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Substituent Effect of Chelated Cobalt.
Part VII. A ^{19}F-NMR Study of *p*- and *m*-Fluorophenylcobalt Chelates [1]

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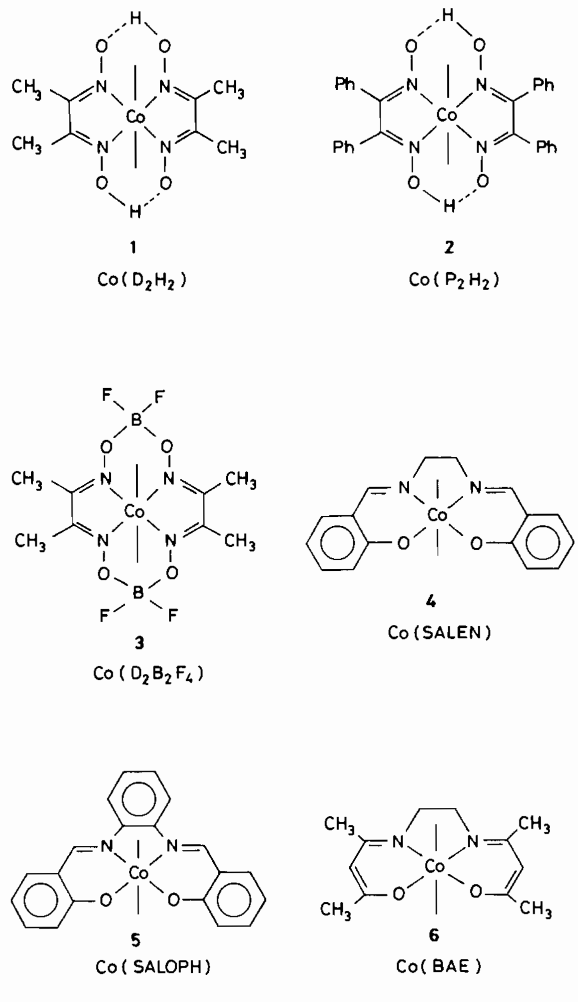
Introduction

In an earlier study [3] we attempted to assess the inductive and resonance interactions of cobaloxime (Scheme 1, chelate *1*) chelated cobalt centers on covalently bound organic groups by investigation of the ^{19}F-NMR chemical shifts of *m*- and *p*-fluorophenylcobaloximes with various axial ligands. We correlated these chemical shifts with those of non-cobalt substituted fluorobenzenes via the Taft dual substituent parameter equation [4] (eq. 1) in which P^i is a

$$P^i = \sigma_I \rho_I{}^i + \sigma_R \rho_R{}^i$$

correlatable property of a substituted benzene derivative (such as the NMR chemical shifts of substituted relative to unsubstituted compounds), σ_I and σ_R are the inductive and delocalization parameters of the substituent, respectively, ρ_I and ρ_R are the susceptibilities of the correlatable parameter to the inductive and resonance effects, and the superscript i refers to the substitution position (*meta* or *para*). These results showed that all neutral and anionic cobaloximes are strongly electron donating both by induction and π-delocalization, that both kinds of electron donation vary considerably with the nature of the *trans* axial ligand, and that a linear relation existed between the σ_R and σ_I values for these cobaloxime chelated cobalt centers. We have now extended this work into an investigation of the effects of equatorial ligand structure on the inductive and resonance substituent parameters of chelated cobalt centers by synthesis and NMR measurements of fluorophenylcobalt chelates in five additional equatorial ligand systems (chelates *2–6*, Scheme 1) including two additional bis(dioximato) chelates and three Schiff's base chelates.



Scheme 1. Structures and abbreviations of the cobalt chelates used in this study. *1*, bis(dimethylglyoximato)cobalt (cobaloxime); *2*, bis(diphenylglyoximato)cobalt; *3*, bis(boron difluoride) derixative of *1* (BF_2–cobaloxime); *4*, bis(salicylaldehyde)ethylenediimine cobalt; *5*, bis(salicylaldehyde)–*o*-phenylenediimine cobalt; *6*, bis(acetylacetone)ethylenediimine cobalt.

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TABLE I. ^{19}F-NMR Chemical Shifts of *m*- and *p*-$FC_6H_4Co(Chel)$ and Calculated Substituent Constants for Cobalt Chelates.[a]

Chelate[b]	Solvent	$\delta_{^{19}F}^{m}$ [c]	$\delta_{^{19}F}^{p}$ [c]	σ_I [d]	σ_R° [d]	$E_{1/2}^{red}$ [e]	$E_{1/2}^{ox}$ [f]	n_{CH_3I} [g]
$Co(D_2B_2F_4)$, *3*	MeOH	0.985[h]	9.671[h]	−0.179	−0.257			12.2[i]
	py	−0.835[h]	7.341[h]	+0.127	−0.272			
	DMSO-S[j]	−0.235[h]	8.320[h]	+0.015	−0.278			
	DMSO-O[k]	0.905[h]	9.298[h]	−0.206	−0.250			
$Co(P_2H_2)$, *2*	MeOH	0.361	8.925	−0.069	−0.264			13.7[i]
	py	0.716	8.913	−0.172	−0.242			
	DMSO	1.046	9.501	−0.232	−0.249			
$Co(D_2H_2)$,[l], *1*	MeOH	0.980	9.750	−0.178	−0.260	−1.40[m]	+1.05	14.3[n]
	py	1.458	9.780	−0.316	−0.231			
	DMSO	1.860	10.270	−0.389	−0.231			
Co(SALEN), *4*	MeOH	1.523	10.563	−0.273	−0.258	−1.57[o]	+0.64	14.6[p]
	py	2.184	11.082	−0.459	−0.234			
	DMSO	2.205	11.129	−0.457	−0.241			
Co(SALOPH), *5*	MeOH	2.008	10.387	−0.358	−0.229	−1.54[q]	+0.87	
	py	2.397	10.568	−0.497	−0.207			
	DMSO	2.329	10.625	−0.479	−0.218			
	$CHCl_3$	0.311	9.707	−0.054	−0.308			
Co(BAE), *6*	MeOH	2.537	11.585	−0.451	−0.240	−1.97[r]	+0.45	
	py	3.211	12.171	−0.657	−0.215			
	DMSO	2.719	12.000	−0.558	−0.242			
	$CHCl_3$	1.504	11.300	−0.290	−0.303			

[a] 27 ± 1 °C. [b] Structures given in Scheme 1. [c] In parts per million from internal monofluorobenzene. Positive shifts are upfield and negative shifts are downfield from the reference. [d] Calculated from eqn. 1 using the ρ values appropriate for each solvent. [e] $E_{1/2}$ (*vs.* S.C.E.) for one electron reduction of the $CH_3Co(Chel)$ at 0° in DMF. [f] $E_{1/2}$ (*vs.* Ag/AgCl) for one electron oxidation of the $CH_3Co(Chel)$ at −20° in DMF, ref. 19. [g] Pearson nucleophilicity constant [20] of the aquo cobalt(I) chelate anion in methanolic base. [h] Additional ^{19}F-resonances are seen upfield due to the equatorial fluorines; see text. [i] Ref. 21. [j] S – liganded DMSO complex; see text. [k] O – liganded DMSO complex; see text. [l] Data from Ref. 3. [m] Ref. 22. [n] Ref. 23. [o] Ref. 24. [p] Ref. 25. [q] For the $CH_3CH_2Co(Chel)$ complex, ref. 26. [r] Ref. 27.

Experimental

Fluorophenylcobalt chelates were, in general, obtained as their aquo complexes by synthesis of the equatorial ligand system, insertion of cobalt(II) and oxidation to the cobalt(III) chelate, followed by arylation with the appropriate fluorophenylmagnesium bromide in THF. The only exceptions were the $FC_6H_4Co(D_2B_2F_4)OH_2$ chelates (*3*, Scheme 1) which were prepared by direct reaction of the $FC_6H_4Co(D_2H_2)OH_2$ compounds with boron trifluoride etherate [5]. $HOCo(P_2H_2)OH_2$ (chelate *2*, Scheme 1) was prepared from diphenylglyoxime and cobaltous chloride by the procedure of Ablov, *et al.* [6] for the analogous cobaloxime. The Schiff's base ligands and their cobalt complexes were obtained by literature procedures [7–9] or slight modifications thereof. All of the purified fluorophenylcobalt chelates were homogeneous on thin layer chromatography, had the expected ^{1}H-NMR spectra, and gave satisfactory elemental analysis.

^{19}F-NMR spectra were obtained on a Nicolet NT-200 superconducting NMR spectrometer operating at 188.23 MHz and 27 °C. 8192 Data points were collected over an 8000 Hz sweep width. Anywhere from several hundred to 150,000 transients were collected with 4.9 μsec 60° pulses and a cycle time of 0.5 sec. Samples (5 mm NMR tubes) were 0.01 *M* or less in fluorophenylcobalt chelate and contained 10–98% deuterated solvent to provide an internal frequency lock. All samples contained monofluorobenzene in three-fold molar excess over cobalt chelate as an internal reference. Chemical shifts from proton-coupled ^{19}F-spectra were determined from the midpoint of the fluorine multiplet envelope of the sample to that of the reference. For internal consistency with previous work, all chemical shifts are reported in parts per million from monofluorobenzene with positive values being upfield and negative values being downfield from the reference, in keeping with the definition of Taft and coworkers [10, 11].

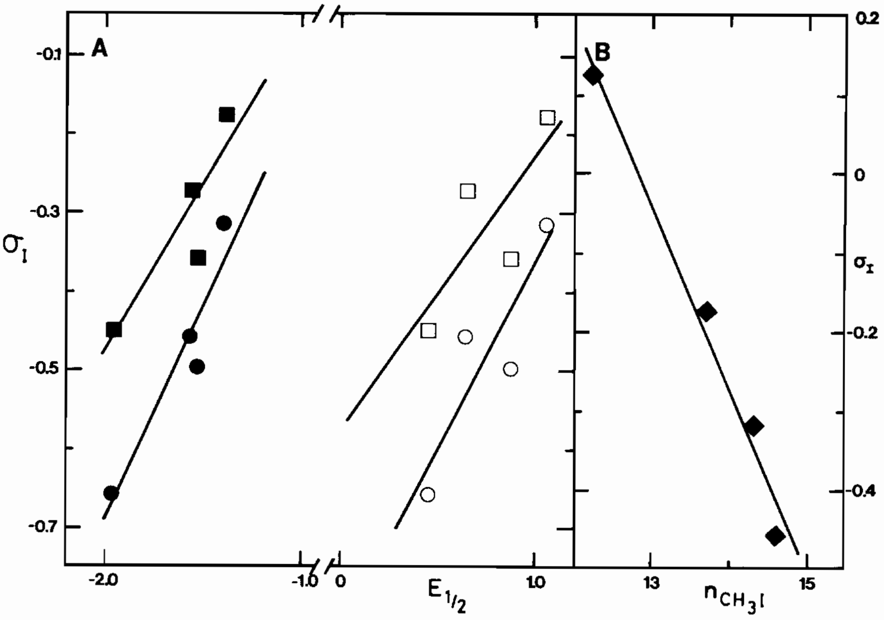

Fig. 1. A. Plots of σ_I for Co(Chel) in pyridine (●), and methanol (■) *vs.* $E_{1/2}$ for the one electron reduction of the $CH_3Co(Chel)$ (*vs.* S.C.E. in DMF at 0 °C), and in pyridine (○) and methanol (□) *vs.* $E_{1/2}$ for the one electron oxidation of the $CH_3Co(Chel)$ (*vs.* Ag/AgCl in DMF at –20 °C). The solid lines are linear regression lines. B. Plot of σ_I for Co(Chel) in pyridine (◆) *vs.* n_{CH_3I}, the Pearson nucleophilicity constant for the anionic $Co^{(I)}(Chel)^-$. The solid line is a linear regression line.

Results and Discussion

All of the purified fluorophenylcobalt chelates had a single ^{19}F-NMR resonance (Table I) with the exception of the $FC_6H_4Co(D_2B_2F_4)$ chelates (*3*, Scheme I) which show additional resonances due to the equatorial fluorines. For example, in methanol, both the *p*- and *m*-$FC_6H_4Co(D_2B_2F_4)$ chelates had additional resonances at about +39.3 and +42.2 ppm each of twice the intensity of the fluorophenyl resonances listed in Table I. This indicates that the two fluorine atoms on each half of the equatorial ligand are non-equivalent, as expected. In DMSO the situation is even more complex, each of these resonances being doubled due to formation of O–liganded and S–liganded isomers which are evidently in slow exchange on the NMR time scale. For example, *p*-$FC_6H_4Co(D_2B_2F_4)$DMSO had two sets of three resonances, one set at +8.320, +20.508 and +38.184 ppm, and one set at +9.298, +24.947 and +40.259 ppm, the former set being more intense than the latter by a factor of 3.5. The *meta*- compound similarly had two sets of three resonances with the more downfield set more intense than the upfield set by a factor of 3.6. We have tentatively assigned the more downfield, more intense members of each such pair of resonances to the S–liganded isomer and the upfield, less intense member to the O–liganded isomer in analogy to the previous assignments of the N– and S–liganded isomers of cobaloximes with axial thiocyanate ligands [3, 12, 13]. This assignment is consistent with the known preference of such chelated organocobalt centers for sulfur *vs.* oxygen ligands [3, 14–17]. It is also consistent with the observed ^{19}F-resonances of both the *meta*- and *para*- compounds in methanol where both compounds must be O–liganded, the resonances assigned to the O–liganded DMSO complexes being very similar to those obtained in methanol (Table I). All of the other fluorophenylcobalt chelates had only a single ^{19}F-resonance in DMSO indicating either that only a single adduct is formed in the case of these chelates, or that the O– and S–liganded isomers are in fast exchange on the NMR time scale, the latter explanation being the more reasonable.

Values for the inductive (σ_I) and resonance ($\sigma_R{}^\circ$) substituent parameters for each chelate (Table I) were calculated from the observed fluorine chemical shifts and eqn. 1 (in the *meta*- and *para*-forms) using the ρ values previously determined [3] from Taft's data [10, 11] on substituted fluorobenzene chemical shifts in $CHCl_3$, DMSO, and methanol, and the values for pyridine (also from fitting Taft's data to eqn. 1) of $\rho_I{}^m = -5.11$, $\rho_R{}^m = 0.68$ (n = 12, f = 0.15) and $\rho_I{}^p = -8.41$, $\rho_R{}^p = -30.90$ (n = 13, f = 0.07), where n is the number of data points in the correlation and f is the ratio of the root mean square of the deviations to the root mean square of the data points [4]. Both of the new correlations in pyridine are adequate using Topsom's criterion [18] of 0.1 <

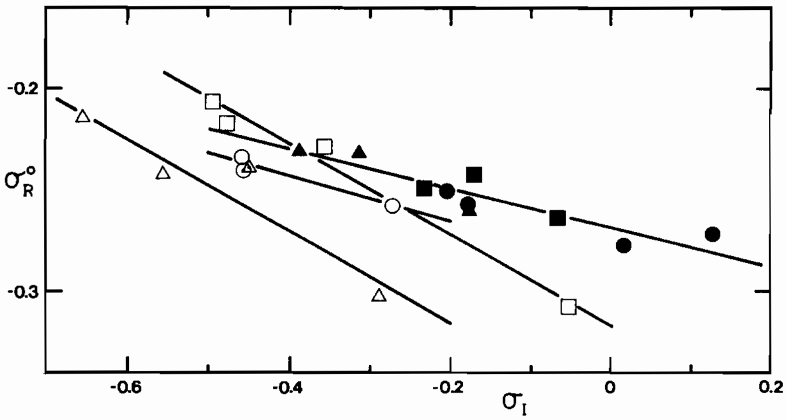

Fig. 2. Plot of $\sigma_R°$ *vs.* σ_I for Co(Chel) in various solvents. Solid symbols are for the dioximato chelates; (●), Co($D_2B_2F_4$); (■), Co(P_2H_2); (▲), Co(D_2H_2); slope = –0.0963, intercept = –0.269, n = 10, f = 0.025. The open symbols are for the Schiff's base chelates; (○), Co(SALEN), slope = –0.111, intercept = –0.288, n = 3, f = 0.011; (□), Co(SALOPH), slope = –0.222, intercept = –0.317, n = 4, f = 0.024; (△), Co(BAE), slope = –0.224, intercept = –0.360, n = 4, f = 0.043.

$f < 0.2$ for an acceptable fit and $f < 0.1$ for an excellent fit, and the ρ values in pyridine are quite similar to those previously obtained in the other solvents [3].

Inspection of the calculated substituent parameters shows that of all the neutral cobalt chelates studied only the extremely electron deficient Co($D_2B_2F_4$) chelates can be inductively electron withdrawing at least with strongly donating (N or S) axial ligands. All of the remaining cobalt centers are extremely inductively donating, the Schiff's base chelates being by far the most inductively donating substituents ever quantitated. The trend of increasing inductive donation among the cobalt chelates is best seen for the pyridine complexes which show the following order: Co($D_2B_2F_4$)py < Co(P_2H_2)py < Co(D_2H_2)py < Co(SALEN)py < Co(SALOPH) < Co(BAE). The same trend is seen for the DMSO liganded complexes but here it must be remembered that these probably consist of mixtures of O– and S– liganded isomers. These trends can be seen to parallel both the trend in the Pearson nucleophilicity constant [19] of the anionic cobalt(I) chelates, and the trend in the relative ease of one electron oxidations and one electron reductions of the methylcobalt chelates (Table) except that the SALEN and SALOPH chelates (whose σ_I values in pyridine and DMSO are very similar) fall in reverse order for these redox potentials. Examples of these correlations of inductive ability with redox potentials and nucleophilicities are shown graphically in Fig. 1. It is also interesting to note that for each cobalt chelate except Co($D_2B_2F_4$) the cobalt center is more inductively donating in strongly coordinating solvents (DMSO, pyridine) than in methanol or $CHCl_3$, as might be expected due to the known ability of such organocobalt chelates to transmit inductive effects from one axial ligand to the other [16, 28]. The reason for the inverse behavior of the Co($D_2B_2F_4$) chelates is not clear.

The overall range of $\sigma_R°$ values for all the chelates is extremely small (with the exception of the two values in chloroform) as was the case for the cobaloximes in our previous study [3]. However, there is clearly a trend among the chelates for less π-electron donation in the same order as the trend for increased inductive donation pointed out above. The values obtained in the non-coordinating $CHCl_3$ solvent for Co(SALOPH) and Co(BAE) are of interest in that these cobalt centers show substantially diminished inductive donating ability (relative to that in coordinating solvents) but increased resonance donating ability. The possible involvement of 5-coordinate species in these cases must be considered [8, 9]. However, although we were able to observe the formation of the green, supposedly 5-coordinate fluorophenylcobalt compounds from the reddish, 6-coordinate aquo complexes of the BAE and SALEN chelates by warming *in vacuo* [8, 9], the SALOPH complexes failed to give the green compounds. While even the red forms of the BAE complexes gave stable green solutions in chloroform, the green solids showed evidence of water in the ^{1}H-NMR spectra of their chloroform solutions. The green forms of the SALEN complexes initially gave green solutions in chloroform which soon precipitated red solids, possibly dimers [29], preventing observation of their ^{19}F-resonances. Hence, the possible involvement of 5-coordinate Schiff's base species in non-coordinating solvents remains unclear.

As was the case with the cobaloximes [3], there is an apparent correlation between $\sigma_R°$ and σ_I for the cobalt chelates presently under study. As seen in Fig. 2, all of the data for the dioximato chelates (solid symbols) fall closely about a line of slope −0.0963 and intercept −0.269 (n = 10, f = 0.025) although this slope is somewhat less negative than that previously obtained for a more extensive set of cobaloxime chelates [3]. It is also possible to correlate the data for all of the Schiff's base chelates (open symbols; slope = −0.168, intercept = −0.314, n = 11, f = 0.073). However, despite the limited amount of data for each chelate, the Schiff's base compounds appear to correlate better individually, with the slopes and intercepts decreasing in the order Co(SALEN) > Co(SALOPH) > Co(BAE) (Fig. 2, legend). These interesting phenomena are currently under further investigation.

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