transition states (because the salt effect on preferential solution will differ for these two states). It is in fact quite interesting that the 1-1 electrolyte effects for the rate of solvolysis of neophyl *p*-toluenesulfonate in 50% (wt.) dioxane-water[16] parallel quite closely (a roughly linear plot results) corresponding salt effects, $K_{\ddagger}$ (or K_g but not $K_g - K_{\ddagger}$) for *t*-butyl chloride solvolysis in water.

(8) **A Comment on Pure Medium Effects.**—Smith, Fainberg and Winstein[41] have recently utilized the conventional rate constant for solvolysis of *p*-methoxy-neophyl *p*-toluenesulfonate as a measure of the ionizing power of a solvent. A close correspondence of the logarithm of the rate constant of pure polar non-hydroxylic solvents with other independent measures of ionizing power is found. The results support the notion that these rates are governed by the ability of the solvent to support a charge separation through non-specific induced polarization of the effective dielectric constant of the medium by the local electric fields of the dipolar transition state (*i.e.*, through coulombic interactions). Since the internal pressures of the solvents investigated vary widely, the partial molal free energy of the dissolved reaction substrate must also vary widely.[42] The success of the treatment implies at least substantial cancellation between ground and transition states of the non-coulombic contributions to the partial molal free energy of these two states. That is, there is apparently involved a cancellation of internal pressure effects between ground and transition states which leaves (for most practical purposes) the rate constant as a coulombic quantity, a situation analogous to the cancellation reported in this paper for kinetic salt effects in pure water. The complication of kinetic salt effects in mixed solvents appears to support the conclusion of the above authors that it can be less certainly accepted that the effects of mixed solvents on the solvolysis rates are purely coulombic quantities.

[41] S. G. Smith, A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

[42] J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," 3rd Ed., Reinhold Publishing Co., New York, N. Y., 1950, pp. 46, 94, 129, 435.

[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Coördination Compounds of Trivalent Metals with Unsymmetrical Bidentate Ligands. I. Benzoylacetonates[1]

BY ROBERT C. FAY[2] AND T. S. PIPER

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The preparation of benzoylacetonates of a number of trivalent metals is described (M = Cr, Co, Rh, Al, Mn, Fe). *cis* and *trans* isomers of the inert complexes (M = Cr, Co, Rh) were separated by utilizing solubility differences in ethanol and column chromatography on alumina. Somewhat less than the statistical amount of *cis* isomer was obtained. In the case of the labile complexes (M = Al, Mn, Fe), only the more stable *trans* isomer could be isolated. The configuration of the diamagnetic complexes was determined by nuclear magnetic resonance; the configuration of the paramagnetic complexes was established on the basis of isomorphism of crystals of the diamagnetic and paramagnetic complexes. Small intensity differences in the electronic spectra suggest that the forbidden d-d transitions obtain intensity by mixing in odd molecular orbitals rather than odd atomic orbitals. *Cis* to *trans* isomerization of the cobalt and chromium complexes takes place at elevated temperatures. The potential importance of n.m.r. in stereochemical studies of metal coördination complexes is emphasized.

Introduction

Coördination compounds in which the central atom is bound to three unsymmetrical bidentate ligands may exist in two geometrically isomeric forms. If the distinguishable ends of an unsymmetrical bidentate ligand are represented by X and Y (see Fig. 1), the X groups may be in the 1,2,3- or 1,2,6-positions. We shall refer to the isomer with X groups in the 1,2,3-positions as the *cis* isomer and the isomer with X groups in the 1,2,6-positions as the *trans* isomer.[3]

The majority of the work reported on isomeric tris-complexes has been concerned with the tris-amino acid chelates of cobalt(III). The glycine and alanine complexes have been known for a long time,[4] but only recently has the configuration of the two isomeric glycine complexes been determined on the basis of visible absorption spectra.[5] Carassiti and co-workers[6,7] using the same technique have determined the configuration of the alanine complexes and also a number of other amino acid chelates of cobalt(III). A tris-(ethanolamine)-cobalt(III) complex has been isolated and assigned the *cis* configuration, also on the basis of absorption spectra.[8] Very recently two tris-(8-quinolinolo)-chromium(III) complexes (one solvated) have been assigned *cis* and *trans* structures.[9] The assignment, however, must be viewed as only tentative because of the lack of experimental evidence.

One class of compounds which ought to give geometric isomers and which has not been previously investigated are tris-complexes of trivalent

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[2] National Science Foundation Fellow, 1960-1962.

[3] W. C. Fernelius, *Adv. in Chem. Series*, **8**, 9 (1953).

[4] H. Ley and H. Winkler, *Ber.*, **42**, 3894 (1909); *ibid.*, **45**, 372 (1912); H. Ley and K. Ficken, *ibid.*, **50**, 1123 (1917).

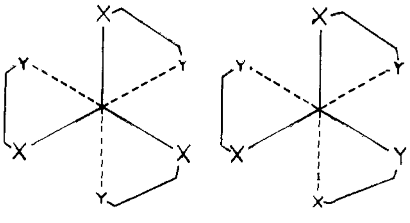
[5] F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

[6] V. Carassiti and M. Claudi, *Ann. Chim. (Rome)*, **50**, 581 (1960).

[7] V. Carassiti and A. M. Marinangeli, *ibid.*, **50**, 593 (1960).

[8] H. Yoneda and S. Kida, *J. Am. Chem. Soc.*, **82**, 2139 (1960).

[9] F. Umland, G. H. Gudmundsson and K. Adam, *Naturwissenschaften*, **48**, 49 (1961).



cis trans

Fig. 1.—Configuration of *cis* and *trans* isomers of metal trischelate complexes in which the ligand is bidentate and unsymmetrical.

metals in which the bidentate ligand is an unsymmetrical 1,3-diketone. In this paper we report the separation and characterization of *cis* and *trans* isomers of tris-(1-phenyl-1,3-butanediono)-metal complexes (hereafter often referred to as $M(bzac)_3$ and called metal benzoylacetonates). The isomers have been separated by utilizing solubility differences in ethanol and column chromatography on alumina. The molecular configuration has been determined with the aid of nuclear magnetic resonance, microscopy and X-ray powder patterns. The electronic and vibrational spectra of the isomers were found to exhibit only small intensity differences.

Experimental

1-Phenyl-1,3-butanedione.—The free diketone was prepared as described by Claisen.[10]

Tris-(1-phenyl-1,3-butanediono)-cobalt(III).—This complex was prepared by reaction of 1-phenyl-1,3-butanedione with $Na_3[Co(CO_3)_3]\cdot 3H_2O$ as described by Bauer and Drinkard.[11]

Tris-(1-phenyl-1,3-butanediono)-chromium(III).[12]—Chromium(III) chloride hexahydrate (13.3 g., 0.050 mole) and urea (100 g.) were dissolved in 250 ml. of water. 1-Phenyl-1,3-butanedione (48.7 g., 0.300 mole) was added, and the mixture was heated on the steam-bath overnight with stirring. The olive-drab precipitate was collected, washed with water and air dried. The yield after rapid chromatography on alumina to remove the excess 1-phenyl-1,3-butanedione was about 25 g. (93%).

Tris-(1-phenyl-1,3-butanediono)-rhodium(III).[13]—Rhodium(III) chloride trihydrate (1.00 g., 0.0038 mole) in 30 ml. of water was treated with 2 *M* sodium hydroxide to precipitate the rhodium as the light yellow hydroxide (or basic chloride). The sodium hydroxide was added at steam bath temperature to *p*H 10; the precipitate was then digested for *ca.* 5 min. during which time the *p*H was appreciably lowered as more of the rhodium precipitated. The sodium hydroxide addition and following digestion was repeated two or three times until the *p*H was constant at *p*H 9–10. The light yellow precipitate which had coagulated was easily separated from the only slightly pink supernatant by filtration. After washing well with 1% ammonium nitrate solution, the yellow hydroxide was redissolved in 3 *N* nitric acid and was reprecipitated with 2 *M* sodium hydroxide as before in order to free the rhodium from all traces of chloride. The hydroxide was again washed with 1% ammonium nitrate solution and was redissolved in a minimum amount of 3 *N* nitric acid. The resulting nitrate solution was neutralized to *p*H 4 with solid sodium bicarbonate at which *p*H the yellow hydroxide (or basic nitrate) begins to precipitate. After addition of 1-phenyl-1,3-butanedione (1.86 g., 0.0114 mole), the mixture was refluxed for 30 min. The *p*H was then readjusted to *p*H 4 by addition of more sodium bicarbonate, and refluxing was continued for 15 min. longer. The yellow-orange gummy product was separated from the slightly yellow supernatant. It was washed with water and air dried. The yield of $Rh(bzac)_3$ after purification by chromatography on alumina was 0.83 g. (37%).

Tris-(1-phenyl-1,3-butanediono)-aluminum(III).[14]—Aluminum isopropoxide (1.01 g., 0.0050 mole) was placed in a dry, stoppered, 200 ml. round bottom flask which had been filled with nitrogen gas and weighed. After weighing the flask and contents, the aluminum isopropoxide was dissolved in 40 ml. of benzene. 1-Phenyl-1,3-butanedione (2.46 g., 0.0152 mole) in 20 ml. of benzene was added. The flask was stoppered and allowed to stand for 15 min. The solvent and isopropanol which was produced were then removed by vacuum distillation. A light yellowish liquid was obtained which, upon standing for 2 hr., crystallized to a white solid. The yield of crude $Al(bzac)_3$ was 2.3 g. (91%).

Tris-(1-phenyl-1,3-butanediono)-manganese(III).[15]—A solution of potassium permanganate (0.32 g., 0.0020 mole) in 10 ml. of water was added to a solution of manganese(II) sulfate monohydrate (1.35 g., 0.0080 mole) in 20 ml. of water. Immediately a solution of 1-phenyl-1,3-butanedione (4.9 g., 0.030 mole) and 2.0 ml. of concentrated ammonium hydroxide in 15 ml. of warm ethanol was added with stirring. The black $Mn(bzac)_3$ formed almost immediately. After cooling the solution and diluting with water to 100 ml., the precipitate was collected, washed with water and air dried. The yield was 4.8 g. (89%).

Tris-(1-phenyl-1,3-butanediono)-iron(III).—1-Phenyl-1,3-butanedione (4.9 g., 0.030 mole) was dissolved in 15 ml. of warm ethanol. Concentrated ammonium hydroxide (4.0 ml.) was added, and the resulting solution was added to a solution of iron(III) chloride hexahydrate (2.7 g., 0.010 mole) in 75 ml. of water. The dark red $Fe(bzac)_3$ began to separate immediately and precipitation was complete within a few minutes. The solution was cooled, diluted to 125 ml. with water and then filtered. After washing with water, the precipitate was air dried. The yield was 4.8 g. (89%).

Separation of *cis* and *trans* Isomers.—In all preparations, the metal benzoylacetonates were isolated from aqueous solutions (or weakly alcoholic aqueous solutions) in which the benzoylacetonates are almost completely insoluble. The crude reaction product was used without purification by recrystallization since this would have led to losses of the more soluble *cis* isomer. The geometric isomers of the cobalt, chromium and rhodium benzoylacetonates were separated by utilizing solubility differences in ethanol and column chromatography on alumina (Merck, acid washed). The same procedure, described in general terms below, was used for all three metals.

The crude reaction product (5 g.) was first purified by rapid chromatography on alumina (100 g., amount not critical). The material was put on the column in 50% benzene–50% hexane solution, and the *cis*- and *trans*-$M(bzac)_3$ complexes were eluted with pure benzene. Unreacted benzoylacetone and other unidentified metal complexes remained on the column. After removing the benzene from the eluent by vacuum distillation, the more soluble *cis* isomer was concentrated by extracting the residue with 20 ml. portions of hot ethanol. The extraction was repeated several times until the extract was only slightly colored. The residue from the ethanol extraction (less soluble *trans*-$M(bzac)_3$) was purified by recrystallizing three or four times from benzene–pentane. The ethanol was removed from the ethanol extract (*cis*-$M(bzac)_3$ and some *trans*-$M(bzac)_3$) by vacuum distillation. Separation of the *cis* isomer was then achieved by careful chromatography on alumina (50–100 g. of alumina/1 g. sample in a 22 mm. outside diameter tube). The sample was put on the column in 20% benzene–80% hexane. The benzene content of the eluting solvent was increased in the order 20, 30, 40, 50 and finally 75% every 100 ml. of eluent. The *cis* isomer was

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(10) L. Claisen, *Ann. Chem. Liebigs*, **291**, 51 (1896).

(11) H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).

(12) The procedure used is similar to that which has been described previously for preparation of chromium(III) acetylacetonate. W. C. Fernelius and J. E. Blanch, *Inorg. Synthesis*, **5**, 130 (1957).

(13) This method is similar to that which has been described previously for preparation of rhodium(III) acetylacetonate; F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **75**, 984 (1953).

(14) A similar procedure but with somewhat more rigorous conditions has been suggested by R. K. Mehrotra and R. C. Mehrotra, *Can. J. Chem.*, **39**, 795 (1961).

(15) G. H. Cartledge, U. S. Patent 2,556,316, June 12, 1951; *C. A.*, **46**, 1585b (1952).

eluted with 75% benzene–25% hexane in the later fractions. Early fractions contained *trans*-M(bzac)$_3$, and the middle fractions contained a mixture of the two isomers. Finally, the *cis* isomer was recrystallized from benzene–pentane.

For the benzoylacetonate complexes of aluminum, manganese and iron chromatography on alumina and also on less basic materials such as silicic acid and magnesium silicate was not successful. These complexes decomposed on the column and could not be eluted even with solvents as polar as methanol. The less soluble *trans* isomers were obtained simply by recrystallizing the crude reaction product three or four times from acetone–hexane or benzene–hexane. Solubility of the *cis*- and *trans*-M(bzac)$_3$ (M = Co, Cr) in benzene and in ethanol indicated that the more soluble *cis* isomer could be obtained in at least 75% purity by extraction of the most soluble material with these solvents. The following procedure was adopted: The crude M(bzac)$_3$ (1–2 g., M = Al, Mn, Fe) was extracted twice with 20 ml. portions of hot ethanol or with 20 ml. portions of 50% benzene–50% hexane at room temperature. The most soluble 100 mg. was extracted. After removing the solvent by vacuum distillation, the residue was recrystallized from acetone–hexane, only *ca.* 3 mg. of M(bzac)$_3$ being left in solution. The crystals obtained had X-ray powder patterns which were identical to the powder patterns of the less soluble *trans* isomers. For the benzoylacetonates of aluminum, manganese and iron, therefore, the *cis* isomer, if present at all, can constitute no greater than 0.3% of the total yield.

Characterization of *cis*- and *trans*-tris-(1,3-butanediono)-metal(III) Complexes.—All of these compounds are easily soluble in chloroform, methylene chloride, benzene and acetone; less soluble in ethanol, ether and carbon tetrachloride; and only sparingly soluble in saturated hydrocarbon solvents.

cis-**Co**(bzac)$_3$.—Crystallization from acetone–hexane or benzene–pentane yields green hexagonal plates which can be grown as large as 1–2 mm. from acetone solution. Microscopic examination along the *c* axis reveals typical uniaxial interference figures and hexagonal etch figures. M.p. was 158–159°; solubility at 30° in benzene, 58 g./l. (gravimetrically); solubility at 30° in ethanol, 0.77 g./l. (spectrophotometrically).

Anal. Calcd. for Co(C$_{10}$H$_9$O$_2$)$_3$: C, 66.43; H, 5.02. Found: C, 66.75, 66.16; H, 4.58, 5.44.

Upon melting, the *cis* complex is converted to the *trans* isomer. In the temperature range 159–165°, at least half of the sample isomerized within 30 seconds.

trans-**Co**(bzac)$_3$.—This compound crystallizes as tiny green plates (monoclinic or triclinic) which give oblique extinction at small angles; m.p., 199.5–200° (with decomposition); solubility at 30° in benzene, 20 g./l.; solubility at 30° in ethanol, 0.14 g./l.

Anal. Calcd. for Co(C$_{10}$H$_9$O$_2$)$_3$: C, 66.43; H, 5.02; Co, 10.87. Found: C, 66.07; H, 5.05; Co, 10.77.

cis-**Cr**(bzac)$_3$.—Two crystalline forms of this compound were obtained. Crystallization from hot benzene–pentane or evaporation of acetone solutions at room temperature usually gives dark red hexagonal plates which are isomorphous with *cis*-Co(bzac)$_3$; m.p., 199.5°; solubility in ethanol at 30°, 0.61 g./l. This crystalline form has been named α-*cis*-Cr(bzac)$_3$. Solution of α-*cis*-Cr(bzac)$_3$ in acetone or benzene–pentane followed by evaporation of the solvent at room temperature sometimes gave back the α crystal, but on other occasions large, dark red prisms (as large as 2–3 mm. from acetone) which have been called γ-*cis*-Cr(bzac)$_3$ were formed. The two crystalline forms appear to be of about equal stability. Usually either one form or the other was obtained upon evaporation although in a few instances the two crystals were found side by side. A systematic study of conditions which favor the stability of one form over the other has not been made. The prismatic crystals of γ-*cis*-Cr(bzac)$_3$ exhibit parallel extinction when viewed perpendicular to the longest axis of the prism and oblique extinction when viewed in the direction which is both perpendicular to the former direction and perpendicular to the longest axis. The crystals, therefore, are probably monoclinic. They also are somewhat dichroic, being bright red when the plane of polarization is parallel to the longest axis of the prism and darker, gray-red when the plane of polarization is perpendicular to this axis. M.p. was 196–196.5°; solubility in ethanol at 30°, 0.68 g./l.

Anal. Calcd. for Cr(C$_{10}$H$_9$O$_2$)$_3$: C, 67.28; H, 5.08; Cr, 9.71. Found: C, 67.53; H, 5.02; Cr, 9.44.

Upon melting, *cis*-Cr(bzac)$_3$ is converted to the *trans* complex. The isomerization was at least 80% complete within 30 sec. at 199.5–205°. In refluxing *o*-xylene at 144°, isomerization takes place within 4 hr. After 4 hr. in boiling benzene or ethanol, however, no isomerization could be detected. *Cis* to *trans* isomerization was studied by recovery of crystals, microscopic examination and X-ray powder patterns.

trans-**Cr**(bzac)$_3$.—This compound crystallizes as dark red needles which are characterized by many faces, curved edges and a number of different habits. These crystals are thought to be monoclinic because some give parallel extinction and others give oblique extinction. They are not isomorphous with *trans*-Co(bzac)$_3$. They show dichroism which is opposite to that of γ-*cis*-Cr(bzac)$_3$, *i.e.*, bright red when the plane of polarization is perpendicular to the long (needle) axis and darker, gray-red when the plane of polarization is parallel to the long axis. M.p. was 235°; solubility at 30° in ethanol, 0.15 g./l.

Anal. Calcd. for Cr(C$_{10}$H$_9$O$_2$)$_3$: C, 67.28; H, 5.08; Cr, 9.71. Found: C, 67.48; H, 5.23; Cr, 9.80.

cis-**Rh**(bzac)$_3$.—Yellow hexagonal plates, isomorphous with *cis*-Co(bzac)$_3$ and α-*cis*-Cr(bzac)$_3$. The melting point of *cis*-Rh(bzac)$_3$ could not be determined. When the sample is plunged into a bath at 218°, it melts almost immediately and then resolidifies within a few seconds. When the sample is plunged into a bath at 180°, it crumbles immediately but does not melt until 258° (with decomposition). Upon gradual heating from room temperature melting does not take place until 258° (near the melting point of the *trans* isomer). These observations may be interpreted in terms of rapid isomerization in the liquid phase to the higher melting *trans* isomer which subsequently freezes and *cis* to *trans* isomerization in the solid upon gradual heating.

Anal. Calcd. for Rh(C$_{10}$H$_9$O$_2$)$_3$: C, 61.44; H, 4.64. Found: C, 62.69; H, 5.07.[16]

trans-**Rh**(bzac)$_3$.—Yellow plates, isomorphous with *trans*-Co(bzac)$_3$; m.p., 260.5–261.5° (with decomposition. Incipient decomposition *ca.* 10° below the melting point resulted in a melting point which was reproducible only to ±3°.).

Anal. Calcd. for Rh(C$_{10}$H$_9$O$_2$)$_3$: C, 61.44; H, 4.64. Found: C, 61.32; H, 4.65.

trans-**Al**(bzac)$_3$.—Colorless needles, isomorphous with *trans*-Cr(bzac)$_3$; m.p., 223.5–224°.

Anal. Calcd. for Al(C$_{10}$H$_9$O$_2$)$_3$: C, 70.58; H, 5.33; Al, 5.29. Found: C, 70.99; H, 5.46; Al, 5.01.

trans-**Mn**(bzac)$_3$.—Black needles, isomorphous with *trans*-Cr(bzac)$_3$; m.p., 173–173.5°.

Anal. Calcd. for Mn(C$_{10}$H$_9$O$_2$)$_3$: C, 66.92; H, 5.05; Mn, 10.20. Found: C, 67.20; H, 5.20; Mn, 10.22.

trans-**Fe**(bzac)$_3$.—Red needles, isomorphous with *trans*-Cr(bzac)$_3$; m.p., 210–211°.

Anal. Calcd. for Fe(C$_{10}$H$_9$O$_2$)$_3$: C, 66.81; H, 5.05; Fe, 10.35. Found: C, 67.06; H, 5.19; Fe, 10.65.

Melting Points.—All melting points were determined with Anschutz thermometers accurate to ± 0.1°. Melting points of compounds most susceptible to decomposition[17] (M = Mn, Co, Rh) were determined under nitrogen (1 atm. at 30°). All other melting points were determined in air.

Vibration and Electronic Spectra.—Infrared spectra in potassium bromide discs were obtained with a Perkin–Elmer Model 21 recording infrared spectrometer. Visible and ultraviolet spectra were studied in chloroform and ethanol solutions in 1 cm. quartz cells with a Cary Model 14 *M* recording spectrophotometer. Samples (30–40 mg.) were weighed to ± 0.1 mg. and were diluted to appropriate

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(16) The reason for the consistently high carbon and hydrogen analyses is not understood. One possibility, clathrate formation with solvent molecules, is suggested by the fact that the carbon content is decreased by 0.6% upon grinding and heating *in vacuo* at 100° for 12 hr. There is little doubt about the identity of the compound, however, since its x-ray powder pattern is very similar to those of *cis*-Co(bzac)$_3$ and α-*cis*-Cr(bzac)$_3$.

(17) R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958); J. von Hoene, R. G. Charles and W. M. Hickam, *ibid.*, **62**, 1098 (1958).

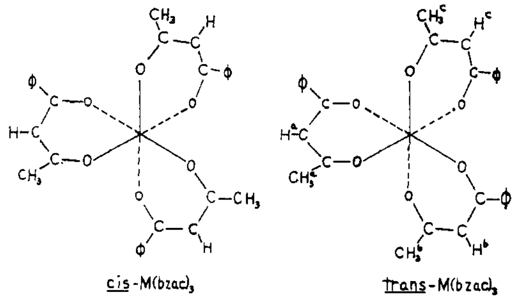

Fig. 2.—Configuration of *cis* and *trans* isomers of $M(bzac)_3$.

volume with standard volumetric flasks at 20 ± 2°. Solutions were 10^{-2}–10^{-3} *M* (vis.) and 10^{-4} – 10^{-5} *M* (u.v.). Extinction coefficients were calculated from $\epsilon = (\log I_0/I)/$molarity. They were reproducible to ± 1%.

N. m. r. Spectra.—Proton resonance spectra were run at 25 ± 2° on a Varian Associates Model V-4300-2 high resolution spectrometer at 60 Mc. The solvent was deuteriochloroform or chloroform which had been passed through an alumina column to remove the ethanol. Concentration of $M(bzac)_3$ was 3–7 wt. %. The chemical shifts were measured relative to tetramethylsilane which was present in *ca.* 2 vol. %. The audio-frequency sideband technique was used for scale calibration. Average of three chemical shift determinations at the same concentration gave a mean deviation of ± 1 c.p.s. The variation in the chemical shift with concentration in the range 3–7 wt. % was less than 2 c.p.s. and in most cases less than 1 c.p.s. The CH_3 and CH detail was run at slow sweep rate (25 c.p.s./min.) which gave *ca.* 6 c.p.s./inch of chart paper. A 20 c.p.s. audio-frequency sideband was used for scale calibration. The difference in chemical shift between non-equivalent protons in the *trans* isomers (0.6–1.5 c.p.s.) was reproducible to ± 10%.

X-Ray Powder Patterns.—X-Ray powder patterns were obtained with iron-filtered Co-Kα radiation using 0.5 mm. glass capillaries and a Debye–Scherrer camera of 14.01 cm. diameter. Special precautions had to be taken in grinding the α crystalline form (α-*cis*-$M(bzac)_3$; M = Cr, Co). When grinding was vigorous, only a very weak pattern could be obtained. Very gentle grinding or shattering the crystal at liquid nitrogen temperature gave a good pattern. The *d* spacings and visually estimated intensities of the stronger lines are tabulated. The Greek letters α, β, γ, and δ refer to the four distinct forms which were found.

α-*cis*-$Cr(bzac)_3$: 10.90(9), 9.43(10), 8.17(2), 7.15(7), 6.00(3), 5.63(2), 5.07(5), 4.73(10), 4.13(2), 3.57(3).

α-*cis*-$Co(bzac)_3$: 11.05(9), 9.36(10), 8.28(1), 7.07(6), 5.99(2), 5.63(2), 5.07(4), 4.70(9), 4.11(1), 3.55(2).

α-*cis*-$Rh(bzac)_3$: 10.90(5), 9.47(10), 8.26(3), 7.20(9), 5.97(2), 5.69(2), 5.08(5), 4.73(6), 4.13(3), 3.58(4).

β-*trans*-$Co(bzac)_3$: 9.72(9), 8.34(9), 7.70(9), 7.13(9), 6.39(5), 5.64(5), 4.78(10), 4.17(8), 3.84(6).

β-*trans*-$Rh(bzac)_3$: 9.68(8), 8.42(10), 7.68(9), 7.15(8), 6.30(5), 5.70(4), 4.76(9), 4.23(3), 3.82(3), 3.65(3).

γ-*cis*-$Cr(bzac)_3$: 9.61(10), 6.73(2), 6.38(8), 5.83(2), 4.79(2), 4.54(3), 4.13(4), 3.62(2).

δ-*trans*-$Al(bzac)_3$: 9.12(10), 7.82(7), 6.96(3), 6.51(2), 4.73(5), 4.49(3), 4.13(8).

δ-*trans*-$Cr(bzac)_3$: 9.12(10), 7.75(8), 6.94(2), 6.48(1), 4.76(4), 4.47(3), 4.13(8).

δ-*trans*-$Mn(bzac)_3$: 9.12(10), 7.77(10), 6.96(2), 6.49(1), 4.73(4), 4.47(3), 4.12(9).

δ-*trans*-$Fe(bzac)_3$: 9.12(10), 7.75(10), 7.00(2), 6.51(1), 4.72(4), 4.49(2), 4.13(10).

Results and Discussion

Relative Yield, Chromatography, Stability and Isomerization.—In the case of $M(bzac)_3$ (M = Cr, Co, Rh), the yield of the *cis* isomer was generally about 20% of the total yield, although in some preparations much less was found. Since the statistical yield of the *cis* isomer is 25%, some preference is exhibited for formation of the *trans* isomer. The *cis* isomer was more strongly adsorbed on alumina than the *trans* isomer. This behavior has been observed previously[18] and is consistent with the greater dipole moment of the *cis* isomer. Failure to obtain any of the *cis* isomer in the case of $M(bzac)_3$ (M = Al, Mn, Fe) reflects both the lability of these complexes and the greater stability of the *trans* isomer. The lability of the aluminum, manganese and iron complexes is consistent with the exchange experiments of Drehmann,[19] who found rapid metal exchange between labeled Mn^{2+} ions and manganese(III) acetylacetonate, and those of Kluiber,[20] who has reported exchange of C-14 labelled acetylacetone with the acetylacetonates of Al(III), Mn(III) and Fe(III) but little or no exchange in the case of Cr(III) and Co(III).

The fact that only the *trans* isomer of the labile complexes can be isolated suggests the greater thermodynamic stability of the *trans* isomer. Moreover, in chloroform solutions, n.m.r. spectra offer no evidence of an appreciable concentration of the *cis* isomer. The *trans* isomer is expected to be somewhat more stable than the *cis* isomer on the basis of its lower dipole moment. The greater stability of the *trans* isomer in the case of the inert benzoylacetonates is further substantiated by the observation that the *cis* complexes isomerize to the corresponding *trans* compounds at elevated temperatures. The *cis* complexes are stable toward isomerization in solution up to at least 80°.

Structural Determination by N.m.r.—Figure 2 shows the configuration of the *cis* and *trans* isomers of a typical metal benzoylacetonate. The *cis* isomer has a threefold rotation axis; whereas the *trans* isomer has no symmetry. In the *cis* isomer, therefore, all three chelate rings are in identical environments, while in the *trans* isomer all three chelate rings are in different environments. Thus, one should observe a proton resonance spectrum for the *cis* isomer which exhibits a single methyl resonance and a single CH resonance, while the proton resonance spectrum of the *trans* isomer ought to exhibit considerable fine structure. If the chemical shifts are large enough, one might expect to observe three methyl and three CH resonances. Even if the chemical shifts are small and the bands are unresolved, the resonances of the *trans* isomer would be expected to be broadened relative to those of the corresponding *cis* isomer.

A typical metal benzoylacetonate spectrum is shown in Fig. 3. The phenyl resonance is at low field and is easily recognized by its complexity. The most intense band is due to the chloroform solvent. The peak at *ca.* −375 c.p.s. is due to the CH proton, and the high field peak, which is approximately three times more intense, is due to the methyl protons. These assignments may be verified by observing that, in the spectrum of tris-(dibenzoylmethano)-cobalt(III), the high field peak assigned to methyl does not appear; whereas in the spectrum of the tris-acetylacetonate, the high

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(18) A. Jensen, J. Bjerrum and F. Woldbye, *Acta Chem. Scand.*, **12**, 1202 (1958); G. B. Kauffman, R. P. Pinnell and L. F. Takahashi, Abstracts of Papers, 140th National Meeting, American Chemical Society, Chicago, Illinois, September 3–8, 1961, p. 45N.

(19) U. Drehmann, *Z. physik. Chem.* (Leipzig), **B53**, 227 (1943).

(20) R. W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).

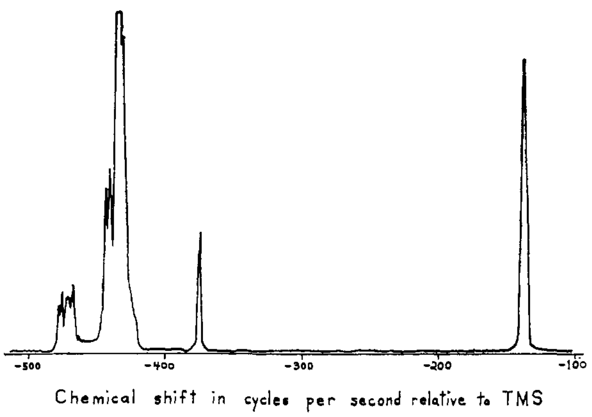

Fig. 3.—Proton resonance spectrum of *cis*-Co(bzac)$_3$ in chloroform at 60 Mc.

field peak has six times the intensity of the peak assigned to the CH proton.

The methyl and CH resonances have been examined in detail at slow sweep rates in order to distinguish the isomers. The results are presented in Fig. 4 for the isomeric diamagnetic benzoylacetonates of cobalt, rhodium and aluminum. The more soluble, less easily eluted isomers exhibit single line resonances; therefore, the more soluble isomers may be assigned the *cis* configuration. The less soluble, more easily eluted isomers give n.m.r. spectra with some of the fine structure expected for *trans* isomers. The aluminum compound clearly shows the expected triplet methyl resonance. In the cobalt compound, two of the methyl peaks nearly coincide and, in the rhodium compound, resolution of these two peaks could not be effected. The rhodium compound shows the nicely resolved three-peak CH resonance expected for a *trans* isomer. In the cobalt and aluminum compounds, resolution of the CH resonance is incomplete. Even in the case of the unresolved bands, however, the widths of the bands at half peak height for the less soluble isomers were about twice those found for the more soluble isomers. There is little doubt that the broader peaks arise from non-equivalent protons and that the less soluble isomers may be assigned the *trans* configuration.

The molecular configuration of the benzoylacetonates of chromium, manganese and iron cannot be determined by n.m.r. because of the paramagnetism of the metal ions. The configuration of these compounds was established on the basis of isomorphism with the diamagnetic compounds, whose configurations had been determined by n.m.r. The results are summarized in Table I where the configuration of all of the compounds studied is listed. The γ-Cr(bzac)$_3$ may be assigned the *cis* configuration because it can be obtained from α-*cis*-Cr(bazc)$_3$ at room temperature where *cis*-Cr(bzac)$_3$ is known to be stable toward isomerization.

The chemical shifts between the non-equivalent protons in the *trans*-benzoylacetonates are indicated in Fig. 4. They are on the order of 0.6–1.5 c.p.s. The chemical shifts of the methyl and CH protons in the *cis*- and *trans*-benzoylacetonates are about the same (see Table II).

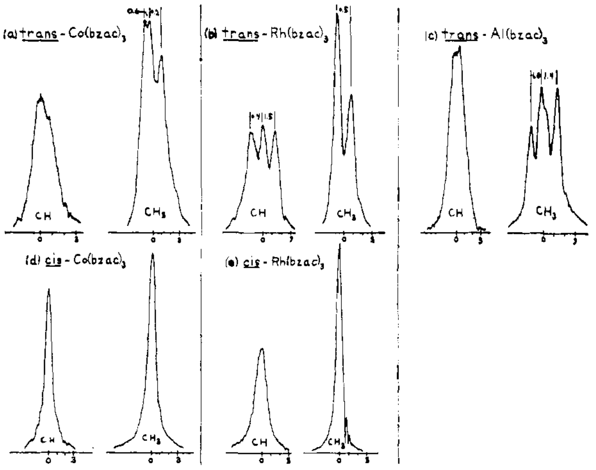

Fig. 4.—CH and CH$_3$ regions of proton resonance spectrum at 60 Mc. and sweep rate of *ca.* 25 c.p.s./min. in chloroform solution: less soluble isomers (a), Co(bzac)$_3$; (b), Rh(bzac)$_3$; (c), Al(bzac)$_3$; more soluble isomers; (d), Co(bzac)$_3$; (e), Rh(bzac)$_3$.

NOTE ADDED IN PROOF.—We have recently demonstrated by fluorine resonance of labile metal trifluoroacetylacetonates that the *cis* isomer does exist in solution at somewhat less than the statistical concentration. The slight shoulder on the center peak of the Al(bzac)$_3$ methyl resonance may well be due to *cis*-Al(bzac)$_3$.

Vibration and Electronic Absorption Spectra.—The infrared spectra of *cis*- and *trans*-Co(bzac)$_3$ were identical in regard to band positions, and only minor intensity differences were observed.

TABLE I

CRYSTAL AND MOLECULAR STRUCTURE OF M(bzac)$_3$ COMPLEXES

Compound	Crystalline form	Configuration
Co(bzac)$_3$	α	*cis*
	β	*trans*
Rh(bzac)$_3$	α	*cis*
	β	*trans*
Al(bzac)$_3$	δ	*trans*
Cr(bzac)$_3$	α	*cis*
	γ	*cis*
	δ	*trans*
Mn(bzac)$_3$	δ	*trans*
Fe(bzac)$_3$	δ	*trans*

TABLE II

CHEMICAL SHIFTS OF CH$_3$ AND CH PROTONS[a]

Compound	CH$_3$ (c.p.s.)	CH (c.p.s.)
cis-Co(bzac)$_3$	−140	−374
trans-Co(bzac)$_3$	−143	−373
cis-Rh(bzac)$_3$	−139	−371
trans-Rh(bzac)$_3$	−141	−371
trans-Al(bzac)$_3$	−131	−373

[a] In the case of the *trans* isomers, the mean chemical shift is reported.

The electronic absorption spectra of *cis*- and *trans*-M(bzac)$_3$ (M = Cr, Co) were examined in the region 220–750 mμ. Three bands were observed: (1) a ligand field band at 563 mμ for Cr(bzac)$_3$ ($^4A_2 \rightarrow {}^4T_2$) and at 598 m$\mu$ for Co(bzac)$_3$ ($^1A_1 \rightarrow {}^1T_1$); (2) an intense band at 355–358 mμ;

and (3) a very intense band near 260 mμ. In addition, the chromium compounds exhibit a shoulder on the low energy side of the 260 mμ band at 292 mμ; the cobalt complexes show a less pronounced shoulder at *ca.* 275 mμ. The lowest energy ligand field bands occur at about 3 mμ longer wave lengths than those observed for the corresponding acetylacetonates; therefore, the ligand field is slightly decreased by the electron withdrawing phenyl group. The very intense band in the 260 mμ region is thought to be a π-π^* transition in the enolate ring. This assignment is based on the great intensity of the band,[21] the absence of a blue shift in polar solvents[21] and the presence of a small red shift (3–9 mμ) upon going from the acetylacetonates[22] to the corresponding benzoylacetonates. A red shift for a π-π^* transition upon introduction of a phenyl group is consistent with the possibility for enhanced delocalization of π electrons in the benzoylacetonates. Since the metal and ligand π levels are mixed, this band may have some charge transfer character.

The energy and shape of the absorption bands of the *cis* and *trans* isomers are nearly identical; the only sizeable difference was found for the most intense ultraviolet band of the cobalt complexes (see Table III). Since the metal ion is surrounded by six oxygen atoms in both isomers, the ligand field in the two isomers is not greatly different; as a result, splitting or broadening of the first ligand field band, which was observed for the *trans*-cobalt(III) amino acid complexes,[5–7] is not observed for the *trans*-benzoylacetonates.

There are significant and interesting intensity differences, however, the *trans* isomers having the more intense absorption bands. Ligand field bands of *cis* isomers have been found to be more intense than those of *trans* isomers. This behavior is expected on the basis of a model in which the *d–d* transition obtains intensity by mixing in odd metal atomic orbitals. According to this model, *cis* isomers, which are farther from a center of symmetry than *trans* isomers, should have more intense absorption bands. The fact that the *d–d* transition to the first excited state is 2–3% more intense for the *trans* benzoylacetonates indicates that the transition does not obtain the majority of its intensity by mixing in odd metal orbitals. Rather, the intensity is believed to result mainly from mixing with the ultraviolet bands which are 8–17% more intense in the case of the *trans* isomers.

TABLE III

ULTRAVIOLET AND VISIBLE SPECTRA OF *cis*-M(bzac)$_3$ AND *trans*-M(bzac)$_3$ IN CHLOROFORM (M = Cr, Co)

Compound	λ_{max}, mμ	ϵ
cis-Cr(bzac)$_3$	563	87.4
	358	22,400
	292(sh)	20,100
	258	27,200
trans-Cr(bzac)$_2$	563	88.9
	358	24,700
	292(sh)	22,300
	259	29,500
cis-Co(bzac)$_3$	598	150
	356	11,300
	262	53,300
trans-Co(bzac)$_3$	598	154
	355	13,400
	267	58,900

In light of the failure of vibrational and electronic spectra to provide stereochemical information, the potential importance of nuclear magnetic resonance for stereochemical studies of metal coördination complexes is worthy of emphasis. Indeed, in some cases, as for example in the present work, n.m.r. is the only technique which can be used to solve a stereochemical problem rapidly and unambiguously.

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