hydrated ruthenium trichloride (0.5 g, ~2 mg - atom Ru), 0.4 g (4 mmol) of potassium bicarbonate and 3 g (18 mmol) of benzoylacetone were ground together and heated at 110° for 72 hr. Excess benzoylacetone was removed by sublimation at 110°/0.1 mm, and the residue was extracted with warm carbon tetrachloride until the extracts were colorless. Removal of solvent afforded a red solid, which was dissolved in benzene and was rapidly chromatographed on Merck acid-washed alumina. The solvent was removed from the eluent to give 0.55 g of a red crystalline material, whose pmr spectrum in deuteriochloroform revealed it to be a statistical mixture of *cis* and *trans* isomers.

Separation of cis– *and* trans–*Ru(bzac)₃.* The isomers were separated by chromatography on Merck acid-washed alumina (100 g/g complex) in a 3.0 cm o.d. tube. The isomeric mixture (0.5 g) dissolved in 15 ml of 1:1 *n*–hexane: benzene (v/v) was put on the column and eluted with 3:7 *n*–hexane: benzene (v/v). Breakthrough of the *trans* isomer occurred after 5 hr. The column was then extruded under nitrogen pressure and cut into sections which were extracted with boiling chloroform. The upper 15% portion and the lower 25% portion yielded the *cis* and *trans* isomers, respectively, and the remaining portion was enriched with *trans*. The *cis* form was recrystallized from benzene-pentane (m.p. 188-190°) and the *trans* form from benzene-heptane (m.p. 254°), and were shown to be isomerically pure by their pmr spectra (*cf.* Table II).

Anal. Calcd for $C_{30}H_{27}O_6Ru$: C, 61.63; H, 4.66. Found: (*cis*) C, 61.81; H, 5.06; (*trans*) C, 61.80; H, 4.56.

The previous preparation[31] of $Ru(bzac)_3$ yielded a product with m.p. 247-249°, indicating that it was mainly the *trans* isomer

(3) *Tris(5–methylhexane–2,4–dionato)V^{III}, V(mhd)₃.* Hexacarbonylvanadium (0.96 g, 4.4 mmol) was added to 1.4 g (11 mmol) of 5–methylhexane–2,4–dione in 75 ml of dry deoxygenated toluene. The reaction mixture was stirred under nitrogen for 36 hr, heated at 50° for 5 hr, and then stirred overnight. Removal of solvent left a brown gum, which was dissolved in a small volume of *n*–pentane and transferred to a molecular distillation apparatus. After evaporation of solvent slow distillation at 130-135°/0.1 mm afforded a viscous brown gum which did not solidify on standing. The pmr spectrum of this material indicated that it was a *cis–trans* mixture.

Anal. Calcd for $C_{21}H_{33}O_6V$: C, 58.22; H, 7.68. Found: C, 58.09; H, 7.67.

(4) *5,5–Dimethylhexane–2,4–dionates. V(dhd)₃.*— This compund was prepared by a procedure analogous to that used for $V(bzac)_3$. The crude product was extracted with benzene, but crystallization could not be induced. The brown gum obtained after removing the solvent at reduced pressure was purified by molecular distillation at 130-135°/0.1 mm yielding a viscous brown gum which, after two years, still had not solidified.

Anal. Calcd for $C_{24}H_{39}O_6V$: C, 60.75; H, 8.28. Found: C, 60.66; H, 8.33.

Co(dhd)₃. This complex was prepared as an isomeric mixture by the same procedure used for $Co(mhd)_3$[4] and was obtained as a green oil which did not crystallize.

Anal. Calcd for $C_{24}H_{39}O_6Co$: C, 59.74; H, 8.14. Found: C, 59.76; H, 8.15.

The preparation of this compound and the separation of its isomers have recently been reported by York *et al.*[20]

(c) *Tris(β–thioketonato)metal(III) Complexes.* Characterization data for new complexes of this type are reported in Table I.

(1) *Vanadium(III) Complexes.* All operations were carried out in the absence of air.

Tris(4-mercaptopent-3-en-2-onato)V^{III}, V(Sacac)₃.— The ligand (7.3 g, 63 mmol) was added to a solution of 3.3 g (21 mmol) of vanadium trichloride in 50 ml of water. Potassium carbonate (4.6 g) was added and a black precipitate formed. The reaction mixture was stirred for 2 hr, the solid collected, washed with water, and dried in vacuum. Two recrystallizations from 1:1 *n*–heptane: toluene afforded 6.2 g (74%) of black crystals.

Tris(4-phenyl-4-mercaptobut-3-en-2-onato)V^{III}, $V(Sbzac)_3$. To a solution of 11 g (60 mmol) of ligand in 20 ml of ethanol was added 22 ml of a 2.7 N sodium hydroxide solution (60 mmol), producing a dark red solution. A solution of 3.0 g (19 mmol) of vanadium trichloride in 50 ml of water was added giving a brown precipitate. Potassium carbonate (1 g) was added and the reaction mixture stirred for 10 min. The solid was collected by filtration, washed with water, and dried in vacuum. The complex was purified by two recrystallizations from 1:1 n–heptane: toluene; 3.9 g (35%) were isolated.

Tris(5-methyl-4-mercaptohex-3-en-2-onato)V^{III}. $V(Smhd)_3$. The preparation was the same as that for $V(Sacac)_3$. Two recrystallizations of the crude product from *n*–heptane afforded the complex as black crystals in 67% yield.

Tris(1,1,1-trifluoro-4-mercaptopent-3-en-onato)V^{III},

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(30) D.J. Machin and K.S. Murray, *J. Chem. Soc., A,* 1498 (1967).
(31) R. Grobelny, B. Jezowska-Trzebietowska, and W. Wojciechowski, *J. Inorg. Nucl. Chem., 28,* 2715 (1966).

$V(tfSac)_3$. A deoxygenated pentane solution of 1,1,1-trifluoro-4-mercaptopent-3-en-2-one (0.95 g, 5.6 mmol) was added to a solution of 0.46 g (2.1 mmol) of hexacarbonylvanadium in toluene and the resulting brown solution stirred for two days at room temperature. Toluene was removed under reduced pressure and excess carbonyl and a yellow liquid were removed at 30°/0.1 mm. The black residue was extracted with 50 ml of petroleum ether and the scaly solid obtained upon cooling the extract was sublimed at 60°/10^{-4} mm. The pmr spectrum of the brown sublimate in $CDCl_3$ solution showed several peaks at −88.0 and −64.8 ppm, respectively, which are assigned to the methyl and ring protons of *cis*–$V(tfac)_3$. Only small amounts of product could be isolated and decomposition occurred before the sample could be purified. Elemental analyses were not carried out.

(2) *Tris(4-phenyl-4-mercaptobut-3-en-2-onato)Cr^{III}*, $Cr(Sbzac)_3$. To a solution of 23 g of urea and 5.0 g (36 mmol) of the ligand in 10 ml of ethanol was added 3.4 g (13 mmol) of chromium trichloride hexahydrate in 2 ml of water. The reaction mixture was stirred at 75-80° for 18 hr, cooled to room temperature, and a brown solid collected. After air-drying the solid was heated to 160° at *ca.* 10^{-3} mm to remove a yellowish-white substance by distillation. The brown residue was recrystallized from 1:1 *n*–heptane:toluene to yield 2.0 g (26%) of small black crystals.

(3) *Tris(4-phenyl-4-mercaptobut-3-en-2-onato)Fe^{III}*, $Fe(Sbzac)_3$ Ferric chloride hexahydrate (3.2 g, 12 mmol) was dissolved in 50 ml of water, 1-2 g of sodium acetate added, and the solution cooled to 15°. A solution of 5.0 g (36 mmol) of the ligand in 350 ml of ethanol was added producing a green solution and a black precipitate. The reaction mixture was stirred for 3 hr, filtered, and the black solid air-dried. The crude product was recrystallized from chloroform-petroleum ether (30-60°); 1.1 g (15%) of black crystals were collected.

(4) *Cobalt(III) Complexes.* These compounds were prepared following the method of Chaston and Livingstone[32] for tris(4-mercaptopent-3-en-2-onato)Co^{III}, $Co(Sacac)_3$ and isolated in good yield as dark green or black crystalline products. Solvents used for recrystallization were the following: $Co(Sacac)_3$ and $Co(Sbzac)_3$, *n*–hexane; $Co(Smhd)_3$, methanol; $Co(Sdhd)_3$, methanol-water; $Co(bzSac)_3$, acetone-ethanol.

Physical Measurements. Pmr spectra were obtained on a Varian HA-HR-100 spectrometer which, for paramagnetic samples, was operated in the HR mode with an external oscillator supplying the audio modulation for base-line stability. Chemical shifts were referenced to TMS as an internal standard. Solution magnetic moments were determined by the usual nmr method and moments of solids were measured by the Gouy method.

Isomerization Kinetics of cis– *and* trans–*Ru(tfac)$_3$.* Rates of isomerization (equation 1) of pure *cis*– and *trans*–$Ru(tfac)_3$ were measured in *sym*–tetrachloroethane solution.

$$cis \underset{k_{TC}}{\overset{k_{TC}}{\rightleftarrows}} trans \qquad (1)$$

The solvent was purified by first washing with concentrated sulfuric acid, passing the product of this step through an alumina column, and finally distilling through a Teflon spinning-band column. A middle cut boiling at 143.5°C was collected. The isomerization rates were measured in the interval 140-170°C. In a typical run an nmr tube containing a solution of one isomer was immersed in a constant temperature bath (±0.1°C) for an appropriate length of time and then quenched by plunging the tube into ice water. The pmr spectrum of the methyl signals at +5.35 and +8.45 ppm was recorded in sextuplicate at the normal probe temperature (~30°) of the Varian HR-100 spectrometer. Relative concentrations of *cis*– and *trans*–isomers were obtained by planimetric integration of the *cis* (+5.35 ppm) and *trans* (+8.45 ppm) peaks. The time dependence of the pmr spectrum of these two methyl peaks is illustrated in Fi-

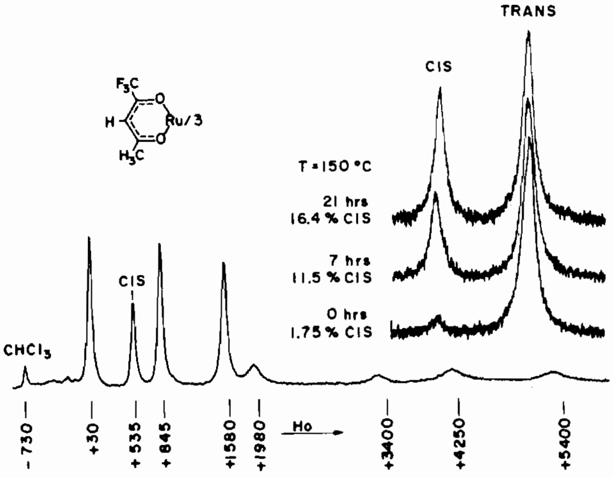

Figure 1. 100 MHz pmr spectrum of an equilibrium mixture of *cis*-and *trans*- $Ru(tfac)_3$ in $CDCl_3$ solution at 30°. Insert: expanded spectra of the *cis* and one of the *trans* methyl signals at various times during an isomerization reaction at 150° in *sym*-tetrachloroethane. The 21 hr. spectrum represents near-equilibrium. Chemical shifts are in Hz.

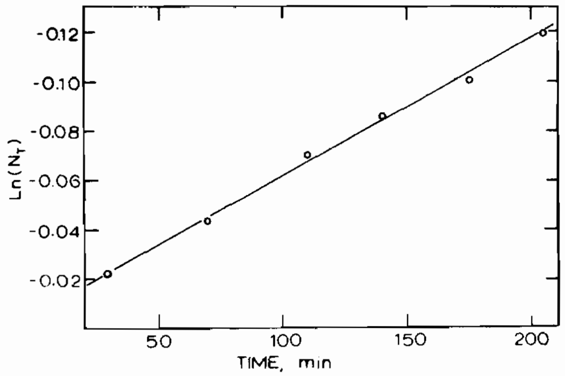

Figure 2. Initial rate plot for the isomerization of *trans*-$Ru(tfac)_3$ in *sym*-tetrachloroethane at 160.6°. N_T = mole fraction of *trans* isomer.

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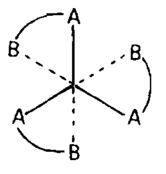
[32] S.H.H. Chaston and S.E. Livingstone, *Austr. J. Chem.*, 20, 1065 (1967).

gure 1 for a run at 150°C starting with the *trans* isomer. Isomerization rates were obtained from the initial slopes of plots of ln(N_C or N_T) *vs.* time, where N is the mole fraction. Initial rates were determined because of the small proportion (*ca.* 16%) of the *cis* isomer at equilibrium. Experimental scatter in determination of equilibrium N_C values produced a large variation in isomerization rates calculated from least squares fit to equation 6 of ref. 4, which takes into account back-reactions. At least five measurements of relative concentrations were made in each kinetic run. A representative initial rate plot, for the isomerization of the *trans* isomer at 160.6°, is displayed in Figure 2. No attempt was made to establish the order of these reactions by concentration variation. Solutions employed (*ca.* 0.04 *M*) were nearly saturated and any appreciable decrease in concentration would have resulted in unacceptable noise levels.

Results and Discussion

Trischelate complexes containing three identical unsymmetrical bidentate ligands are of the general type $M(A–B)_3$ and can exist as *cis* and *trans* isomers, each of which is enantiomeric. The *cis*–λ and *trans*–λ forms are illustrated by 6 and 7, respectively. The three chelate rings in 6 are equivalent whereas those in 7 are inequivalent, thus allowing detection of one isomer in the presence of the other by nmr provided chemical shift differences are large enough. This has proven to be the case for all complexes examined in this work which were not undergoing rapid rearrangement reactions (isomerization, inversion) throughout the temperature interval of measurement. Furthermore, for those systems not subject to exchange broadening of their nmr spectra, Keq for reaction (1) can be obtained from measurement of signal intensities and the signals of the individual isomers identified when Keq $\neq$ 3, the statistical value. Results dealing with equilibrium distribution of isomers and isomerization rates for the two general classes of complexes 1 and 5 are described below.



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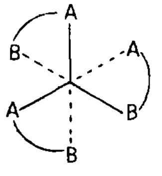

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Tris(β–*diketonates*) (1). Chemical shifts in deuteriochloroform at *ca.* 29° are listed in Table II.

(a) *Vanadium*(*III*) *Complexes.* These species possess spin-triplet ground states[12,30] and exhibit pmr spectra which are isotropically shifted to low field relative to the free ligands or diamagnetic Co^{III} complexes. As is the case for other β–diketonate[12] and related V^{III} complexes[7b,9,33,34] isomerization of the four complexes in Table II is slow on the pmr time scale. One of these, $V(bzac)_3$, was isolated in two forms by fractional sublimation. The lower and higher melting modifications have been tentatively identified as the *cis* and *trans* isomers, respectively. Fresh solutions of each give identical pmr spectra, shown in Figure 3, which reveal the presence of both isomers. Signals due to each isomer could not be definitely identified. Signal identification of the isomers of $V(mhd)_3$, $V(dhd)_3$, and $V(tfac)_3$ was possible, and Keq and thermodynamic parameters for the latter complex were obtained from planimetric integration of signal intensities in the –55° to 60° range. These data are given in Table III. Similar results could not be obtained for the other two complexes because of unfavorable signal

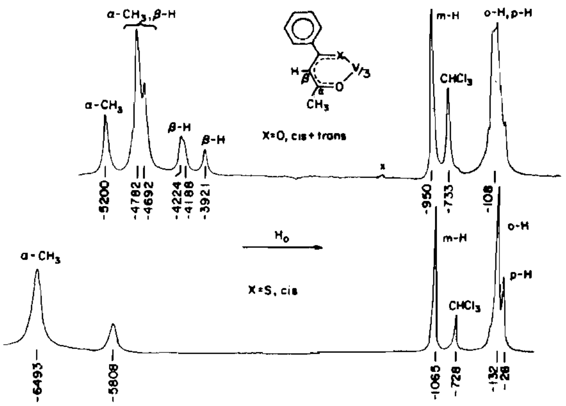

Figure 3. 100 MHz pmr spectra of a *cis-trans* mixture of $V(bzac)_3$ (top) and *cis*-$V(Sbzac)_3$ (bottom) in $CDCl_3$ solution at ~ 30°. Chemical shifts are in Hz.

Table I. Characterization Data for Tris(β-thioketonato)Metal(III) Complexes.

Complex	m.p.,°C	μ_{eff}(BM) 30°	Calcd., % C	Calcd., % H	Calcd., % S	Found, % C	Found, % H	Found, % S
$V(Sacac)_3$	175-176 [a]	2.75 [b]	45.44	5.34	24.26	45.31	5.28	24.78
$V(Sbzac)_3$	219-220 [a]	2.75 [b]	61.84	4.67	16.51	62.06	4.83	16.12
$V(Smhd)_3$	108-110 [a]	2.77 [b]	52.48	6.92	20.01	52.42	6.52	19.95
$Cr(Sbzac)_3$	234-235	3.78 [b]	61.72	4.66	—	61.94	4.86	—
$Fe(Sbzac)_3$	171-172	5.91 [c]	61.32	4.63	—	61.47	4.42	—
$Co(Sbzac)_3$	213-214	dia.	61.00	4.61	16.29	61.55	4.68	16.35
$Co(Smhd)_3$	155-156	dia.	51.62	6.81	19.69	51.19	6.77	19.84
$Co(Sdhd)_3$	160-161	dia.	54.31	7.41	18.13	54.32	7.36	17.50
$Co(bzSac)_3$	224-225	dia.	61.00	4.61	16.29	61.24	5.11	15.97

[a] In vacuo. [b] Measured by mmr in 15% v/v $TMS/CHCl_3$. [c] Solid.

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(33) Y.T. Chen and G.W. Everett, Jr., *J. Amer. Chem. Soc.*, *90*, 6660 (1968); G.W. Everett, Jr., and Y.T. Chen, *ibid.*, *92*, 508 (1970).

(34) R.H. Holm, *Acocunts Chem. Res.*, *2*, 307 (1969).

Table II. Chemical Shifts of Tris(β-diketonato)metal(III) Complexes (*1*) in $CDCl_3$ Solution at ~ 29°.

	Shift, ppm							
Complex [a]	R_α		β-H			R_γ [b]		
$V(Me,H,CF_3)_3$ [c]	—54.3,	—57.8(c),	—25.5,	—39.3(c),			*d*	
	—62.7,	—71.0	—47.0,	—57.8				
$V(Me,H,Ph)_3$	—46.9,	—47.8(2),	—39.2,	—41.9,		— 1.08(3),	— 9.50(2)	
	—52.0		—42.2	*e*				
$V(Me,H,iPr)_3$ [c]	—42.3,	—44.1	—35.9,	—37.5	Me:	— 1.15,	— 2.14,	— 2.50(2)
	—45.5(c),	—55.4	—39.6		CH:	—21.8(2),	—22.5,	—27.4
$V(Me,H,tBu)_3$ [c]	—41.4,	—43,3	—36.4,	—38.5,		— 2.10,	— 2.45(2),	— 2.85
	—46.3(c),	—57.3	—40.8(c),	—46.3				
$Mn(Me,H,CF_3)_3$	—33.4(c+t),		— 4.27,	—10.1,		+10.3,	+ 3.40,	— 5.18
	—40.5,	—42.4	—11.8,	—20.3		—16.0 [f]		
$Mn(Me,H,Ph)_3$	—25.9(2),	—30.2(2)	—14.9(2),	—20.5(2)		— 3.50 to	— 7.80 [g]	
$Fe(Me,H,CF_3)_3$		—28.9	+40.0				*h*	
$Fe(Me,H,Ph)_3$		—18.0	*i*			+ 0.50,	— 3.80,	—12.0
$Co(Me,H,tBu)_3$ [c]	—2.11,	—2.15(c+t),	— 5.55,	— 5.57(c),		— 1.09,	— 1.11(c+t)	
	—2.22		— 5.61,	— 5.63				
$Ru(Me,H,CF_3)_3$ [c]	+0.30,	+5.35(c),	+19.8,	+34.0(c),			*h*	
	+8.45,	+15.8	+42.5,	+54.0				
$Rn(Me,H,Ph)_3$ [c]	+3.17,	+ 5.45,				— 6.83,	— 8.69,	— 8.88(c),
	+6.55(c),	+10.7	*h*			— 9.00,	— 9.42,	—11.6(c),
						—11.7		

[a] Abbreviated in terms of substituents as $M(R_\alpha,H,R_\gamma)_3$. [b] Approximate centers of multiplets given for $R_\gamma = Ph$. [c] Signals of *cis* (c) isomers are indicated, others are due to *trans* (t). [d] Cf. ref. 12. [e] Remaining signal in the —46.9 to —47.8 ppm region (*cf.* Fig. 3). [f] ^{19}F spectra measured at 94.1 MHz, 1,1,1-trifluorotoluene internal reference. [g] *Cf.* Fig. 4. [h] Not measured. [i] Not observed.

Table III. Thermodynamic Parameters for the *Cis*⇆*Trans* Equilibrium of Tris(β-diketonato)metal(III) Complexes (*1*).

Complex	Solvent	ΔH kcal/mole	ΔS eu	Keq [a]
$Al(tfac)_3$ [b]	$CDCl_3$	—0.24±0.19	+2.2±0.6	4.5
$Ga(tfac)_3$	$CDCl_3$	—0.47±0.22	+1.5±0.7	4.7
$V(tfac)_3$	$CDCl_3$	—1.4 ±0.3 [c]	—1.0±1.0 [c]	6.1
$Mn(tfac)_3$	$CDCl_3$	—1.1 ±0.4 [c]	—0.7±1.2 [c]	4.4
$Co(tfac)_3$ [b]	$CDCl_3$	—0.34±0.71	+1.8±2.4	4.1 (79°)
$Ru(tfac)_3$	*Sym*-$C_2H_2Cl_4$	—1.1 ± 0.6 [c]	+0.6±1.4 [c]	4.9 (150°)
$Co(bzac)_3$ [d]	C_6H_5Cl	+0.17±0.33	+2.5±0.9	2.6 (56°)
$Co(mhd)_3$ [e]	C_6H_5Cl	—	—	2.1 (90°)
$Al(pmhd)_3$ [f]	C_6H_5Cl	+0.15±0.50	+2.3±1.5	2.5
$Ga(pmhd)_3$ [f]	C_6H_5Cl	+0.38±0.50	+3.1±1.5	2.5

[a] (*trans*)/(*cis*), value refer to 25° unless otherwise stated. [b] Data from ref. 14. [c] Estimated maximum error. [d] Data from ref. 13. [e] Data from ref. 4. [f] Data from ref. 5.

overlap. Values of Keq were obtained from the 30° spectra in deuteriochloroform: $V(mhd)_3$, 2.0 (~33% *cis*), and $V(dhd)_3$, 1.4 (~41% *cis*). The spectrum of $V(tfac)_3$ was examined up to 100°; no changes attributable to exchange broadening were found. The observation of separate *cis* and *trans* resonances in all cases indicates that the rate of isomerization must be slower than *ca.* 10^2 sec^{-1} at room temperature.

(b) *Manganese(III) Complexes.* Reasonably well resolved spectra, which are shown in Figure 4, were obtained for $Mn(tfac)_3$ and $Mn(bzac)_3$ at ambient temperature. All shifts are downfield, as has been observed for $Mn(acac)_3$[35] and certain of its mixed ligand complexes[36] which also possess a spin-quintet ground state. For both complexes the number and relative intensities of the signals are consistent only with the presence of both *cis* and *trans* isomers.[37] Below about —20° the spectra of both complexes show four distinct methyl peaks. The *cis—trans* equilibrium constant for $Mn(bzac)_3$ is very close to the statistical value and none of the peaks could be unambiguously assigned to *cis*. However, the *cis*—$Mn(tfac)_3$ peak was easily identified by its low intensity and the *cis—trans* equilibrium constant was determined in deuteriochloroform over the range —51° to +37°. Keq was calculated from the relation Keq = 3A/(2B—A), where A is the area of the α—Me signals at low field (2 *trans*) and B is the area of the higher field α—methyls (*cis* + *trans*). Areas were determined by planimetry. Thermodynamic parameters and the equilibrium constant at 25° are reported in Table III. Above ~40°, effects of rapid environmental exchange are noticeable in the pmr spectra and by 100° the α—Me

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(35) D.R. Eaton, *J. Amer. Chem. Soc.*, *87*, 3097 (1965).
(36) D.R. Eaton, W.R. McClellan, and J.F. Weiher, *Inorg. Chem.*, 7, 2040 (1968).

(37) It is noted that any distortion which might occur as a consequence of the ^5E ground states of $Mn(acac)_3$ (D_3) and above *cis* isomers (C_3) are probably too slight to produce significant inequivalence of chelate rings in static structures, for which rapid equilibration in solution is anticipated anyway. The most important difference between the structure of $Mn(acac)_3$ and other crystalline $M(acac)_3$ species is a slight trigonal twist of 8-9° [38] which preserves the three-fold axis.
(38) B. Morosin and J.R. Brathovde, *Acta Cryst.*, *17*, 705 (1964); T.S. Davis, J.P. Fackler, and M.J. Weeks, *Inorg. Chem.*, 7, 1994 (1968).

signals of both complexes have coalesced to a single line. The temperature dependences of the α–Me regions of $Mn(tfac)_3$ and $Mn(bzac)_3$ are illustrated in Figure 5. Plots of chemical shift *vs.* 1/T show that the formation of only two α–Me resonances prior to complete collapse is attributable to accidental chemical shift degeneracy, and not to a rapid exchange process. Rough estimates of isomerization rates can be obtained by treating the process as a simple two site exchange problem and using the approximate relationship $\tau_c = \sqrt{2}/2(\nu_A - \nu_B)$[39] to obtain the exchange rate at coalescence. The chemical shift differences in the absence of exchange, $\nu_A - \nu_B$, were obtained by extrapolating chemical shift *vs.* 1/T plots to the coalescence temperature. Differences in relative populations are neglected in this approach. Taking 80° as the coalescence temperature of $Mn((bzac)_3$ and 70° for $Mn(tfac)_3$ yields $\tau_c \sim 6 \times 10^{-4}$ and $\sim 4 \times 10^{-4}$ sec, respectively. Rearrangement rates are then simply, $k = 1/2\tau_c$: $\sim 8 \times 10^2$ sec^{-1} for $Mn(bzac)_3$ and $\sim 1 \times 10^3$ sec^{-1} for $Mn(tfac)_3$.[40]

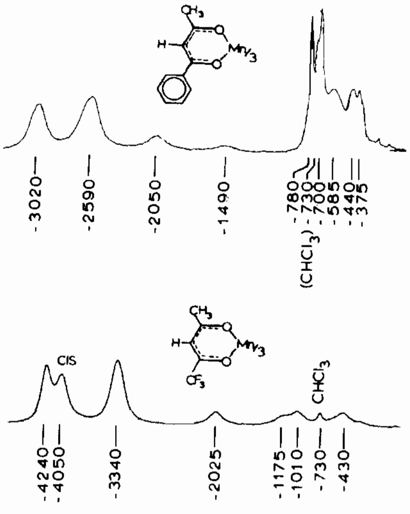

Figure 4. 100 MHz pmr spectra of a *cis-trans* mixture of $Mn(bzac)_3$ (top) and $Mn(tfac)_3$ (bottom) in $CDCl_3$ solution at ~ 29°. Chemical shifts are in Hz.

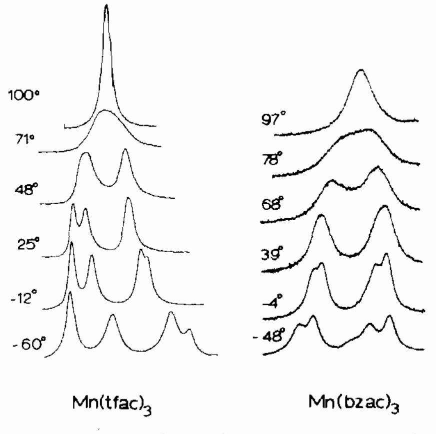

Figure 5. Temperature dependence of the α-methyl resonances of $Mn(tfac)_3$ (left) and $Mn(bzac)_3$ (right) in $CDCl_3$ solution.

(c) *Iron(III) Complexes.* The two complexes examined, $Fe(bzac)_3$ and $Fe(tfac)_3$ gave very broad, poorly resolved pmr spectra. The half-widths of the α–Me signals were 800-1000 Hz at 30°. Eaton[35] reported a width of ~800 Hz for the methyl resonance of $Fe(acac)_3$, which as the preceding species, has a spin-sextet ground state. Lowering the temperature to –70° produced no spectral evidence of a *cis–trans* mixture. Although the broad lines may have masked any multiple resonances present, the observations are tentatively taken to imply rapid isomerization. An alternative explanation, that only the *cis* form exists in solution, is considered unlikely. Evidence presented here and elsewhere[4,5,12-14,29,41] demonstrates that equilibrated solutions of all other tris(β–diketonates) thus far studied contain both isomers. Furthermore, crystalline $Fe(tfac)_3$[14] and $Fe(bzac)_3$[29] contain the *trans* isomer only.

(d) *Ruthenium(III) Complexes.* $Ru(bzac)_3$ and $Ru(tfac)_3$ were separated into their pure *cis* and *trans* isomers by fractional crystallization and/or chromatography. Consistent with previous results,[4,14,20,29] the *trans* isomer was the more easily eluted and the *cis* isomer lower melting. The complexes are low spin and display positive isotropic shifts. The pmr spectrum of a mixture of $Ru(tfac)_3$ isomers is shown in Figure 1; line widths are about 50 Hz for the α–Me and 100-200 Hz for the β–H resonances. The spectrum of an isomeric $Ru(bzac)_3$ mixture is similar (*cf.* Table II). Chemical shifts of $Ru(acac)_3$ were also determined (α–Me, +5.40, β–H, +29.3 ppm, ~29°, $CDCl_3$) and are in excellent agreement with those reported elsewhere.[35] Attempts to measure isomerization rates of $Ru(bzac)_3$ were unsuccessful. The high temperature required (~180°) led to partial decomposition. Isomerization of $Ru(tfac)_3$ was found to occur at lower temperatures without noticeable decomposition, and was studied over the range 140-175° in *sym*–tetrachloroethane solution using *cis* and *trans* forms as the initial isomers. Initial rate constants and activation parameters are collected in Table IV. Thermodynamic data for equilibrium (1) are given in Table III.

The general analysis of the kinetics of intramolecular rearrangements of $M(A–B)_3$ complexes developed recently and applied to $Co(mhd)_3$[4] could not be employed with $Ru(tfac)_3$. This analysis, which can permit reasonable deduction of the pathways of rearrangement processes, requires as minimum kinetic information rates of isomerization and racemization of the *cis* and *trans* isomers.

Exhaustive attempts to resolve by chromatography $Ru(tfac)_3$ optical isomers failed, although alkyl- or aryl-substituted Cr^{III},[41,42] Co^{III},[4,13] Rh^{III} [42] β–diketonates can be resolved by similar methods. Attempts to resolve several tifluoromethyl-substituted Co^{III} complexes of type 1 have also been unsuccessful.[41,42]

$Ru(tfac)_3$ was found to undergo the reversible reduction reaction (2) which can be effected chemically or electrochemically. The reaction was investigated

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[39] J.A. Pople, W.G. Schneider, and H.J. Bernstein, «High Resolution Nuclear Magnetic Resonance», Mc-Graw-Hill, N.Y., 1959, p. 223.

[40] A more detailed analysis of the spectrum of this complex is being carried out elsewhere (G.N. LaMar, private communication).

[41] R.C. Fay and T.S. Piper, *Inorg. Chem.*, 3, 348 (1964).

[42] R.C. Fay, A.Y. Girgis, and U. Klabunde, *J. Amer. Chem. Soc.*, 92, 7056 (1970), and references therein.

Table IV. Rate Constants and Activation Parameters for the Isomerization of $Ru(tfac)_3$ in *sym*-Tetrachloroethane Solution.

T, °C	*cis*→*trans* $k_{CT} \times 10^5$, sec^{-1} [a]	T, °C	*trans*→*cis* $k_{TC} \times 10^5$, sec^{-1} [a]
140.5	1.24±0.03	140.0	0.193±0.004
151.8	3.96±0.11	150.1	0.439±0.009
162.7	9.66±0.15	160.3	1.07 ±0.02
174.5	26.9±0.5	160.6	0.925±0.018
		170.4	2.02 ±0.06 [b]
ln A [c]	28.9±0.9		21.2±1.3
E_a, kcal $mole^{-1}$	33.0±0.8		28.2±1.1
ΔH^*, kcal $mole^{-1}$	32.1±0.8		27.3±1.1
ΔS^*, eu	−7.5±2.0		−23 ±3

[a] Quoted errors are one esd calculated from residuals of the least squares fit to the initial rate data; 5-6 measurements of relative concentration per run. [b] Based on three relative concentration measurements. [c] A expressed in sec^{-1}.

using the *trans*–isomer and

$$\underset{\text{(red-brown)}}{trans\text{- }Ru(tfac)_3} \underset{O_2}{\overset{Na,\ EtOH}{\rightleftarrows}} \underset{\text{(purple)}}{trans\text{- }[Ru(tfac)_3]^-} \qquad (2)$$

$$E_{1/2} = -0.04$$

retention of configuration was established over the course of a redox cycle. This observation reflects the general non-lability of $Ru^{II,III}$ chelates, a property which in at least one case[43] permits retention of absolute configuration in electron transfer processes. The monoanion also resisted resolution by chromatography or by formation of diastereoisomeric salts. Polarographic half-wave potentials for processes of type (2) have been found to exhibit a marked dependence on chelate ring substituents and these electron transfer reactions are being further investigated.[44]

(e) *Cobalt(III) Complexes.* Detailed studies of equilibrium isomer distributions and isomerization kinetics of $Co(tfac)_3$,[14,41] $Co(mhd)_3$,[4] and $Co(bzac)_3$[13] have been reported. Isomerization is quite slow at normal temperatures, with rate constants on the order of 10^{-3} sec^{-1} for $Co(tfac)_3$ in chloroform and 10^{-4}–10^{-5} sec^{-1} in chlorobenzene for the other two complexes. Equilibrium constants and thermodynamic data are given in Table III.

Trends in Isomer Distribution and Isomerization Rates. An adequate number of measurements of these properties, especially for $M(tfac)_3$ complexes, is now available and allows recognition of certain trends. Equilibrium data in Table III were obtained from measurements of pmr signal intensities, usually over a temperature range. The small intensity changes with temperature render ΔH and ΔS values rather inaccurate. Most of the Keq values quoted are derived from direct measurements at the indicated temperatures and are more precise. The limited data available for alkyl– or phenyl–substituted tris(β–diketonates) reveal that $\Delta H = 0$ within experimental uncertainty and Keq is slightly less than the statistical value of 3. In addition Keq ~3 for $Mn(bzac)_3$ and $Co(dhd)_3$ in deuteriochloroform. In contrast, ΔH values are negative and ΔS values positive for nearly all $M(tfac)_3$ complexes, resulting in $Keq > 4$. The *trans* form is thus the thermodynamically more stable form in weakly polar media, presumably because of its lower dipole moment.[14,45]

Relative rates of rearrangement (isomerization, inversion) of tris(β–diketonates) are observably dependent upon both ligand structure and metal ion. Rates for $M(tfac)_3$ complexes are invariably faster than those for other complexes of type 7 with R_α, R_γ=alkyl, Ph as shown by the orders $M(tfac)_3 > M(pmhd)_3$[5,41] ($M = Al$, Ga) and $Co(tfac)_3 > Co(mhd)_3$, $Co(bzac)_3$.[4,13,41] A simple rationale for these observations is that the highly electronegative CF_3 weakens and lengthens the M—$OCCF_3$ bonds, thereby facilitating rearrangement by either bond rupture or twist mechanisms.[4]

In terms of metal ion dependence this work establishes relative isomerization rates of $M(tfac)_3$ complexes as Fe>Mn>V>Ru. When related to the results of Fay and Piper[41] obtained in weakly polar solvents, a more extensive rate order for $M(tfac)_3$ may be deduced: Fe,In>Mn>Ga>Al>V>Co>Ru>Rh. This order is consistent with the relative isomerization rates of $M(bzac)_3$ (Mn>V>Co[13]), and the inversion rates of $M(acac)_3$[42] (Co>Cr>Ru, Rh), and rearrangement rates of $M(pmhd)_3$[5] (Ga>Al) in chlorobenzene.

A detailed interpretation of this rate order requires a knowledge of the isomerization mechanism of each complex. This information is not presently available and cannot be obtained[4] for the more inert complexes until a procedure for resolution of optical isomers has been developed. At this point it can only be noted that the close correspondence of activation parameters for the *cis*→*trans* reaction of $Co(tfac)_3$[41] with those for the intramolecular rearrangements of $Co(mhd)_3$[4] and $Co(bzac)_3$[13] via bond rupture suggests that this reaction may follow a similar path. Activation energies for the two isomerization reactions of $Ru(tfac)_3$ are comparable with those for the Co^{III} complexes (E_a=31-33 kcal/mole). However, the smaller ln A values (*ca.* 35 for Co^{III} complexes) and the apparent inequality of E_a and ln A for the forward and reverse isomerization reactions (equation 1) permit no informative comparison to be drawn with the Co^{III} systems. The present results show that $M(tfac)_3$ complexes represent a useful series for establishment

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

(44) For comparison, $E_{1/2}$ for the $Ru(acac)_3^- = Ru(acac)_3$ couple in DMF is —0.76v: G.S. Patterson and R.H. Holm, work in progress. $Ru(SacSac)_3$ has also been found to undergo polarographic reduction: G.A. Heath and R.L. Martin, *Austr. J. Chem.*, *23*, 1721 (1970).

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

Table V. Chemical Shifts of Tris(β-thioketonato)metal(III) Complexes (5) in CDCl$_3$ Solution at ~ 29°.

Complex [a]	Shift, ppm R_α	β-H	R_γ
V(Me,H,Me)$_3$	—66.8 [b]	—58.4	—55.9 [b]
V(CF$_3$,H,Me)$_3$ [g]	c	—64.8	—88.0
V(Me,H,Ph)$_3$	—64.9	—58.1	—0.26, —1.32, —10.7
V(Me,H,*i*Pr)$_3$	—65.8	—57.7	Mc, —5.08; CH, —22.3
Co(Me,H,Me)$_3$	— 2.20	— 6.16	—2.20
Co(Me,H,Ph)$_3$	— 2.16	— 6.68	—7.22, —7.26
Co(Ph,H,Me)$_3$	— 7.45	— 7.10	—2.38
Co(Me,H,*i*Pr)$_3$	— 2.23	— 6.37	Me, —1.20 [d]; CH, —2.80 [e]
Co(*t*Bu,H,*t*Bu)$_3$ [f]	— 1.08 [b]	— 6.62	—1.28 [b]

[a] Abbreviated in terms of substituents as M(R_α, H, R_γ)$_3$ (5). [b] Assignment uncertain. [c] Not measured. [d] Center of doublet (J=6.0 Hz). [e] Center of septet (J=6.0 Hz). [f] Compound prepared by Dr. D.H. Gerlach. [g] Impure compound, identified by pmr spectrum.

of metal ion dependence of relative isomerization rates, which are likely to extend to other groups of complexes. However, the M(tfac)$_3$ series does not appear to be of any present utility in the study of intramolecular rearrangement mechanisms by methods developed for complexes undergoing slow[4] or fast[5] rearrangements under ordinary conditions. Consequently, mechanistic investigations of this process have recently[4,5] been and currently[46] are being carried out with complexes whose structural and physical properties permit examination of both isomerization and inversion reactions.

Tris(β*–thioketonates*) (5). Detailed studies of these complexes were confined to V^{III} and Co^{III} species. Proton chemical shifts are set out in Table V and magnetic moments are given in Table I. As reported earlier[19] all complexes display one resonance per substituent, indicating exclusive population of the *cis* isomer. Pmr data for several of the Co^{III} complexes investigated here have also been published by others[47] but without comment concerning structure. Spectra of V(Sbzac)$_3$ and Co(Sbzac)$_3$ are compared with those of their oxygen analogs in Figures 3 and 6, respectively. The large isotropic shifts in the vanadium complexes render spectral simplification due to accidental chemical shift degeneracies highly improbable. The structural lability of V^{III} species further ensures that an equilibrium distribution of isomers was observed. In addition, heating deuteriochloroform solutions of V(Sacac)$_3$ and V(Smhd)$_3$ at 118° for 24 hr produced no changes in the pmr spectrum of either complex. It is also probable that the isomer distribution of the cobalt(III) complexes is thermodynamically controlled. The synthetic procedure results in the formation of labile Co^{II} complexes (some of which have been isolated[18b]), which are slowly oxidized in air to the inert Co^{III} complexes.

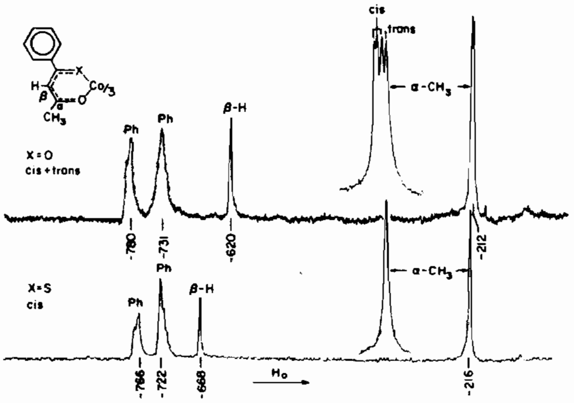

Figure 6. 100 MHz pmr spectra of a *cis-trans* mixture of Co(bzac)$_3$ (top) and *cis*-Co(Sbzac)$_3$ (bottom) in CDCl$_3$ solution at ~29°. Chemical shift are in Hz.

In an attempt to stabilize detectable amounts of *cis* and *trans* isomers, V(tfSac)$_3$ was prepared. The presence of a trifluoromethyl group destabilizes the *cis* isomers of M(tfac)$_3$ complexes (*cf.* Table III), and it was thought that this effect might partially counteract the *cis*-stabilizing ability of the sulfur atoms. The pmr spectrum of a somewhat impure sample of the complex clearly revealed the presence of only the *cis* isomer, however.

The pmr spectra are consistent with C_3 or C_{3v} (*cis*-trigonal prismatic) symmetry. In order to distinguish between these structures, 50 mg of Co(Sacac)$_3$ was eluted from a column of D–lactose with 1:1 *n*–hexane/benzene. Fractions of *ca.* 7 ml were collected and rotations measured at 546 nm in a 10 cm cell. The following results (fraction, rotation) were obtained: 1, –0.044°; 2, –0.085°; 8, +0.017°; 9, +0.010°. The C_{3v} structure is thus excluded for this and, presumably, the other Co^{III} complexes.

A possible source of the stabilization of the *cis* form of tris(β–thioketonates) is the existence of weak S---S interactions similar to those postulated to account for the trigonal prismatic coordination of some tris(dithiolenes).[17] Further consideration of the factors responsible for *cis* isomer stabilization and of the detailed structure of tris(β–thioketonates) must await X-ray results. In this regard the structure of V(Sacac)$_3$ would be particularly valuable inasmuch as resolution experiments on labile V^{III} chelates are likely to be unsuccessful and an accurate structure of V(acac)$_3$ has recently been reported.[48]

Finally, Cr(Sbzac)$_3$ and Fe(Sbzac)$_3$ were briefly examined. Both are high spin and afforded pmr spectra

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(46) S.S. Eaton, J.R. Hutchison, R.H. olm, and E.L. Meutterties, work in progress.
(47) A. Yokoyama, S. Kawanishi, M. Chikuma, and N. Tanaka, *Chem. Pharm. Bull.* (Tokyo), *15*, 540 (1967); A. Yokoyama, S. Kawanishi, and H. Tanaka, *ibid.*, *18*, 356, 363 (1970).
(48) B. Morosin and H. Montgomery, *Acta Cryst.*, *B25*, 1354 (1969).
(49) M. Cox, J. Darken, B.W. Fitzsimmons, L.F. Larkworthy, K.A. Rogers, and A.W. Smith, *Chem. Commun.*, 105 (1970).

which were too broad and poorly resolved to be structurally diagnostic. The only available information bearing on the structure of type 5 complexes of these metal ions is the recent claim from Mössbauer data that Fe^{III} in the low-spin isomer of $Fe(Sacac)_3$ is located at a site of near-cubic symmetry.[49] If correct, this result when related to the structure of $Fe(SacSac)_3$[50] indicates that no gross structural change results upon altering the coordination from O_3S_3 to S_6, at least with low-spin Fe^{III}.

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(50) R. Beckett, G.A. Heath, B.F. Hoskins, B.P. Kelly, R.L. Martin, I.A.G. Roos, and P.L. Weickhardt, *Inorg. Nucl. Chem. Letters*, *6*, 257 (1970).