Fluorinated Alkoxides. Part IX. The Resolution of Perfluoro(2,3-diphenylbutane-2,3-diol) and its use in preparing Optically Active Complexes of Ni^{2+} and Cu^{2+} [1]

W. Stafford Cripps and Christopher J. Willis

Department of Chemistry, University of Western Ontario, London, Ontario N6A 3K7

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Perfluoro(2,3-diphenylbutane-2,3-diol), $CF_3(C_6F_5)C(OH)C(OH)(C_6F_5)CF_3$, prepared by the reductive dimerization of $C_6F_5COCF_3$, has been separated into *meso*- and DL-isomers and the latter resolved via its cinchonidine salt into optical enantiomers. The doubly ionized diol, $PDBD^{2-}$, acts as a dinegative, chelating, ligand, and neutral complexes of the form (PDBD)-ML_2 may be isolated, where L is a neutral nitrogen- or phosphorus-containing ligand and $M = Ni^{2+}$ or Cu^{2+}. Use of the resolved diol enables optically active metal complexes to be prepared, and from their o.r.d./c.d. spectra we assign an absolute configuration to the diol. The partially fluorinated diols $CF_3(C_6H_5)C(OH)C(OH)(C_6H_5)CF_3$ and $CH_3(C_6F_5)C(OH)$-$C(OH)(C_6F_5)CH_3$ have also been prepared from the appropriate ketones. The former, which appears to be exclusively the *meso*-isomer, has more limited chelating ability than the fully fluorinated analog, while the latter shows no ligand properties; these differences are ascribed to the reduced acidity resulting from the lower degree of fluorination.

Nuclear magnetic resonance studies suggest hindered rotation of the C_6F_5 groups through steric interaction with CF_3 groups in perfluoro(2,3-diphenylbutane-2,3-diol); an alternate explanation involving hydrogen bonding from the hydroxylic proton to aromatic fluorine atoms is considered less likely.

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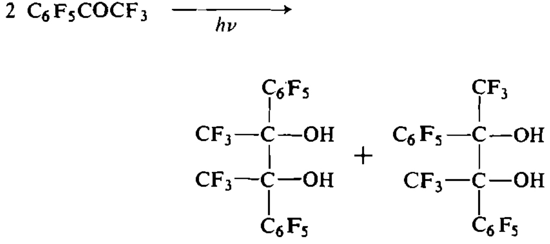
On a préparé les perfluoro (diphényl-2,3 butanediol-2,3), $CF_3(C_6F_5)C(OH)C(OH)(C_6F_5)CF_3$, par dimérisation réductrice de $C_6F_5COCF_3$; on a séparé les isomères *meso* et DL et ce dernier a été résolu en antipodes optiques par l'intermédiaire de son sel de cinchonidine. Le diol doublement ionisé, $PDBD^{2-}$ agit comme ligand dinégatif chélatant et on peut isoler des complexes neutres de la forme (PDBD)ML_2 dans lesquels L est un ligand neutre contenant de l'azote ou du phosphore et $M = Ni^{2+}$ ou Cu^{2+}. Si l'on utilise du diol résolu en antipodes optiques, on peut préparer des complexes métalliques optiquement actifs et en se basant sur les spectres o.r.d./c.d. on peut attribuer une configuration absolue au diol. On a aussi préparé, à partir des cétones appropriées, les diols partiellement fluorés $CF_3(C_6H_5)C(OH)C(OH)(C_6H_5)CF_3$ et $CH_3(C_6F_5)$-$C(OH)C(OH)(C_6F_5)CH_3$. Le premier, qui semble être exclusivement l'isomère *méso*, a des propriétés chélatantes plus limitées que son analogue complètement fluoré alors que le dernier ne présente aucune propriété comme ligand; on attribue ces différences à une acidité réduite résultant du degré plus bas de fluoration.

Des études par résonance magnétique nucléaire suggèrent une rotation empêchée des groupes C_6F_5 due à des interactions stériques du groupe CF_3 dans le perfluoro diphényl-2,3 butanediol-2,3; on considère comme moins probable l'explication impliquant des liens hydrogène entre les protons hydroxyliques et les atomes de fluor du noyau aromatique.

[Traduit par le journal]

We have previously (1) reported the preparation of perfluoro(2,3-diphenylbutane-2,3-diol) (**1**) by the reductive dimerization of octafluoroacetophenone, and noted that the product appeared to contain more than one isomer. We now confirm this by the separation of the *meso*-isomer (**1***a*) and the DL-isomer (**1***b*), followed by


1*a* **1***b*

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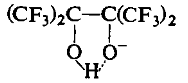
the resolution of the latter into optical enantiomers. The initial product of dimerization was separated by fractional crystallization into approximately equal amounts of two compounds; one melting at 119–120° and the other at 129–130°. Both had elementary compositions and molecular weights corresponding to the formula $C_{16}H_2F_{16}O_2$. Their infrared spectra, while not identical, were very similar, both showing strong absorption near 3630 cm^{-1} characteristic of free O—H stretching modes.

We therefore concluded that these two compounds were the *meso-* and DL-forms of the diol. In order to decide which fraction was which isomer, we studied their interaction with a variety of optically active organic bases. The usual method of separating optical enantiomers of diols is to make an ester, *e.g.*, the phthallate, to provide an acidic function from which salts may be prepared. In the present work, this was not necessary, because the fluorination of the molecule increases the acidity of the hydroxyl group to the point where a salt may be made directly, even though the aromatic diol (pK_a = 8.85 (1)) is a considerably weaker acid than perfluoropinacol (pK_a = 5.95 (2)).

Of various bases tried, L-strychnine gave a crystalline derivative with the lower m.p. diol isomer, but fractional crystallization, followed by regeneration of the diol on acidification, gave no indication of the separation of enantiomers. This suggests that this is the *meso*-isomer (**1***a*). With the higher m.p. isomer, strychnine gave no solid derivative, but L-cinchonidine readily formed crystals which were shown by analysis to be a 1 : 1 adduct. This dissociated in methanol to give a conducting solution and the infrared spectrum of the solid showed no O—H absorption peaks. We therefore formulate it as an ionic salt, although the possibility of solid-state interactions through hydrogen-bonding cannot be eliminated.

The cinchonidine salt was fractionally crystallized to constant optical rotation, and acidification of the less soluble fraction yielded resolved (+)-diol, m.p. 89–90°, $[\alpha]^{20}_{589}$ = 96.6°. This separation shows unambiguously that the higher m.p. fraction from the dimerization product is the DL-isomer (**1***b*), and the fact that it has a m.p. 40° higher than that of the resolved enantiomer characterizes it as a racemic compound, rather than a mixture.

The pK_a values, measured in aqueous ethanol, are 8.7 for the *meso*-isomer and 9.1 for the DL-isomer. This difference, although slight, is surprising, since the acidic nature of fluorinated diols of this type was originally ascribed to intramolecular hydrogen-bonding in the anion (2):



$$\begin{array}{c}(CF_3)_2C-C(CF_3)_2\\ \mid \qquad \mid \\ O \cdots H \cdots O^-\end{array}$$

Although the need for an explanation of this "enhanced" acidity of perfluoropinacol was removed by the subsequent revision of the accepted value of the pK_a of perfluoro(*t*-butanol) (3), there has been no reason to doubt the existence of intramolecular hydrogen-bonding, on which basis one would expect a greater acidity for **1***b*, the DL-isomer, since the steric interaction between the bulky pentafluorophenyl groups required to bring the two oxygen atoms into a *syn*-conformation would appear to be less than that in the *meso*-isomer, **1***a*. The greater acidity found in the latter would suggest that hydrogen-bonding, if present, is intermolecular to solvent molecules, rather than intramolecular.

Metal Complexes

The overall objective of this work is to study the formation of complexes between highly fluorinated molecules and metal ions, as we have previously done for perfluoropinacol (4, 5). We have therefore studied the reaction of **1** with Ni^{2+} and Cu^{2+}, but we find that the fluorinated aromatic diol does not form complexes as readily as does H_2PFP. Thus, we were unable to isolate anionic complexes of either **1***a* or **1***b* of the type $[M(PDBD)_2]^{2-}$ [where $PDBD^{2-}$ = dianion of perfluoro(2,3-diphenylbutane-2,3-diol)] under conditions where perfluoropinacol readily forms $[M(PFP)_2]^{2-}$ (4), and this can be ascribed in part to the reduced acidity of the aromatic diol. Using resolved (+)-diol in solutions containing Ni^{2+} in various concentration ratios, we varied the p*H* while monitoring the optical rotary dispersion (o.r.d.) of the solutions, but in no case was any evidence seen of interaction between the ligand and the metal ion, up to the point where decomposition of the ligand began.

However, the use of a neutral co-ligand enabled us to isolate a number of stable complexes of $PDBD^{2-}$ with Ni^{2+} and Cu^{2+}, similar to those formed by perfluoropinacol (6). Nickel complexes isolated were $[(C_2H_5)_3P]_2Ni(PDBD)$, $[(CH_3)_2PC_6H_5]_2Ni(PDBD)$, (TMED)Ni(PDBD) (TMED = tetramethylethylenediamine), and

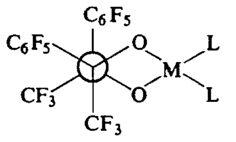
TABLE 1. Visible, optical rotary dispersion, and circular dichroism spectra (in methanol)

Compound	Visible		Optical rotary dispersion		Circular dichroism	
	λ_{max}	ε	λ_{max}	[α]	λ_{max}	Δε
(TMED)Ni[(+)-PDBD]	510	82	438	−598	474	+1.07
			504	+144	527	−0.42
			554	−407	576	+0.82
			618	+121		
(TMED)Ni[(−)-PDBD]*	510	82	439	+546	474	−0.91
			504	−134	527	+0.28
			554	+382	576	−0.72
			618	−114		
$[(C_2H_5)_3P]_2Ni[(+)\text{-PDBD}]$	470	205	387	−1200	421	+2.31
			453	+550	478	−1.00
			505	−340	531	+0.14
$[(CH_3)_2PC_6H_5]_2Ni[(+)\text{-PDBD}]$	460	286	380	−1110	412	+2.52
			446	+598	472	−0.98
			502	−272	520	+0.22
(TMED)Cu[(+)-PDBD]	561	77	544	−202	503	−0.22
			616	+51	577	+0.24
					654	−0.12

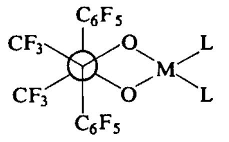
*Comparison with the data for the (+)-diol complex indicates about 93% optical purity.

(TEED)Ni(PDBD) (TEED = tetraethylethylenediamine). These four complexes were diamagnetic and had visible absorption spectra similar to those of the analogous PFP^{2-} derivatives (6); they were therefore assumed to have a square-planar coordination of ligands around nickel. Bulkier phosphine ligands, such as triphenylphosphine, did not yield stable complexes. Copper (II) gave the complex (TMED)Cu(PDBD).

Several competitive reactions were examined in which more than one potential ligand was present in solution with the metal ion. Clearcut selective chelation occurred, and the order of complexing ability was found to be PFP^{2-} > DL-$PDBD^{2-}$ > *meso*-$PDBD^{2-}$. The preferential coordination of PFP^{2-} was expected, in view of the known properties of this compound, while the superiority of the DL-isomer of the aromatic diol, although contrary to the slight difference in acidity between the two isomers, is entirely consistent with steric requirements. Consideration of Newman projections along the C—C axes of the aromatic diols shows the relative steric interactions in the coordinated ligands:



2a
coordinated *meso*-diol



2b
coordinated DL-diol

Whereas the coordination of the *meso*-diol (**2**a) requires an axial-equatorial conformation of the C_6F_5 groups, the DL-diol may adopt a conformation in which they are *trans*-diaxial (**2**b), with reduced steric interaction.

Dissymmetric Complexes

The availability of resolved enantiomers of the aromatic diol enabled us to prepare optically active complexes of Ni^{2+} and Cu^{2+}. It is apparent from structure **2**b that the preferred conformation of the C_6F_5 groups will impose chirality on the chelate ring, and it is accepted (7) that chirality of this type is dominant over the vicinal effect of asymmetric centers in determining the optical rotatory power of a metal complex. Using the (+)-diol, dissymmetric complexes of the two metals were prepared, and essential features of the o.r.d. and c.d. (circular dichroism) spectra are shown in Table 1, while representative spectra are illustrated in Figs. 1 and 2.

These complexes represent an unusual example of a series of stable, isolable, compounds in which a chelate ring derived from a 2,3-diol contains two adjacent asymmetric carbon atoms. Although many other examples of interactions between metal ions and optically active diols are known, they mainly occur in solution without yielding solid products of established stoichiometry. It was of interest, therefore, to establish

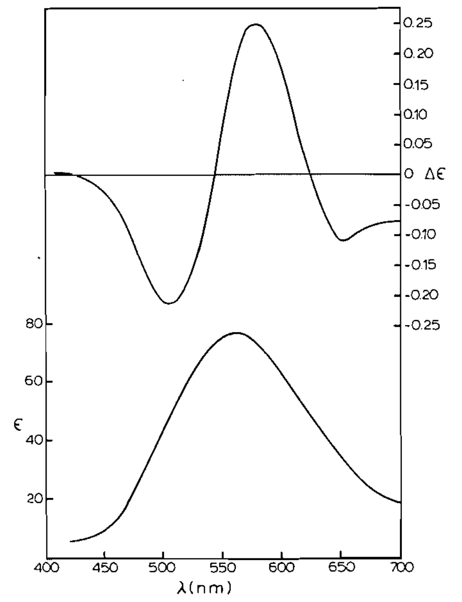


FIG. 1. Circular dichroism and visible spectra (methanol solution) of (TMED)Cu[(+)-PDBD].

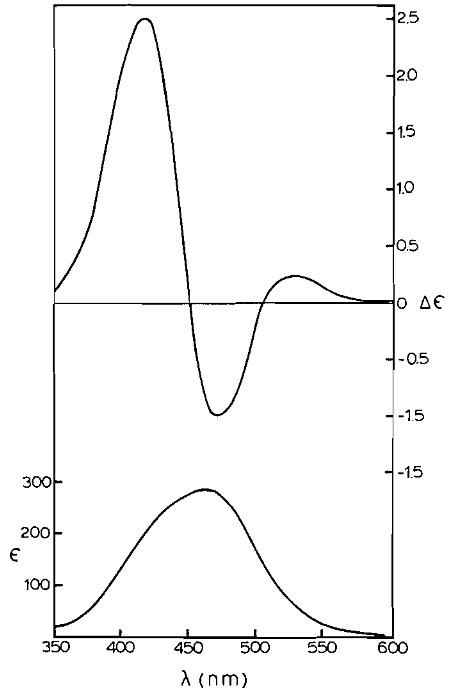
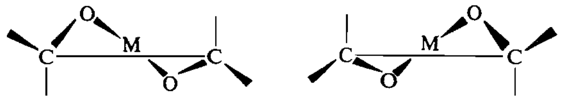


FIG. 2. Circular dichroism and visible spectra (methanol solution) of [$(CH_3)_2PC_6H_5]_2Ni[(+)$-PDBD].

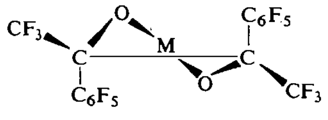
the absolute configuration of the chelate ring (and hence of the ligand itself) in the present complexes, and we have attempted to do this by a comparison of the o.r.d. spectra of the complexes with those of analogous systems of known absolute configuration.

It is convenient to refer to the conformations of the chelate rings as δ and λ



δ-conformation λ-conformation

Reeves (8) investigated the configuration of a number of optically active ligands by their interaction with Cu^{2+} in ammoniacal solution ("cupra A"), where a 1:1 complex is formed, but not isolable. Using a conformationally rigid diol of known structure, subsequent workers (9) found that these solutions show a weak c.d. band at 580–600 nm and a more intense band of opposite sign near 280 nm, and established that a positive value of the former peak is associated with the δ-conformation of the chelate ring. The c.d. spectrum of our (+)-diol in cupra A shows a positive peak at 610 nm and a more intense negative peak below 300 nm, the reverse being shown by the (−)-diol. We therefore assign the δ-conformation to the coordinated (+)-isomer of $PDBD^{2-}$, *i.e.*



3

Additional evidence comes from studies on the conformations of a number of optically active Schiff base complexes of Ni^{2+} and Cu^{2+}. Downing and Urbach (10) found that a δ conformation in the ring of a copper complex led to a c.d. spectrum with a negative peak at 630–700 nm, a positive peak at 550–590 nm, and a further negative peak at 475–500 nm. The c.d. spectrum of (TMED)Cu[(+)-PDBD] (Table 1) is entirely consistent with this pattern, conforming our assignment of the δ-conformation to its chelated diol ring.

With the similar complexes of Ni^{2+}, several workers (11, 12) have drawn attention to the difficulty of assigning absolute configurations, so we do not feel justified in using data from the c.d. spectra of the Ni^{2+} complexes of $PDBD^{2-}$ to support our arguments.

The extension from the assignment of a ring conformation to the assignment of an absolute configuration of each diol isomer depends on our assumption that the steric interaction between two vicinal C_6F_5 groups is greater than that between two CF_3 groups, so that the (+)-diol has the configuration illustrated in **3**. Since the difference in size between the two substituent groups is quite considerable, we consider that this assumption may be accepted with some confidence.

Partially Fluorinated Diols

In an attempt to extend the range of diols of the type RR′C(OH)C(OH)RR′ which might form stable complexes with metal ions, we prepared the partially fluorinated compounds where $R = C_6F_5$, $R' = CH_3$ (**4**), and $R = C_6H_5$, $R' = CF_3$ (**5**) by reductive dimerization of the ketones $C_6F_5COCH_3$ and $C_6H_5COCF_3$ respectively.

Compound **5** had been prepared previously by Mosher and Heindel (13) who reported only one isomer, without identifying it as the *meso-* or DL-form. We also found evidence for only one isomer, which we attempted to separate into optical enantiomers as we had the fully fluorinated diol. Although strychnine gave a solid adduct with **5**, fractional crystallization showed no sign of resolution, from which we assumed it was the *meso*-form. Consistent with this, the singlet observed in the ^{19}F n.m.r. spectrum was not split when the compound was dissolved in an optically active solvent. After this work was completed, an alternate preparation of diol **5** was published (14) quoting a crystal structure on a derivative in which it was shown to have the *meso*-configuration.

Diol **5** was much less acidic than its fully fluorinated analog, having a pK_a of about 11.4. Nevertheless, it did form stable metal complexes such as $(TMED)\overline{NiOC(CF_3)(C_6H_5)C(CF_3)(C_6H_5)O}$. In competitive reactions, the fully fluorinated *meso*-diol (**1***a*) coordinated in preference to **5**, indicating that the effect of the greater acidity of the former predominated over the smaller degree of steric hindrance between the unfluorinated phenyl rings in the latter. However, diol **5** did form a complex with Ni^{2+} in the absence of any co-ligand when a solution of the diol and Ni^{2+} was made highly alkaline ($[OH^-] > 5\ M$). The resulting clear blue solution had a visible spectrum very similar to that of $Ni(PFP)_2^{2-}$ in noncoordinating solvent (6), and presumably contained a square-planar anionic complex of Ni^{2+} with diol **5**, although no solid compound could be isolated. The formation of a nickel complex under these conditions with diol **5**, but not with the other diols included in this study, may be attributed to the ligand's stability under highly basic conditions, where the diols containing pentafluorophenyl groups decomposed.

Diol **4** was produced in poor yield by the photolytic dimerization of $C_6F_5COCH_3$. As would be expected, it was less acidic than any of the other diols included in this study. It did not give an end-point on titration, nor could any evidence be found for the existence of isolable metal complexes. In the absence of salt formation with organic bases, no attempt was made to identify **4** as a *meso-* or DL-isomer.

The order of coordinating ability of the fluorinated diols covered in this study is therefore $[(CF_3)_2C(OH)—]_2$ > DL-$[(C_6F_5)(CF_3)C(OH)—]_2$ > *meso*-$[(C_6F_5)(CF_3)C(OH)—]_2$ > *meso*-$[(C_6H_5)(CF_3)C(OH)—]_2$ > $[(C_6F_5)(CH_3)C(OH)—]_2$. With the exception of the slight difference between isomers **1***a* and **1***b*, this is the order of decreasing acidity of the diols.

^{19}F Nuclear Magnetic Resonance Spectra

We have previously (1) reported the ^{19}F n.m.r. spectra of a variety of fluorinated aromatic alcohols. The compound $C_6F_5C(CF_3)_2OH$ (**6**), for example, shows one peak associated with the CF_3 group and three others, with intensities in a 2:2:1 ratio, corresponding to the *ortho-*, *meta-*, and *para*-fluorine atoms of the aromatic ring (Table 2). By contrast, the spectra of the fully fluorinated aromatic diols studied in the present work contained the expected peak from the CF_3 groups and five equal-intensity peaks from the fluorine atoms of the aromatic rings, indicating that all five aromatic fluorine atoms were nonequivalent.

The following numbering scheme will be used to discuss these spectra; this diagram is not intended to show the conformation of the molecule.

The peak corresponding to each fluorine atom was split by fluorine–fluorine coupling and the

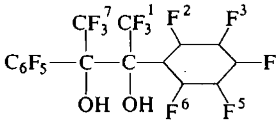
TABLE 2. ^{19}F nuclear magnetic resonance chemical shifts*

		meso-diol (1*a*)	DL-diol (1*b*)	$[(CH_3)_2PC_6H_5]_2Ni[(+)\text{-PDBD}]$	$[C_6F_5C(CH_3)(OH)—]_2$	$C_6F_5C(CF_3)_2OH$ (6)
CF_3	F^1,F^7	71.6	73.3	67.4	—	76.2
ortho-F	F^2	129.3	129.9	132.6	138.0	135.3
	F^6	140.5	143.2	133.4		
para-F	F^4	149.6	148.7	157.4	154.7	149.5
meta-F	F^5	160.3	159.3	164.2	162.3	160.6
	F^3	160.6	160.2	166.9		

*In p.p.m. from $CFCl_3$.

TABLE 3. Analytical data

Compound	Formula	Carbon		Hydrogen		Fluorine	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
meso-diol (1*a*)	$C_{16}H_2F_{16}O_2$	36.3	36.4	0.4	0.3	57.3	57.6
DL-diol (1*b*)	$C_{16}H_2F_{16}O_2$	36.3	36.0	0.4	0.3	57.3	57.1
DL-diol, cinchonidine salt	$C_{35}H_{24}F_{16}N_2O_3$	51.0	51.8	2.9	2.9	36.9	37.8
(TMED)Ni[(+)-PDBD]	$C_{22}H_{16}F_{16}N_2NiO_2$	41.2	41.2	3.2	3.3	40.0	40.1
(TEED)Ni[(+)-PDBD]	$C_{26}H_{24}F_{16}N_2NiO_2$	40.9	40.7	3.7	3.8	36.9	36.7
$[(C_2H_5)_3P]_2Ni[(+)\text{-PDBD}]$	$C_{28}H_{30}F_{16}NiO_2P_2$	37.6	37.4	2.3	2.5	43.2	43.5
$[(CH_3)_2PC_6H_5]_2Ni[(+)\text{-PDBD}]$	$C_{32}H_{22}F_{16}NiO_2P_2$	44.5	44.9	2.6	2.8	35.2	34.2
(TMED)Cu[(+)-PDBD]	$C_{22}H_{16}CuF_{16}N_2O_2$	37.2	36.7	2.3	2.2	42.8	42.7
$[CH_3C(C_6F_5)OH—]_2$	$C_{16}H_8F_{10}O_2$	45.5	45.5	1.9	2.2	45.0	44.9
$(TMED)Ni[CF_3(C_6H_5)CO—]_2$	$C_{22}H_{26}F_6N_2NiO_2$	50.5	50.4	5.0	4.9	21.8	22.0



various peaks were identified by examination of the coupling pattern and use of standard decoupling techniques. The following ranges of coupling constants were found: $J(F^2\text{–}F^3) = J(F^3\text{–}F^4) = J(F^4\text{–}F^5) = J(F^5\text{–}F^6) = 21\text{–}23$ Hz; $J(F^2\text{–}F^4) = J(F^2\text{–}F^5) = J(F^3\text{–}F^6) = J(F^4\text{–}F^6) = 6\text{–}7$ Hz; $J(F^3\text{–}F^5) = 1$ Hz; $J(F^2\text{–}F^6)$ not resolved.

Coupling was also observed from the *ortho*-fluorine atoms to one of the CF_3 groups (F^1 or F^7), whose absorption peaks consisted of a complex multiplet. Irradiation of F^2 caused this to collapse to a broad singlet, while irradiation of F^6 produced a doublet ($J = 24$ Hz), indicating preferential coupling to each CF_3 group from one of the *ortho*-fluorine atoms.

The nonequivalence of the aromatic fluorine atoms indicates restricted rotation of the phenyl ring. Previous workers (15) have suggested the possibility of hydrogen-bonding from the hydroxyl group of an alcohol to an adjacent fluorine atom, but we may eliminate that in this case because the same pattern is observed in the coordinated ligand, where no hydroxyl group is present. We suggest, therefore, that the restricted rotation results from steric interaction between the *ortho*-fluorine atoms of the ring and those of one of the CF_3 groups (assuming that the diol adopts a conformation with the two phenyl rings too far apart to interact). Examination of molecular models shows that the greater degree of steric interaction is between the C_6F_5 group and the CF_3 in the vicinal position to it, rather than the *gem*-CF_3 group, and this is consistent with our observation that no such interaction is observed in **6** or in similar monohydric fluorinated alcohols. The coupling from F^2 to the CF_3 group may therefore be through-space coupling to F^7, rather than to F^1.

Additional evidence favoring our suggestion that steric interaction between C_6F_5 and CF_3 groups is dominant comes from the ^{19}F n.m.r. spectrum of the partially fluorinated diol $[C_6F_5C(CH_3)(OH)\text{—}]_2$. This shows a typical 2:2:1 set of peaks for *ortho*-, *meta*-, and *para*-fluorine atoms, indicating that the presence of the smaller CH_3 group allows free rotation of the phenyl ring.

Infrared Spectra

The infrared (i.r.) spectra of the diols **1***a* and **1***b* were very similar. The O—H stretching frequency appeared as a sharp absorption peak at 3640 cm^{-1} (**1***a*) and 3627 cm^{-1} (**1***b*) (mulls), showing the absence of hydrogen-bonding. A similar peak at 3630 ± 5 cm^{-1} has been noted previously (16) in a series of unfluorinated 1,2-diols.

Peaks associated with ring skeletal modes were seen at 1651 and 1534 cm^{-1} (**1***a*) and 1654 and 1535 cm^{-1} (**1***b*), and strong C—F stretching absorptions were present in the region 1100–1300 cm^{-1} in both compounds. The major difference in the i.r. spectra between the two isomers occurred near 1000 cm^{-1}. Whereas the *meso*-diol, **1***a*, had two sharp peaks at 995 and 945 cm^{-1}, the DL-diol had a broad, poorly resolved pair of peaks at 1010 and 990 cm^{-1}. The overall complexity of the spectra precluded any definite assignment of these peaks, but their presence provided a useful guide to the purity of the isomers.

The absence of any peaks corresponding to intramolecularly hydrogen-bonded O—H is in accord with previous work (17), which demonstrated that the fluorination of this type of molecule, while having little effect on the frequency of the O—H absorption, reduced the tendency towards hydrogen bonding.

Metal complexes of the diol isomers showed very similar i.r. spectra (the O—H peaks being, of course, absent) with the same difference in the appearance of the spectrum around 1000 cm^{-1} between complexes of **1***a* and **1***b*.

Experimental

General

Infrared spectra were recorded on a Beckman IR-10 instrument; u.v.–visible spectra on Beckman DK or Cary 14 instruments; o.r.d./c.d. spectra on a Durrum–Jasco ORD-UV-5 spectropolarimeter. Microanalyses (Table 3) were performed by Alfred Bernhardt Laboratories, West Germany.

Perfluoro(2,3-diphenylbutane-2,3-diol) (*1*).

The synthesis of the diol, as a mixture of isomers, has been described previously (1). The crude product was separated by fractional crystallization from light petroleum (b.p. 30–60°) into approximately equal amounts of two fractions; the less soluble *meso*-diol (**1***a*), m.p. 119–120°, and the more soluble DL-diol (**1***b*), m.p. 130–131°. Molecular weights (osmometric in benzene) were 535 and 543 respectively (calcd., 530).

Resolution of the DL*-diol*

Diol **1***b* (16 g, 30 mmol) and L-cinchonidine (9.0 g, 30 mmol) in a mixture of chloroform (150 ml) and hexane (20 ml) deposited a crystalline solid over a period of 3 days at 25°. Analysis showed this to be a 1:1 adduct. It had an equivalent conductance of 40 $\mathrm{ohm}^{-1}\ \mathrm{cm}^2$ in methanol and a molecular weight of 405 (calcd. for complete dissociation: 412) extrapolated to infinite dilution in methanol. The diol was regenerated by acidification with aqueous hydrochloric acid and extraction with dichloromethane; it had $[\alpha]^{20}_{589} = +62°$. The process was repeated to constant rotation to yield resolved (+)-diol, $[\alpha]^{20}_{589} = +96.6°$, m.p. 89–90°. Residues from the recrystallization gave an oil which yielded diol of specific rotation −42°, indicating about 45% concentration of the (−)-diol. This was used for the preparation of the metal complexes, described below, whose recrystallization provided a further degree of purification to give substantially pure (−)-diol derivatives.

Preparation of Nickel Complexes of PDBD^{2-}

(+)-Diol (0.30 g, 0.57 mmol) and nickel nitrate hexahydrate (0.17 g, 0.57 mmol) were dissolved in ethanol (15 ml) and TMED (0.15 g, 1.3 mmol) added slowly. Ethanolic potassium hydroxide was added dropwise to p*H* 8 and the resulting red solution filtered and evaporated to dryness. Recrystallization from ethanol gave (TMED)Ni[(+)-PDBD], red, m.p. 148° (decomp). The same procedure gave (TEED)Ni[(+)-PDBD], red.

The same procedure was used with partially resolved (−)-diol and the complex recrystallized from dichloromethane/hexane to constant rotation, yielding essentially pure (TMED)Ni[(−)-PDBD].

For both the DL-diol and the *meso*-diol, the following procedure was used. Equimolar amounts of diol and nickel nitrate were dissolved in aqueous methanol and a slight excess of TMED added. The solution was brought to p*H* 8 with methanolic potassium hydroxide and the resulting red precipitate removed by filtration, extracted with dichloromethane, and recrystallized from dichloromethane/hexane. Products were red, with m.p. 138–139° (DL-diol) and 130–131° (*meso*-diol).

The complex $[(C_2H_5)_3P]_2Ni[(+)\text{-PDBD}]$ was prepared by the slow addition of triethylphosphine (0.095 g, 0.80 mmol) under nitrogen atmosphere to a solution of (+)-diol (0.20 g, 0.38 mmol) and nickel nitrate hexahydrate (0.11 g, 0.38 mmol) in methanol, followed by the addition of methanolic potassium hydroxide to p*H* 8.5. The orange solution was evaporated to dryness and the residue extracted with dichloromethane and recrystallized from dichloromethane/hexane to yield $[(C_2H_5)_3P]_2Ni[(+)\text{-PDBD}]$, orange, m.p. 137–138°. The similar derivative of the *meso*-diol was prepared in the same way; orange, m.p. 124–125°.

The dimethylphenylphosphine complex was prepared by dissolving (+)-diol (0.30 g, 0.57 mmol) and nickel nitrate hexahydrate (0.17 g, 0.57 mmol) in ethanol under nitrogen, and slowly adding dimethylphenylphosphine (0.20 g, 1.5 mmol) followed by ethanolic potassium hydroxide to p*H* 8. The resulting solution was filtered and evaporated to dryness and the product recrystallized from 95% ethanol to give $[(CH_3)_2PC_6H_5]_2Ni[(+)\text{-PDBD}]$, orange, m.p. 143°. The similar derivative of the *meso*-diol was prepared by the same route and recrystallized from dichloromethane/hexane; orange, m.p. 116°.

Preparation of (TMED)Cu[(+)-PDBD]

Copper sulfate pentahydrate (0.15 g, 0.60 mmol) and (+)-diol (0.30 g, 0.57 mmol) were dissolved in aqueous ethanol and TMED (0.20 g, 1.7 mmol) added, followed by aqueous potassium hydroxide to p*H* 8. The desired compound precipitated on concentrating the solution; it was recrystallized from ethanol to give (TMED)Cu[(+)-PDBD], purple, m.p. 88–90° (decomp).

2,3-Bis(pentafluorophenyl)butane-2,3-diol

Methyl pentafluorophenyl ketone was prepared by the Grignard reaction of acetyl chloride with pentafluorophenyl magnesium bromide (18). A solution of the ketone (5.1 g) in 2-propanol (25 ml) in a quartz tube was degassed and irradiated with ultraviolet light for 7 days. Removal of volatile material left a solid product which was recrystallized from dichloromethane/hexane to give 2,3-bis(pentafluorophenyl)butane-2,3-diol (2.1 g), m.p. 173–174°. The ^{19}F n.m.r. spectrum ($CHCl_3$ solution) showed three multiple peaks in a 2:1:2 ratio at 138.0, 154.7, and 162.3 p.p.m. from $CFCl_3$. Attempts to form nickel complexes of this diol, using methods successful with other diols, showed no evidence of interaction.

1,1,1,4,4,4-Hexafluoro-2,3-diphenylbutane-2,3-diol

Trifluoroacetophenone was prepared by the Grignard reaction of trifluoroacetic acid with phenylmagnesium bromide (19). The ketone (10 g) was dissolved in 2-propanol (22 ml) acidified with hydrochloric acid (0.2 ml) in a quartz tube, the mixture outgassed and irradiated with ultraviolet light for 8 days. Removal of solvent left a solid residue which was recrystallized from benzene/hexane to give 1,1,1,4,4,4-hexafluoro-2,3-diphenylbutane-2,3-diol (7.0 g), m.p. 154–155° (lit. m.p. (13), 155–156°). Fractional crystallization from a variety of solvents gave no evidence of the presence of more than one isomer. The ^{19}F n.m.r. spectrum showed a single peak both in chloroform (at 70.2 p.p.m. from TMS) and in (+)-α-phenethylamine (at 67.8 p.p.m.). Titration in a 1:1 ethanol/water solution gave a pK_a of about 11.4.

When equimolar quantities of this diol and L-strychnine were dissolved in a chloroform/hexane mixture, a crystalline precipitate formed. Its infrared spectrum showed the presence of both diol and strychnine, but no O—H stretching band. Fractional crystallization, followed by regeneration of the free diol by acidification and ether extraction, showed no evidence for the separation of an optically active form of the diol.

The complex $(TMED)Ni[CF_3(C_6H_5)CO\text{—}]_2$ was prepared similarly to (TMED)Ni[(+)-PDBD] and recrystallized from ethanol to give a red complex, m.p. 196–200° (decomp.).

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