of II in benzonitrile: $\Delta H^{\ddagger} = 10.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -42$ eu. Large negative activation entropies are consistent with highly ordered transition states.

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Fully Fluorinated Alkoxides. III. Perfluoropinacol, a Useful Bidentate Ligand

Sir:

The perfluoropinacol molecule, $(CF_3)_2C(OH)C(OH)(CF_3)_2$, is known to form the basis of a number of five-membered heterocycles of type $\overline{OC(CF_3)_2C(CF_3)_2OM}$, where the element M is Si,[1] Ge, Sn, B, or S.[2]

Previously reported compounds of this type have been made by the reaction of the appropriate dihalides with the ionic alkoxides of perfluoropinacol in anhydrous donor solvent, such as tetrahydrofuran. However, the stability of perfluoropinacol in water, combined with its acidic nature (pK = 5.95[3]), suggests that it should be possible to prepare complexes in which the pinacol ion is acting as a bidentate ligand to a metal ion.

This we have found to be the case, and we now report that stable complexes with a variety of metals may readily be made in aqueous solution. Complex ions of the type $[M(PFP)_3]^{3-}$, where PFP represents the perfluoropinacolato ion, $[OC(CF_3)_2C(CF_3)_2O]^{2-}$, have been made where M = Fe^{3+} or Al^{3+}, while complexes of the type $[M(PFP)_2]^{2-}$ are formed where M = Mn^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}.

The most general method of preparation was to add the aqueous metal ion (as the metal sulfate) to the calculated amount of perfluoropinacol in a 1:1 methanol/water mixture (the pinacol having only limited solubility in water). No reaction was observed, but the introduction of aqueous potassium hydroxide produced immediate color changes in those solutions which were colored, and, by addition of base to a pH of about 7.5, the complex ions were formed according to the equation

$$nH_2PFP + M^{n+} + 2nOH^- \longrightarrow [M(PFP)_n]^{n-} + 2nH_2O$$

where n = 2 or 3.

In some cases, *e.g.*, iron and manganese, it was possible to prepare the complex ions by dissolving the freshly precipitated metal hydroxide in partially neutralized pinacol

$$3H_2PFP + Fe(OH)_3 + 3OH^- \longrightarrow [Fe(PFP)_3]^{3-} + 6H_2O$$

but this route was not suitable for all the metals studied.

Solid products were obtained by filtration of the above solutions to remove any metal hydroxides, followed by crystallization by evaporation at 25° of aqueous or methanolic solutions and drying at 25° *in vacuo*. The following compounds were characterized.

Potassium tris(perfluoropinacolato)ferrate(III) deposited as very pale yellow crystals from water. *Anal.* Calcd for $C_{18}F_{36}O_6FeK_3$: C, 18.49; F, 58.50. Found: C, 18.36; F, 58.38; magnetic moment, 6.0 BM.

Potassium tris(perfluoropinacolato)aluminate(III) deposited as colorless crystals from water. *Anal.* Calcd for $C_{18}F_{36}O_6AlK_3$: C, 18.95; F, 59.97. Found: C, 19.03; F, 59.54.

Potassium bis(perfluoropinacolato)manganate(II) formed brown crystals from water, dehydrating *in vacuo* to a pale yellow solid. *Anal.* Calcd for $C_{12}F_{24}O_4MnK_2$: C, 18.08; F, 57.20; Mn, 6.89. Found: C, 18.12; F, 57.02; Mn, 6.85; magnetic moment, 5.2 BM.

Potassium bis(perfluoropinacolato)nickelate(II) formed a yellow aqueous solution giving purple crystals of a dihydrate, dehydrating *in vacuo* to deep blue-purple anhydrous compound (diamagnetic). *Anal.* Calcd for $C_{12}F_{24}O_4NiK_2$: C, 17.99; F, 56.93; Ni, 7.33. Found: C, 17.56; F, 56.71; Ni, 7.28.

Potassium bis(perfluoropinacolato)cuprate(II) formed a deep blue aqueous solution giving deep blue crystals of stable dihydrate. *Anal.* Calcd for $C_{12}H_4F_{24}O_6CuK_2$: C, 17.12; H, 0.48; F, 54.16; Cu, 7.55. Found: C, 16.92; H, 0.64; F, 54.10; Cu, 7.61; magnetic moment, 2.0 BM.

Potassium bis(perfluoropinacolato)zincate(II) deposited as colorless crystals from water. *Anal.* Calcd for $C_{12}F_{24}O_4ZnK_2$: C, 17.84; F, 56.46. Found: C, 17.88; F, 56.49.

A brief investigation was made of some complexes containing other cations. When perfluoropinacol was added to an aqueous stirred suspension of iron(III) hydroxide and silver oxide, reaction occurred to give silver tris(perfluoropinacolato)ferrate(III), as pale yellow crystals from water, rapidly darkening on exposure to light. *Anal.* Calcd for $C_{18}F_{36}O_6FeAg_3$: C, 15.71; F, 49.72. Found: C, 15.65; F, 49.60.

Metathetical reaction of the aqueous silver salt with aqueous tris(ethylenediamine)cobalt(III) iodide gave tris(ethylenediamine)cobalt(III) tris(perfluoropinacolato)ferrate(III), $[Co(en)_3][Fe(PFP)_3]$. *Anal.* Calcd for $C_{24}H_{24}F_{36}O_6N_6CoFe$: C, 22.32; H, 1.87; F, 52.97; N, 6.51. Found: C, 22.01; H, 2.08; F, 52.68; N, 6.18.

The cesium salts appeared to be much less soluble than the potassium salts. With the bis(perfluoropinacolato)cuprate(II), for example, addition of aqueous cesium chloride to an aqueous solution of the potassium salt gave an immediate precipitate of the deep blue cesium salt, which was then recrystallized from methanol. *Anal.* Calcd for $C_{12}F_{24}O_4CuCs_2$: C, 14.51; F, 45.89. Found: C, 14.45; F, 45.62.

In the iron and aluminum compounds described above, where the metal atom is chelated by three pinacol ligands, there is no reason to doubt that the structure is basically octahedral, similar to the well-known trioxalatoferrate or -aluminate ions, and the magnetic moment of the iron complex is that to be expected from a high-spin d^5 species. Similarly, the magnetic moment of the ion $[Cu(PFP)_2]^{2-}$ is within the range usually found for d^9 species of copper(II), and that of the ion $[Mn(PFP)_2]^{2-}$ is consistent with d^5 manganese(II). With the nickel complex $[Ni(PFP)_2]^{2-}$, the diamagnetism would suggest a square-planar configuration, but more detailed interpretations of the structures of all these

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species must await the results of work now in progress on their electronic absorption spectra.

From the species described above, it would appear that perfluoropinacol is a valuable addition to the range of bidentate oxygen-containing ligands and may be expected to form a variety of complexes with many metal ions.

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An Anomalous Sign Reversal in the Circular Dichroism Spectra of Tetradentate Schiff Base Complexes of Nickel(II) and Copper(II)

Sir:

In the course of an investigation of the circular dichroism (CD) spectra of a series of square-planar metal complexes with tetradentate Schiff base ligands, we have found a correlation between the sign of the Cotton effects in the d–d transition region and the presence of substituents at the azomethine carbon atoms. This observation suggests that the chelate ring conformation, rather than the absolute configuration of the amine, is of primary importance in the induction of optical activity in the metal ion chromophore by these asymmetric ligands. These results may be rationalized by assuming a corresponding inversion in the conformation of the central chelate ring, similar to that employed to detect apical coordination in tridentate amino acid chelates.[1]

The d–d band in the visible absorption spectrum of N,N′-bis(salicylidene)-*R*-(−)-propane-1,2-diaminonickel(II) (Ni(sal)$_2$(−)pn)[2] occurs as a shoulder at 18,500 cm^{-1} ($\epsilon_{\max}$ 150) on the more intense charge-transfer band. The spectra of the corresponding complexes derived from *o*-hydroxyacetophenone (Ni(7-CH$_3$sal)$_2$(−)pn) and 2,4-pentanedione (Ni(acac)$_2$(−)pn) also exhibit single d–d bands[3] at 18,080 cm^{-1} ($\epsilon_{\max}$ 170) and 17,730 cm^{-1} ($\epsilon_{\max}$ 65), respectively. The CD spectra of these chelates in the d–d region are presented in Table I. For the latter two complexes, which have methyl groups on their azomethine carbons, the pattern of the CD bands in the d–d region is reversed, compared to Ni(sal)$_2$(−)pn. In addition, the magnitude of the CD bands is greater for the methyl-substituted compounds. Such sign reversals may be observed in previously reported ORD spectra.[3] The reversal in the CD spectra is more definitive, however, since in these closely related complexes it is reasonably certain that the low-energy CD bands correspond to the same transitions.

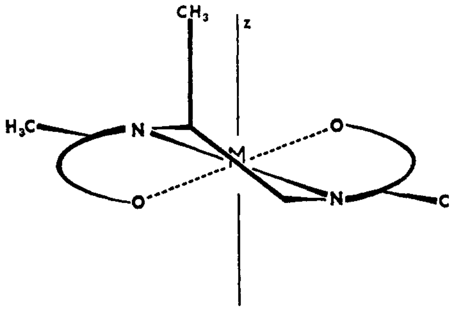
Table I. Circular Dichroism Spectra of Nickel(II) Chelates

	ν, cm^{-1}	$\Delta\epsilon_{\max}$
Ni(sal)$_2$(−)pn[2]	17,570	+0.6
	20,700	−0.4
Ni(7-CH$_3$sal)$_2$(−)pn	17,670	−5.3
	20,410 (sh)	+1.0
Ni(acac)$_2$(−)pn	17,360	−2.1
	20,200	+0.6
	22,420[a]	−2.0

[a] This band obscured by charge-transfer bands in the other compounds.

A number of crystallographic investigations have shown the central ring of these tetradentate Schiff base chelates to be nonplanar.[4] The CD results given above may be interpreted by assuming that the sign of the Cotton effect of a given d–d transition is determined by the preferred conformation of the central chelate ring. If, by analogy with coordinated 1,2-diaminopropane[5] (pn), it is assumed that in Ni(sal)$_2$(−)pn the λ conformation,[6] with the methyl group pseudo-equatorial, is favored, then the sign reversal in the CD is explained by a preference for the δ (methyl-axial) conformation in Ni(7-CH$_3$sal)$_2$(−)pn and Ni(acac)$_2$(−)pn. This methyl-axial preference in these compounds is reasonable, owing to the severe interaction between the methine methyl and an equatorial pn methyl group. The increase in magnitude of the CD is a consequence of the stronger conformational preference in the case of the methyl-substituted complexes.

The assumption of a λ conformation for the central ring in Ni(sal)$_2$(−)pn may be questioned, however, since those interactions which favor an equatorial orientation for the methyl group in chelated pn are absent in these Schiff base chelates. The crystal structure[7] of Cu(sal)$_2$(−)pn·H$_2$O in fact shows the pn methyl to be pseudo-axial, although this may be due to interaction with the coordinated water molecule. Inspection of a model of Ni(sal)$_2$(−)pn suggests that the only appreciable steric interaction is that between the methine hydrogen and pn methyl, and should tend to favor the methyl-axial, δ conformation. Similar conformational reasoning can also be used to explain the fact that the complexes Cu(gly)$_2$S(+)pn and Cu(gly)$_2$RR(−)chxn (gly = glycyl, chxn = 1,2-diaminocyclohexane) have low-energy CD bands with the same sign.[8] In-plane methyl–oxygen interaction may favor the axial position for the pn methyl, so that Cu(gly)$_2$(+)pn will have a central ring



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