Optical Resolution of Tris(pentane-2,4-dionate) Complexes of Transition-metal Ions

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Optically pure $\Delta(-)[Cr(pd)_3]$ and partly resolved $[Ru(pd)_3]$ with the $\Delta(+)$isomer in excess are afforded by an asymmetric synthesis from the corresponding (+)-tartrate complex (pd = pentane-2,4-dionate). Complexes *rac*-$[M(pd)_3]$ (M = Co^{III}, Cr^{III}, Rh^{III}, or Ru^{III}) partition between diethyl (+)-tartrate and (−)-α-pinene with a partial resolution of the optical isomers, the Λ isomer being generally the more soluble in the ester layer. The optical isomers of $[Rh(pd)_3]$ have been obtained from the *racemic* complex through the optically enriched fractions provided by the differential partitioning.

HITHERTO the principal method available for the optical resolution of the electrically neutral tris(pentane-2,4-dionates) $[M(pd)_3]$ and related complexes of trivalent metal ions has been chromatography on a (+)-lactose column. Introduced by Moeller and Guylas,[1] the method as developed by Collman *et al.*[2] and by Fay *et al.*[3] involves protracted elution of small fractions and, while useful for small-scale substitution [2] or racemisation [3] studies, it is less convenient for larger-scale preparative purposes.

It was found in the present work that the treatment at ambient temperature of aqueous solutions of the (+)-tartrate complexes of Cr^{III}, Co^{III}, or Ru^{III} at high pH with pentane-2,4-dione (Hpd) yields the tris(pentane-2,4-dionate) of the metal ion with one of the optical isomers in excess. The optical yields of the initially formed complex were modest, being 24% for $[Cr(pd)_3]$ and *ca.* 50% for $[Ru(pd)_3]$, but in the former case the mixture of isomers was readily prepared in quantity and subsequently enriched optically by recrystallisation. Optically pure $\Delta(-)[Cr(pd)_3]$ was obtained by this method (Figure 1).

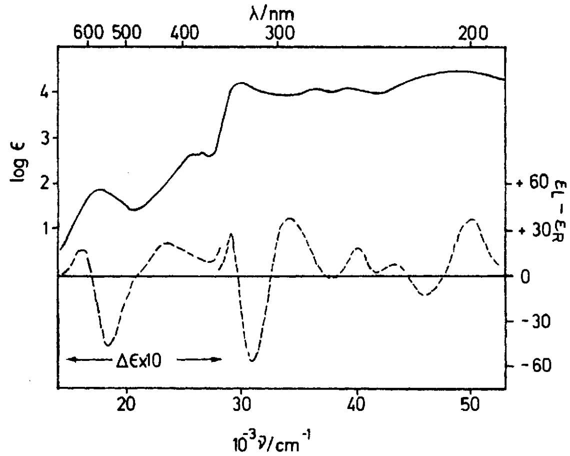

FIGURE 1 Absorption (upper curve) and c.d. spectra (lower curve) of $\Delta(-)[Cr(pd)_3]$ in ethanol

Attempts to prepare the optical isomers of $[Rh(pd)_3]$ and $[Ir(pd)_3]$ by this route were unsuccessful and in the case of $[Co(pd)_3]$ the optical yields were low (2—5%) and erratic, being sensitive to the pH of the cobalt(III) (+)-tartrate solution and to trace amounts of Co^{II}. However, the dissymmetric partitioning of *rac*-$[M(pd)_3]$ between two immiscible chiral liquids provides a further and more general method for the partial resolution of these complexes into optical isomers.[4,5] It is found that the optical isomers of $[M(pd)_3]$ have a differential solubility in diethyl (+)-tartrate and in chiral liquid hydrocarbons which are not miscible with the ester, such as α- or β-pinene, cedrene, or limonene. The differential partitioning of the optical isomers of a *rac*-$[M(pd)_3]$ complex between diethyl (+)-tartrate and a given terpene is dependent on the optical enantiomer of the latter employed and, for example, it is larger for (−)- than for (+)-α-pinene. The optical yield of the differential partitioning is low, some 5%, but again relatively large amounts of the partially resolved complex may be obtained and optically enriched by recrystallisation. Optically pure $\Lambda(-)[Rh(pd)_3]$ was isolated by this method and characterised by recrystallisation to a constant circular dichroism (c.d.) spectrum (Figure 2). Each of the observed c.d. bands has the same sign and a similar magnitude to the c.d. band at the corresponding frequency in the spectrum of

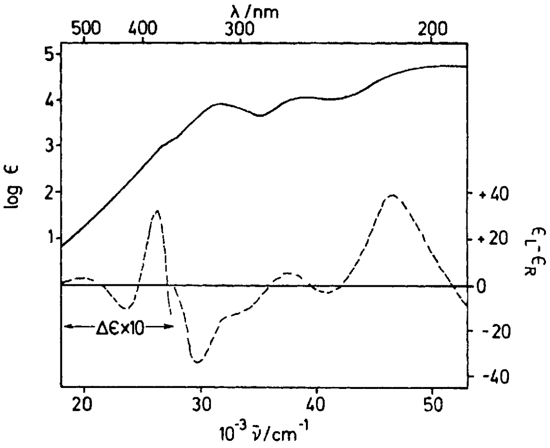

FIGURE 2 Absorption (upper curve) and c.d. spectra (lower curve) of $\Lambda(-)[Rh(pd)_3]$ in ethanol

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[1] T. Moeller and E. Guylas, *J. Inorg. Nuclear Chem.*, 1958, **5**, 245.

[2] J. P. Collman, R. P. Blair, R. L. Marshall, and L. Slade, *Inorg. Chem.*, 1963, **2**, 576.

[3] R. C. Fay, A. Y. Girgis, and U. Klabunde, *J. Amer. Chem. Soc.*, 1970, **92**, 7056.

[4] F. P. Dwyer and E. C. Gyarfas, *Nature*, 1951, **168**, 29.

[5] N. S. Bowman, V. G'ceva, G. K. Schweitzer, and I. R. Supernaw, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 351.

the (+)-3-acetylcamphor [(+)atc] complex,[6] Λ-*trans*- or Λ-*cis*-[Rh{(+)atc}$_3$].

The optical enrichment of (+)- or (−)-[Ru(pd)$_3$] by recrystallisation is limited by the instability of the complex which progressively darkens in colour and separates from solution as a viscous oil. The major c.d. band at 275 nm in the spectrum of Λ(−)[Ru(pd)$_3$] obtained by the differential-partitioning method has the value at its maximum of $\Delta\varepsilon = -28$ dm^3 mol^{-1} cm^{-1} (Figure 3), and while the corresponding value for the Δ(+) isomer obtained by chromatography on a (+)-lactose column [3] has a similar magnitude ($\Delta\varepsilon = +26$) [7] the comparable values for both Λ-*trans*- and Λ-*cis*-[Ru{(+)atc}$_3$] are somewhat larger with $\Delta\varepsilon_{\text{max.}} = -33$ in each case.[8] Using $\Delta\varepsilon_{\text{max.}}$ of the last two complexes as a guide, the optical purity of Δ(+)[Ru(pd)$_3$] prepared from the ruthenium(III) (+)-tartrate complex was *ca.* 50% (Figure 3).

As yet no tris complexes of Ir$^{\text{III}}$ with chiral β-dicarbonyl ligands are available for an estimate of the optical purity of the partly resolved [Ir(pd)$_3$] complex (Figure 4) and for an assignment of the configuration of the major isomer. The probable optical purity is *ca.* 5—10% as the optical enrichment by recrystallisation, following differential partitioning of the enantiomers between diethyl (+)-tartrate and (−)-α-pinene, was limited by the small quantity of *rac*-[Ir(pd)$_3$] available, the latter being the product of the attempted asymmetric synthesis from the corresponding (+)-tartrate complex.

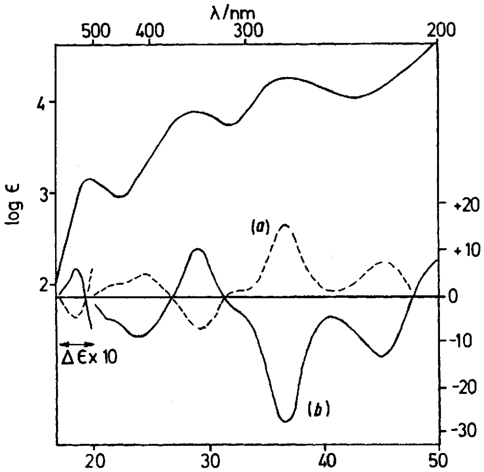

FIGURE 3 Absorption (upper curve) and c.d. spectra (lower curves) of [Ru(pd)$_3$]: (*a*) enriched in the Δ(+) isomer by asymmetric synthesis from the corresponding (+)-tartrate complex; (*b*) enriched in the Λ(−) isomer from the ester layer of a differential partitioning of the *racemic* complex between diethyl (+)-tartrate and (−)-α-pinene

The stereochemical configurations assigned to the optically pure isomers or the major isomer of the partly resolved mixtures obtained are based on the correspondence between the c.d. spectrum of the isomer isolated and that of a [M{(+)atc}$_3$] analogue of known configuration. The absolute configuration of[9] Λ(−)[Co(pd)$_3$] and of[10] Λ(+)-*trans*-[Cr{(+)atc}$_3$] have been determined by *X*-ray diffraction analysis, from which the configurations of the four isomers of[11,12] [Co{(+)atc}$_3$] and of[12] [Cr{(+)atc}$_3$] have been characterised. The relative abundance order and the chromatographic elution order of the four isomers are similar in the two series,[11,12] and from the assumption that the same orders obtain for the corresponding four isomers of the [Rh{(+)atc}$_3$][6] and of the [Ru{(+)atc}$_3$] series[8] the configurations of the isomers in the last two series have been assigned. The c.d. spectra of the [M{(+)atc}$_3$] isomers [6,8,11,12] then provide standards for the estimation of the optical purity of corresponding [M(pd)$_3$] isomers and a reference for the determination of the absolute configuration of the latter.

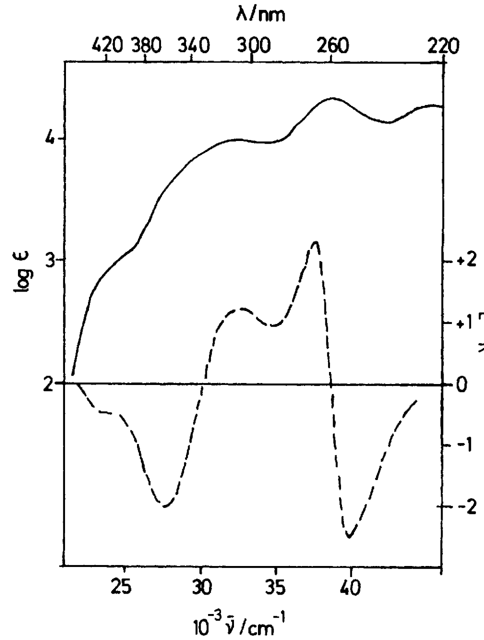

FIGURE 4 Absorption (upper curve) and c.d. spectra (lower curve) of partly resolved [Ir(pd)$_3$]

The configurations assigned in the present work indicate that the Λ isomers of the [M(pd)$_3$] complexes are generally more soluble than their enantiomers in diethyl (+)-tartrate, while the Δ isomers are preferentially formed with Hpd from the (+)-tartrate complexes of Cr$^{\text{III}}$ and Ru$^{\text{III}}$. A theoretical study [13] of the dispersion and induction energies between two chiral molecules in the gas phase shows that the interactions

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[6] G. W. Everett, jun., and A. Johnson, *Inorg. Chem.*, 1974, **13**, 489.

[7] R. C. Fay, personal communication.

[8] G. W. Everett, jun., and R. M. King, *Inorg. Chem.*, 1972, **11**, 2041.

[9] R. B. Von Dreele and R. C. Fay, *J. Amer. Chem. Soc.*, 1971, **93**, 4936.

[10] W. DeW. Horrocks, jun., D. L. Johnstone, and D. MacInnes, *J. Amer. Chem. Soc.*, 1970, **92**, 7620.

[11] C. S. Springer, jun., R. E. Sievers, and B. Feibush, *Inorg. Chem.*, 1971, **10**, 1242.

[12] R. M. King and G. W. Everett, jun., *Inorg. Chem.*, 1971, **10**, 1237.

[13] D. P. Craig, E. A. Power, and T. Thirunamachandran, *Proc. Roy. Soc.*, 1971, **A322**, 165.

are discriminatory between a pair of molecules with the same sign for the optical rotation, where the energy is repulsive, and the corresponding pair with rotations of the opposite sign where the energy is attractive. The generalisation is not expected to apply to condensed phases, particularly to a hydrogen-bonding solvent and an oxygen-containing solute. Thus the $\Lambda(+)[Cr(pd)_3]$ isomer is the more soluble in diethyl (+)-tartrate where it is stabilised relative to its enantiomer.

EXPERIMENTAL

$\Delta(-)[Cr(pd)_3]$.—Pentane-2,4-dione (Hpd) (100 cm^3) was left stirring for 2 d with a 4 mol dm^{-3} solution (100 cm^3) of potassium (+)-tartrate containing chrome alum (6 g) and potassium hydroxide (3 g). Removal of the excess of Hpd from the organic layer with a rotatory evaporator at room temperature, followed by recrystallisation of the solid residue from cyclohexane–hexane (2 : 1), gave violet needles, 0.60 g (14.3%) (Found: C, 51.4; H, 6.00. $C_{15}H_{21}CrO_6$ requires C, 51.6; H, 6.00%). The c.d. spectrum of the initially formed $[Cr(pd)_3]$ gave $\Delta\varepsilon_{540} = -1.05$, corresponding to a 24% optical yield relative to the theoretical $\Delta\varepsilon_{540}$ values of [14] -4.3 or [15] -4.43 calculated for the (−) isomer from photoresolution studies. Recrystallisation of the partly resolved complex from benzene–hexane (1 : 4) gave *racemic* crystals for the first 75% of the total $[Cr(pd)_3]$, while the c.d. of the mother liquor increased progressively to the limiting value of $\Delta\varepsilon_{540} = -4.785$. Subsequent crystals of $\Delta(-)[Cr(pd)_3]$ had the same limiting c.d. value.

$\Delta(+)_{546}[Ru(pd)_3]$.—Formaldehyde (1.2 cm^3, 45%) was added to an aqueous solution (35 cm^3) of (+)-tartaric acid (1.3 g) and $[NH_4]_2[RuCl_6]$ (1.0 g), the mixture being heated under reflux for 45 min. Potassium hydrogencarbonate (1.8 g) was added over 30 min and reflux distillation was continued until the colour of the mixture changed from red to olive-green. Pentane-2,4-dione (20 cm^3) was added to the cooled solution, after adjusting to pH 11 by the addition of K[OH], and the mixture was stirred for 24 h. Removal of the excess of Hpd from the organic layer and chromatography of the residue on a silica-gel column, eluted with benzene–hexane (1 : 1), afforded partly resolved $[Ru(pd)_3]$ with the $\Delta(+)$ isomer in excess, characterised by the absorption [16] and the c.d. spectrum [3,7] (Figure 3).

$\Lambda(-)[Rh(pd)_3]$.—The complex [17] *rac*-$[Rh(pd)_3]$ (1 g) in diethyl (+)-tartrate (100 cm^3) was stirred with aliquot portions (50 cm^3) of (−)-α-pinene until the complex extracted into the hydrocarbon layer contained no excess of the $\Delta(+)$ isomer detectable by c.d. spectroscopy. Ten successive extractions were required. The combined (−)-α-pinene extracts were passed down a silica-gel column and, after washing the column with hexane, the retained complex was eluted with methylene dichloride. Removal of the solvent and fractional recrystallisation of the residue from benzene–hexane (1 : 1) afforded in the final fractions $\Delta(+)[Rh(pd)_3]$ with a c.d. spectrum enantiomeric to that illustrated for the $\Lambda(-)$ isomer (Figure 2). After the (−)-α-pinene extractions the diethyl (+)-tartrate layer was diluted with an equal volume of water and the mixture was extracted with toluene. Removal of the toluene and fractional recrystallisation of the residue from benzene–hexane (1 : 1) gave initially *racemic* crystals and a progressive rise in the c.d. of the mother liquor to the limiting spectrum recorded (Figure 2) when crystals of $\Lambda(-)[Rh(pd)_3]$ with the same c.d. spectrum were produced.

Other $[M(pd)_3]$ *Complexes*.—Similar differential-partitioning studies afforded, from the diethyl (+)-tartrate layer, $\Lambda(+)[Cr(pd)_3]$, $\Lambda(-)[Co(pd)_3]$, and the partly resolved $[Ir(pd)_3]$ with the c.d. spectrum reported (Figure 4).

Spectra.—Absorption spectra were recorded with a Cary 17 spectrophotometer and c.d. spectra with a Jasco J 40 instrument.

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[14] K. L. Stevenson, *J. Amer. Chem. Soc.*, 1972, **94**, 6652.

[15] B. Norden, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 387.

[16] R. Grobelny, B. Jezowska-Trzebiatowska, and W. Wojciechowski, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2715.

[17] F. P. Dwyer and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1953, **75**, 984.