of the first wave, which is reversible, resulted in discoloration of the solution with disappearance of the intervalence bands, showing that the structure is not retained. In this case also, the electron transfer is followed by chemical reactions leading to a breakdown of the structure.

Conclusion

The present study has shown the stability of the $V_2O_3^{3+}$ mixed-valence core with the trans geometry. Electronic and ESR spectra are consistent with a large amount of ground-state delocalization, especially in the $[V_2O_3(pmida)_2]^-$ ion for which the two vanadium sites are chemically equivalent. With the bdta ligand, a complicated structure with four mixed-valence units is observed. The interactions between these units are believed to be responsible of the differences in behavior with respect to "normal" binuclear mixed-valence systems: the splitting of the intervalence band, the broadening of the ESR spectrum, and finally the presence of several waves in electrochemical oxidation.

Acknowledgment. We thank A. De Kozak for magnetic susceptibility measurements.

Registry No. $H[V_2O_3(pmida)_2]\cdot 4H_2O$, 84049-50-3; $K[V_9O_{16}(bdta)_4]\cdot 27H_2O$, 94904-37-7; $VOSO_4$, 27774-13-6; $[V_2O_3(pmida)_2]$, 94904-38-8; $[V_2O_3(pmida)_2]^{2-}$, 94904-39-9; $[V_2O_3(pmida)_2]^-$, 84032-45-1.

Supplementary Material Available: Listings of anisotropic thermal parameters and observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Synthetic and NMR Studies on Fluorinated Alkoxides of Platinum(II): An Investigation of the Trans Influence of Alkoxides and the Nature of the Pt–O Bond, Using Phosphine and Thioether Complexes

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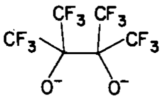
A number of new cis platinum(II) complexes have been synthesized incorporating the chelating dianion of perfluoropinacol, $[-OC(CF_3)_2C(CF_3)_2O-]^{2-}$, PFP, in conjunction with phosphine and thioether coligands. The general formula is $(PFP)PtL_2$, where L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, SMe_2, MeSEt, SEt_2, or S-bonded Me_2SO or L_2 = $MeS(CH_2)_2SMe$. The last complex exists as two stereoisomers, with the *S*-methyl groups in syn or anti conformations. Through the use of NMR measurements, in particular the value of $^1J(Pt,P)$ in the phosphine complexes, the static trans influence of the fluorinated alkoxy group has been estimated for the first time. It is similar to that of the halides and pseudohalides, the ordering being $Cl^- < -C(CF_3)_2O^- \approx Br^- < I^-$. By contrast, measurements of the barrier to inversion in the thioether complexes show $-C(CF_3)_2O^-$ to have a dynamic trans effect less than that of Cl^-. These observations are interpreted on the basis that platinum(II) forms bonds to alkoxides with a higher degree of electrostatic character than those to chloride, but a lower degree of covalent character.

Introduction

In our previous studies on fluorinated alkoxides of transition metals, we have demonstrated the use of the dianion of perfluoropinacol, PFP^{2-} (**1**), as a bidentate ligand forming a wide range of complexes.[1] In particular, we were able to prepare a stable fluorinated alkoxide of platinum(II) with phosphines as coligands, **2**; the geometry of PFP^{2-} requires that these be cis.[2]



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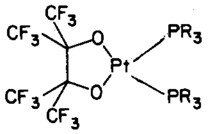

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At the time when we reported the synthesis of **2**, few alkoxides of platinum were known, an effect attributed to the incompatibility between the hard alkoxy ligand and the soft Pt^{2+} ion.[3] Subsequent work has somewhat extended the range of this type of compound, but stable alkoxy platinum complexes are still described as "rare".[4] The stability and ready accessibility of the PFP^{2-} derivatives therefore make this ligand particularly suitable for the investigation of compounds containing the platinum–oxygen linkage. In this paper, we report an extension of the range of type **2** complexes using different phosphines as coligands, together with the synthesis of new Pt^{2+} complexes where a thioether or sulfoxide is used as a coligand with PFP^{2-}. By the use of NMR methods, including the measurement of coupling constants and, in the case of the thioether complexes, the observation of inversion at sulfur, the trans influence and the trans effect of the fluorinated alkoxy ligand may then be estimated relative to other common ligands, enabling the Pt–OR bond to be contrasted with the Pt–halide bond.

Experimental Section

General Information. Organophosphines and dimethyl thioether were commercial samples (Alfa, Aldrich). Diethyl thioether, ethyl methyl thioether, and 2,5-dithiahexane were prepared by standard methods.[5] Perfluoropinacol (H_2PFP) was prepared as described previously.[2] Microanalysis was performed by Guelph Analytical Laboratories, Guelph, Ontario; all analytical data are in Table I. Infrared spectra were recorded on a Beckman 4250 spectrometer, mass spectra on a Varian Mat 311A instrument, and NMR spectra on a Varian XL-100 spectrometer at 100.1 MHz for ^1H, 94.1 MHz for ^{19}F, and 40.5 MHz for ^{31}P. Variable-temperature NMR spectra were recorded over the range −120 to +160 °C; temperature settings of the spectrometer were checked with a Doric Trendicator 400 type T digital thermometer calibrated to ±0.5 °C at the ice point.

Preparation of Complexes. $Pt(PFP)(PMe_3)_2$ (3). *cis*-$PtCl_2(PMe_3)_2$ was prepared by a modification of the literature method.[6] A mixture of K_2PtCl_4 (1.9 g) and $(AgI\cdot PMe_3)_4$ (2.5 g) was refluxed in water (50 mL) for 1 h; some decomposition was observed. After removal of water by rotary evaporation, extraction with boiling methanol followed by cooling to 0 °C gave *cis*-$PtCl_2(PMe_3)_2$ (1.4 g, 83%) as flaky white crystals, mp 345 °C dec.

cis-$PtCl_2(PMe_3)_2$ (0.670 g, 1.45 mmol) was suspended in CH_2Cl_2 (80 mL) and H_2PFP (0.48 g, 1.45 mmol) added with stirring, followed by KOH (2.69 mmol) in ethanol. (In this and the following reactions, it was found convenient to measure out KOH volumetrically with a standardized solution, about 0.6 M, in ethanol.) After stirring for 2 h, the reaction

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Table I. Analytical Data

compd	formula	% C calcd	% C found	% H calcd	% H found	% other calcd	% other found	color	mp, °C
$Pt(PFP)(PMe_3)_2$ (3)	$C_{12}H_{18}F_{12}O_2P_2Pt$	21.22	21.23	2.67	2.66	9.12	8.21[c]	colorless	257-260
$Pt(PFP)(PMe_2Ph)_2$ (4)	$C_{22}H_{22}F_{12}O_2P_2Pt$	32.89	32.71	2.76	2.76	7.71	7.76[c]	colorless	176-179[d]
$Pt(PFP)(PMePh_2)_2$ (5)	$C_{32}H_{26}F_{12}O_2P_2Pt$	41.44	41.50	2.83	2.86	6.68	7.02[c]	colorless	171-173
$Pt(PFP)(PPh_3)_2$ (6)	$C_{42}H_{30}F_{12}O_2P_2Pt$	47.97	47.89	2.88	2.74	5.89	5.76[c]	colorless	278-280
$Pt(PFP)(SMe_2)_2$ (7)	$C_{10}H_{12}F_{12}O_2PtS_2$	18.44	18.67	1.86	1.75	9.84	9.63[e]	tan	60
$Pt(PFP)(SEt_2)_2$ (9)	$C_{14}H_{20}F_{12}O_2PtS_2$	23.77	23.96	2.85	2.74	9.06	8.93[e]	pale yellow	103-105
Pt(PFP)(DTH)[a] (10)	$C_{10}H_{20}F_{12}O_2PtS_2$	18.50	18.55	1.55	1.55	9.87	9.71[e]	pale yellow	288-290
$Pt(PFP)(Me_2SO)_2$[b] (11)	$C_{10}H_{12}F_{12}O_4PtS_2$	17.58	17.53	1.77	1.81	9.38	8.60[e]	white	225-226

[a] DTH = 2,5-dithiahexane. [b] Me_2SO = dimethyl sulfoxide. [c] Phosphorus content. [d] Lit. mp 174-175 °C. [e] Sulfur content.

mixture was filtered to remove KCl and evaporated and the product recrystallized from $CHCl_3$.

$Pt(PFP)(PMe_2Ph)$ (4). *cis*-$PtCl_2(PMe_2Ph)_2$ was prepared by the literature method[6] as modified by Thompson.[7] Treatment with H_2PFP and base as before gave **4**, recrystallized from CH_2Cl_2.

$Pt(PFP)(PMePh_2)$ (5) was prepared in a similar manner from *cis*-$PtCl_2(PMePh_2)_2$[8] and recrystallized from $CH_2Cl_2/CHCl_3$.

$Pt(PFP)(PPh_3)_3$ (6) was prepared from *cis*-$PtCl_2(PPh_3)_2$[8] by the same method, except that overnight stirring was used following the addition of the H_2PFP and base. The product was recrystallized from CH_2Cl_2.

$Pt(PFP)(SMe_2)_2$ (7). The reported procedure[9] for the preparation of *cis*-$PtCl_2(SMe_2)_2$ gave a product shown by ^1H NMR to be contaminated by ~10% of the trans isomer. Further purification was effected by dissolving in the minimum quantity of CH_2Cl_2 and adding an excess of benzene, when the less soluble cis isomer precipitated; its purity was established by NMR. The cis complex (0.38 g, 0.97 mmol) was dissolved in CH_2Cl_2 (20 mL) and H_2PFP (0.32 g, 0.97 mmol) added, followed by KOH (1.94 mmol) in ethanol. After stirring for 18 h, the solution was filtered and evaporated; the residual tan solid was extracted with ether, then passed through Fluorosil in acetone solution, and evaporated. The product was recrystallized from toluene and washed with 40–60 petroleum ether.

$Pt(PFP)(MeSEt)_2$ (8). *cis*-$PtCl_2(MeSEt)_2$ had not previously been reported. It was prepared following the procedure used by Kauffman[10] for the preparation of the diethyl thioether analogue and characterized by the mass spectrum and ^1H NMR. ^1H NMR (δ): 1.30 (t, $^3J(H,H)$ = 7.0 Hz, CH_3 of ethyl group), 2.1–3.4 (m, CH_2 of ethyl group), (s, $^3J(Pt,H)$ = 49.5 Hz). Cis geometry was established by comparison with $^3J(Pt,H)$ of $PtCl_2(SMe_2)_2$, 49.0 Hz for cis and 41.5 Hz for trans.[11] The dichloride was converted to the PFP derivative, **8**, following the same procedure as for **7**. The product was a waxy solid that could not be recrystallized; its identity and purity were established by infrared, mass, and NMR spectra.

$Pt(PFP)(SEt_2)_2$ (9). *cis*-$PtCl_2(SEt_2)_2$ was made as described previously[10] and the PFP derivative prepared as for **7**.

Pt(PFP)(DTH) (10). $PtCl_2$(DTH) was made by the method of Tschugaeff.[12] Because of its low solubility in common solvents, a suspension of the dichloro complex (0.30 g, 0.78 mmol) in CH_2Cl_2 (150 mL) was treated with excess H_2PFP (0.4 g, 1.2 mmol) and ethanolic KOH (1.55 mol) added. After stirring for 2 days, the suspension of KCl was filtered through Celite and evaporated to yield a brown semisolid. This was extracted with acetone, from which ether addition produced a green solid that was washed with CH_2Cl_2 and recrystallized from acetone/toluene to give **10** as pale yellow flakes.

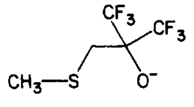
$Pt(PFP)(Me_2SO)_2$ (11). $PtCl_2$ (0.200 g, 0.75 mmol) was dissolved in dimethyl sulfoxide (20 mL) and H_2PFP (0.25 g, 0.75 mmol) added, followed by ethanolic KOH (1.50 mmol). The solution was stirred for 5 days at 25 °C, and then precipitated KCl removed by centrifugation and solvent removed under vacuum at ~80 °C. The residual solid was extracted with acetone, centrifuged, and evaporated to give a pale yellow residue. Recrystallization from acetone/chloroform gave colorless crystals of **11**.

Characterization. The identity of new complexes was established by elemental analysis (Table I) with the exception of **8**, which could not be obtained in crystalline form. Infrared spectra showed absorptions associated with the PFP ligand near 860, 910, 940, 1105, 1140, and 1160–1250 (C–F stretch) cm^{-1}.

All complexes gave mass spectra consistent with their proposed structures. The peak at highest mass number corresponded to the molecular ion in all cases except for **6**, where loss of F^- occurred. All nine complexes gave peaks corresponding to loss of CF_3^-, loss of $[(CF_3)_2CO + F^-]$, and loss of PFP^-.

Results and Discussion

Our previous work on complexes of the perfluoropinacol ligand, PFP^{2-}, has demonstrated that the most stable complexes of divalent metal ions are usually those where neutral coligands are present, giving a neutral complex $M(PFP)L_2$. In the case of Pt^{2+} complexes where cis geometry is imposed by the PFP^{2-} ligand, stability would be expected when soft coligands are present (the "antisymbiotic effect"[14]). We have previously demonstrated a preference for cis geometry in the Pt^{2+} complex of ligand **12**, where cis–trans isomerism is possible with the O_2S_2 donor set.[15]



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Our previous studies on platinum derivatives of PFP^{2-} had been restricted to the complex $Pt(PFP)(PMe_2Ph)_2$, and it was clearly of interest to extend this to cases where other phosphines, thioethers, or related compounds were used as coligands. We have therefore synthesized a range of complexes in which the coligand is PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, SMe_2, MeSEt, SEt_2, $MeS(CH_2)_2SMe$ (2,5-dithiahexane, DTH), or S-bonded $(CH_3)_2SO$ (Me_2SO). The general synthetic approach was to take the appropriate $PtCl_2$ complex in CH_2Cl_2 solution and treat it with the stoichiometric quantitites of H_2PFP and KOH, causing KCl to precipitate and leaving the desired product in solution; in the case of $Pt(PFP)(Me_2SO)_2$, the reaction was carried out in Me_2SO solution without isolation of the $PtCl_2$ adduct.

NMR Studies. The presence in these complexes of three NMR-active nuclei (^1H, ^{19}F, ^{31}P), each of which may couple to ^{195}Pt, renders them particularly suitable for investigation by this technique. In the case of the thioether ligands, additional information may be obtained from NMR studies of inversion at sulfur. General features of the NMR spectra, summarized in Tables II and III, will be discussed first, followed by a more detailed consideration of their implications in terms of the trans-influence of the PFP^{2-} ligand.

(i) Phosphine Complexes. The ^{19}F spectrum of each of the four phosphine complexes, **3**–**6**, consists of a single peak at ambient temperature (~32 °C), indicating equivalence between the four CF_3 groups on the NMR time scale. Solid-state studies on other chelated PFP^{2-} derivatives have shown that the CF_3 groups become inequivalent through twisting of the five-membered rings, e.g. in $[Ni(PFP)_2]^{2-}$[16] or in $S(PFP)_2$.[17] However, the environment of

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Table II. ^{1}H and ^{19}F NMR Spectra: General Features

complex	conditions	$\delta(CF_3)$ $(\nu_{1/2})^a$	^4J(Pt,F), Hz	$\delta(CH_3)^b$	^2J(P,H), Hz	^3J(Pt,H), Hz
Pt(PFP)$(PMe_3)_2$ (**3**)	$CDCl_3$, 60 °C	−71.2 (1.0)	2.8	1.54^c	11.3	32.9
Pt(PFP)$(PMe_2Ph)_2$ (**4**)	$CDCl_3$	−71.1 (2.3)	≤2	1.56^c	11.6	31.4
Pt(PFP)$(PMePh_2)_2$ (**5**)	$CDCl_3$, 32 °C	−70.9 (2.0)	≤2	1.73^c	11.0	30.1
Pt(PFP)$(PPh_3)_2$ (**6**)	CD_2Cl_2, 32 °C	−70.4 (2.0)	≤2	*e*		
Pt(PFP)$(SMe_2)_2$ (**7**)	$CDCl_3$	−71.0 (0.9)	6.5	2.51		44.0
Pt(PFP)$(MeSEt)_2$ (**8**)	$CDCl_3$, 32 °C	−71.0 (1.8)	≤5	2.48		44.0
Pt(PFP)$(SEt_2)_2$ (**9**)	$CDCl_3$, 32 °C	−71.0 (1.2)	5.0			
Pt(PFP)(DTH) (**10**)	$(CD_3)_2SO$, 180 °C	~−69 (7.5)	*f*	2.60		46.7
syn, 36%	$(CD_3)_2SO$, 60 °C	−69.46 (~6)	*f*	2.65		46.4
anti, 64%	$(CD_3)_2SO$, 60 °C	−69.48^d	*f*	2.52		48.7
syn, 48%	$(CD_3)_2CO$, 32 °C	−69.52 (5.5)	≤5	2.74		46.7
anti, 52%	$(CD_3)_2CO$, 32 °C	−69.50^g	*f*	2.61		48.3
Pt(PFP)$(Me_2SO)_2$ (**11**)	$(CD_3)_2CO$, 32 °C	−70.1 (1.0)	3.7	3.50		20.5

^{a} δ in ppm from $CFCl_3$; ν in Hz. ^{b} δ in ppm from Me_4Si. ^{c} CH_3 signal "filled-in doublet". ^{d} Doublet of quartets, J_{AB} = 10 Hz, Δ_{AB} = 42 Hz. ^{e} Aromatic ^{1}H signal, 7.1–7.7 ppm. ^{f} Not resolved. ^{g} Doublet of quartets, J_{AB} = 9 Hz, Δ_{AB} = 36 Hz.

Table III. ^{31}P NMR Parameters^a

complex	$\delta(^{31}P)^b$	^1J(Pt,P), Hz	$\delta(\text{free})^c$	$\Delta\delta^d$
Pt(PFP)$(PMe_3)_2$ (**3**)	−32.3	3414	−62.0	29.7
Pt(PFP)$(PMe_2Ph)_2$ (**4**)	−22.5	3490	−47.0	24.5
Pt(PFP)$(PMePh_2)_2$ (**5**)	−8.7	3578	−28.0	19.3
Pt(PFP)$(PPh_3)_2$ (**6**)	+5.4	3669	−6.0	11.4

^{a} Proton decoupled, in CH_2Cl_2, 0.1 M, at 30 °C. ^{b} From external $(MeO)_3PO$; positive shifts to low field. ^{c} Data for free phosphines.[13] ^{d} The coordination shift, [δ(coord) − δ(free)].

the CF_3 groups in **3–6** may be rendered equivalent through simple ring flexion, and it is not surprising that this occurs readily in solutions at room temperature. In an attempt to slow down the interconversion process, the temperature was lowered. Significant broadening was observed, but in no case did we see a separation of signals due to nonequivalent CF_3 groups. Inequivalent CF_3 groups giving rise to distinct ^{19}F NMR signals have been observed at −100 °C in the PFP derivative $S(PFP)_2$,[18] but the bonding at sulfur is based on trigonal-bipyramidal geometry and the interconversion process is therefore not strictly comparable to that occurring in a square-planar metal complex.

Previous reports of the value of four-bond coupling between ^{19}F and ^{195}Pt (in complexes of nonaromatic ligands) have varied over the range 4–30 Hz. In the Pt^{2+} complexes of the chelating ligands $[O-O-C(CF_3)_2-O]^{2-}$ and $[O-C(CF_3)_2-O]^{2-}$ (PPh_3 coligand), which are closely analogous to our complexes, ^4J(Pt,F) values are 6.1 and 6.8 Hz, respectively.[19] In our phosphine complexes, the ^4J(Pt,F) coupling is somewhat lower than this, being 2.8 Hz in compound **3** and less than 2 Hz (unresolved) in the other three.

The ^{1}H spectra of the phosphine complexes are very similar to those of their *cis*-$PtCl_2(PR_3)_2$ analogues. Coupling constants given in Table II represent *apparent* ^2J(P,H) and ^3J(Pt,H) values, since all complexes exhibit $X_nAA'X'_n$ spectra, where X = ^{1}H, A = ^{31}P, and n = 9, 6, and 3 for **3–5**, respectively.[20] It has been shown[21] that the appearance of this type of spectrum is critically dependent on the value of ^2J(P,P′), which is in the range 14–19 Hz in *cis*-$PtX_2(PR_3)_2$ complexes.[20]

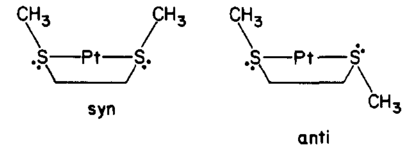
In each of the four complexes, the ^{31}P resonance consists of a singlet with ^{195}Pt satellites. There is a linear correlation between the coordination shift, $\Delta\delta$, and the free-ligand resonance positions of the respective phosphines, an effect that has been noted before in several cases, and it has been suggested that it is associated with the increase in the C–P–C bond angle on coordination.[22]

(ii) Thioether Complexes. For the three complexes of the monodentate thioethers, **7–9**, the ^{19}F NMR spectrum shows a singlet in each case, indicating that, as with the phosphine complexes, the PFP^{2-} ring is dynamically planar. The values of ^4J(Pt,F) are significantly greater than in the phosphine complexes. The ^{1}H spectra of the SMe_2 complex, **7**, and the MeSEt complex, **8**, are consistent with a cis structure. In each, the CH_3 group gives a singlet (δ 2.51 and 2.48, respectively) with ^{195}Pt satellites, ^3J(Pt,H) = 44.0 Hz. These values may be compared with those reported for the isomers of the analogous complex $PtCl_2(SMe_2)_2$:[11] δ 2.55 (^3J(Pt,H) = 49.0 Hz), cis and δ 2.45 (^3J(Pt,H) = 41.5 Hz, trans).

The ^{1}H spectrum of the ethyl group of the thioether in complex **8** consists of a CH_3 triplet [δ 1.40 ppm (^3J(H,H) = 7.4 Hz)] and an ABM_3 multiplet for the methylene protons, which become magnetically inequivalent on coordination [δ 2.85 (Δ_{AB} = 39.9 Hz, ^2J(A,B) = 12.2 Hz in $CDCl_3$)].

The ^{1}H spectrum of Pt(PFP)$(SEt_2)_2$ (**9**) is similarly complicated by the fact that the protons of the methylene groups in the thioether become magnetically inequivalent on coordination. They show the same ABM_3 pattern: δ 2.85 (Δ_{AB} = 47.2 Hz, ^2J(A,B) = 12.2 Hz). This problem has been considered in detail by Haake[23] for $PtCl_2(SEt_2)_2$, for which both cis and trans isomers show an ABM_3 spectrum, superimposed on a smaller ABM_3X spectrum due to coupling with ^{195}Pt. The AB/ABX envelope in the chloro complex is found to coalesce at 60 °C for the cis isomer and 1 °C for the trans; below the coalescence point, the chemical shift separation Δ_{AB} is ~31 Hz for the cis isomer and ~18 Hz for the trans at the same temperature. Data for **9**, which is unambiguously cis, are in good agreement with this work; allowing for a change in field strength, *cis*-$PtCl_2(SEt_2)_2$ would show Δ_{AB} = ~49 Hz at 100 MHz.

Assignment of the ^{1}H and ^{19}F NMR spectra of the DTH complex, **10**, is complicated by the existence of conformational isomers different in the relative orientation of the methyl groups on the two pyramidal coordinated sulfur atoms; these may conveniently be referred to as syn and anti isomers:



At elevated temperature [180 °C, $(CD_3)_2SO$ solution], interconversion of these is rapid on the NMR time scale and averaged signals are seen. The CH_3 groups give a singlet with ^{195}Pt satellites [δ 2.60, ^3J(Pt,H) = 46.7 Hz], while the CH_2 groups give a singlet at δ 2.96 (^3J(Pt,H) = 47.8 Hz). A detailed analysis of the NMR

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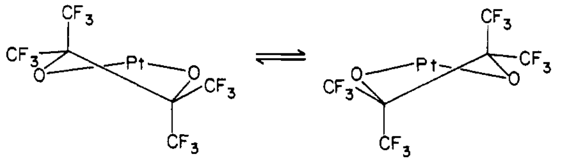
parameters of $PtCl_2(DTH)$ has been made by Abel,[24] who reports a high-temperature spectrum with CH_3 singlet at δ 2.61 ($^3J(Pt,H) = 47$ Hz) and a CH_2 singlet at δ 2.95 ($^3J(Pt,H) = 46$ Hz), in close agreement with out data on **10**.

At ambient temperature [32 °C, $(CD_3)_2CO$ solution], the spectra of **10** clearly show the existence of two isomers. The ^{19}F signal contains a singlet superimposed on a doublet of quartets, the latter suggesting inequivalent pairs of CF_3 groups in PFP^{2-}. The CH_3 signals are singlets (with ^{195}Pt satellites) at 2.74 and 2.61 ppm, while the CH_2 groups give rise to complex multiplets. Abel has used steric arguments to assign the lower field CH_3 signal to the syn isomer of $PtCl_2(DTH)$, which shows peaks at 2.72 and 2.60 ppm,[24] and the close agreement in the positions of the peaks in **10** suggests that we are observing an analogous situation. Accurate integration of the CH_2 and CF_3 signals was difficult, and we have relied on the marked difference in population of the two isomers between acetone-d_6 and Me_2SO-d_6 to assign the peaks. Integration of the clearly visible SCH_3 signals from the two isomers was 48:52 in the former and 36:64 in the latter solvent. When the relative size of the doublet of quartets and the singlet signals in the ^{19}F spectra was noted, it was then possible to assign the former to the CF_3 groups in the anti isomer and the latter to those in the syn isomer.

The difference in the ^{19}F spectra of the two isomers may be rationalized by assuming that the lowest energy conformation of a chelate PFP^{2-} ring is twisted so as to divide the four CF_3 groups into two axial and two equatorial pairs:



It is clear that, in the syn isomer of the complex Pt(PFP)(DTH), these two conformations of the PFP ring will be of equal energy. However, in the anti isomer (where the DTH ligand adopts a chiral conformation) the two conformations of the PFP ring will differ in energy because of differing steric interactions between the CH_3 and CF_3 groups. The PFP ring therefore adopts a preferred chiral conformation in the anti isomer, and the CF_3 groups are in two different environments.

(iii) Sulfoxide Complexes. During the high-temperature NMR study on the DTH complex, **10** in Me_2SO-d_6 solution, an additional peak was observed to be gradually developing at slightly higher field in the ^{19}F spectrum. Workup of the sample showed the presence of the new compound, $Pt(PFP)(Me_2SO\text{-}d_6)_2$, identified by its mass spectrum, and its protonated analogue, **11**, was subsequently made directly. Its ^{19}F spectrum shows a singlet with ^{195}Pt satellites [δ −70.1, $^4J(Pt,F) = 3.7$ Hz], while the ^1H spectrum shows a singlet at δ 3.50 ($^3J(Pt,H) = 20.5$ Hz).

It has been established that, in O-bonded sulfoxide complexes of Pt^{2+} such as $[PtCl(Me_2SO\text{-}O)diphos]PF_6$,[25] there is a coordination shift of less than 0.5 ppm from the resonance of the free ligand (δ 2.53) and no observed coupling to ^{195}Pt. In contrast, the compound *cis*-$PtCl_2(Me_2SO)_2$, where an S-bonded structure has been established,[26] has a methyl resonance at δ 3.55 ($^3J(Pt,H) = 23$ Hz).[27] On this basis, we may confidently assign an S-bonded structure to $Pt(PFP)(Me_2SO)_2$.

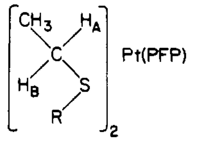
Trans Influence of Phosphines and Thioethers. The trans influence of various ligands in palladium(II) and platinum(II) complexes has been the subject of considerable interest, and the field has been comprehensively reviewed.[28] Our compilation of data on this series of new complexes enables us to attempt a ranking of the coligands trans to the fluorinated alkoxy group, based on the observed values of $^4J(Pt,F)$. Since the trans influence implies a static *weakening* of the opposite bond, the ligand with the greater influence will cause a *smaller* value of the coupling constant. The latter is not resolved in every case, but the observed order is $SMe_2 < MeSEt < SEt_2 < OSMe_2 < PMe_3 < PPh_nMe_{3-n}$, where $^4J(Pt,F) = 6.5$, ~5.5, 5.0, 3.7, 2.8, and ~2 Hz, respectively.

The value of $^4J(Pt,F)$ provides a useful discriminator among ligands of *weak* trans influence, and general trends in this series are in accord with ratings based on *trans*-(Pt–Cl) stretching frequencies[29] or on trans $^1J(Pt,P)$ coupling constants.[30] The relative ordering among the phosphines is not so reliable, because of the small values of ^4J, but it appears that trimethylphosphine has a weaker trans influence than the alkylarylphosphines. This is contrary to the ordering based on other criteria,[28] but a similar inversion has been noted by Kemmit,[31] based on observations of trans $^2J(Pt,F)$ in a series of $Pt(C_2F_4)L_2$ complexes.

On the basis of metal–chlorine bond lengths, Davies[25] has concluded that Me_2SO has a somewhat greater trans influence than thioethers. A recent study of the kinetic trans effect[32] shows that SEt_2 has a greater labilizing effect on a trans chloride ligand than SMe_2, a difference attributed to the better σ-donor power of the ethyl-substituted compound; here, the trans effect and the trans influence run in parallel.

Inversion in Thioether Complexes. As mentioned in the above discussion of the NMR spectra of the thioether complexes, the presence of pyramidal coordinated sulfur leads to the existence of conformational isomers, which may be interconverted by inversion at the sulfur atom. This process is conveniently followed by dynamic NMR spectroscopy, since the barrier to inversion is frequently such that the process occurs at a measurable rate over temperature ranges accessible by the NMR method.[29] In this way, the height of the inversion barrier may be estimated.

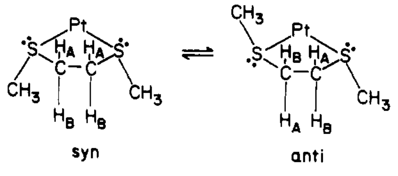
The four thioether complexes studied in the present work fall into three categories when the inversion process is investigated by NMR. In **7**, where the ligand is $(CH_3)_2S$, all three protons of each methyl group are rendered equivalent by rotation about the C–S bond, so only one signal is observed and no information about inversion at sulfur may be obtained. When ethyl groups are present in the thioether, as in **8** and **9**, the two methylene protons H_A and H_B are interconverted by inversion at sulfur, but *not* by rotation about the C–S bond. If the inversion process is slow on the NMR time scale, the methylene protons will give an ABM_3 pattern.



8, R=CH_3
9, R=C_2H_5

In these compounds, the inversion process gives a species chemically identical with the original molecule (and degenerate with it in energy), a process called *mutual inversion*. Clearly, the rate constant and activation energy for the forward and reverse reactions will be the same in this situation.

In the DTH compound, **10**, inversion at one sulfur atom will convert the syn to the anti isomer, or vice versa. Since these species are chemically distinct, they are of different energies and populations, and the interconversion process is known as *nonmutual inversion*.



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In this case, the rate constants and activation energies for forward and reverse reaction will be different.

A detailed discussion of the experiment has been given by several authors,[33-35] and our treatment follows that of Sandström.[35] The most accurate method of obtaining thermodynamic parameters requires computer fitting of line shapes as a function of temperature. However, the treatment of experimental data may be very much simplified by considering the line shape of the resonance at the coalescence temperature, T_c. This may be defined as the temperature at which NMR signals due to two exchanging nuclei have just coalesced to give the widest peak with no residual splitting effects. At this temperature, the rate constant, k, for exchange between two uncoupled, equally populated, sites undergoing mutual exchange may be related to the difference between their chemical shifts. Δ_{AB}, by the classical expression of Gutowsky and Holm:[36]

$$k = \pi\Delta_{AB}/\sqrt{2} \qquad (1)$$

The half-height line width of the peak at coalescence temperature, W^*, is often used as an approximation for Δ_{AB} in this equation on the basis of Lorentzian line shapes.

Similar approximations have been applied to systems undergoing two-site, nonmutual exchange of two uncoupled spin systems with unequal populations. With the populations denoted as p_a and p_b and the difference $\Delta p = (p_a - p_b)$, where $p_a > p_b$, then it may be shown that

$$\Delta p = [(X^2 - 2)/3]^{3/2}(1/X) \qquad (2)$$

where $X = 2\pi\tau_c\Delta_{AB}$ and τ_c is the lifetime at coalescence:

$$\tau_c = (k_a + k_b)^{-1} = p_a/k_a = p_b/k_b$$

Egan and Mislow[37] have solved eq 2 for X at various values of Δp, and a convenient tabulation of their results is given by Sandström.[38]

The rate constants may then be evaluated from

$$k_a = p_a(2\pi)W^*/X \qquad k_b = p_b(2\pi)W^*/X \qquad (3)$$

The last equation has been used in this study for the DTH complex, which is undergoing nonmutual exchange of uncoupled CH_3–S signals.

From the measured rate constants, the activation energy of the inversion process, $\Delta G^\ddagger$, may then be found from the Eyring equation

$$k = \chi(k_b/h)Te^{-\Delta G^\ddagger/RT} \qquad (4)$$

where k is the rate constant, χ is the transmission coefficient, k_b is the Boltzmann constant, and the other symbols have their usual significance. For polyatomic molecules undergoing thermal rearrangement, χ may be taken as unity and the activation energy at a given temperature T may be obtained by rearrangement of (4) to give

$$\Delta G^\ddagger = (1.914 \times 10^{-2})T(10.319 + \log|T/k|) \qquad (5)$$

In the present work, this equation has been used to find the activation energy for the inversion process in each complex at its coalescence point, T_c. The largest source of error in the method is the measurement of T_c, which we estimate to be accurate to ±5 K. In the temperature range 300–400 K, this will give a resulting uncertainty of about ±1 kJ/mol in $\Delta G^\ddagger$. (The effect on $\Delta G^\ddagger$ of error in k is much less significant and may be neglected.)

For compounds **8** and **9**, ^1H spectra were recorded in Me_2SO-d_6 solution over the temperature range 30–180 °C and T_c was found to be 72 °C (347 K) for each. The chemical shift difference Δ_{AB} was measured in the temperature region 30–52 °C; no appreciable variation with temperature was noted, and these values were therefore used for Δ_{AB} at T_c in solving for k. Values of Δ_{AB} were 7.5 Hz for **8** and 11.8 Hz for **9**, and use of eq 1 and 5 gives $k = 16.7\ s^{-1}$, $\Delta G^\ddagger = 77 \pm 1$ kJ/mol for the MeSEt complex, **8**, and $k = 26.1\ s^{-1}$, $\Delta G^\ddagger = 75.5 \pm 1$ kJ/mol for the SEt_2 complex, **9**. These activation energies are significantly greater than the figure of 70.3 kJ/mol calculated by the same approach for *cis*-$PtCl_2(SEt_2)_2$.[23]

As mentioned above, there are two isomers, syn and anti, present in the complex Pt(PFP)(DTH) (**10**). At the coalescence temperature of 114 °C (391 ± 5 K), the proportions are as follows: anti, 0.60 (p_a); syn, 0.40 (p_b). Substituting the value of W^* (14 Hz) into eq 4 gives $k_a = 18.6\ s^{-1}$, $\Delta G^\ddagger(A \rightarrow B) = 87.1 \pm 1$ kJ/mol and $k_b = 28.0\ s^{-1}$, $\Delta G^\ddagger(B \rightarrow A) = 85.8 \pm 1$ kJ/mol.

An approximate value of $\Delta G^\ddagger$ may also be obtained from the ^{19}F spectrum of **10**. Because the fluorine nuclei in this complex are coupled in an A_3B_3 system, the spectrum is not first order. The signal from the anti isomer is a doublet of quartets, while that from the syn isomer is a singlet. By assuming that the former collapses to a singlet, which then merges with the latter at the coalescence point, a rough estimate of 120 °C (393 ± 5 K) may be made for T_c, at which point $W^* = 12$ Hz. This leads to $k_b = 27\ s^{-1}$ and $\Delta G^\ddagger(B \rightarrow A) = 86 \pm 1$ kJ/mol, within experimental error of the value obtained from the ^1H spectra. The agreement between the $\Delta G^\ddagger$ values independently determined from the proton and fluorine NMR spectra suggests that the same process produces simultaneous interconversion of the inequivalent hydrogen and fluorine atoms, consistent with the previously suggested differentiation between inequivalent groups in coordinated PFP^{2-} imposed by the chirality of the DTH coligand in the anti isomer.

The height of the barrier to inversion in **10** may be compared with those in the complexes $PtCl_2$(DTH) and PtI_2(DTH), which are respectively 81.4 ± 0.1 and 75.3 ± 0.2 kJ/mol.[39] In both the SEt_2 and the DTH complexes, the barrier is ~5 kJ higher for the PFP^{2-} complex than for the Cl^- analogue. (The increase in $\Delta G^\ddagger$ of ~10 kJ for the same anion when passing from the monodentate SEt_2 to the chelating DTH is due to the introduction of angle strain, which hinders the obtaining of a planar transition state.[39] A similar difference is found between the SEt_2 and DTH complexes of $PtCl_2$.)

Variations in $\Delta G^\ddagger$ with the nature of the coligands have been noted previously in DTH complexes but have not been quantitatively assessed.[40] Much of the discussion has focused on the very large depression of the coalescence temperature resulting from the introduction of a trans-disposed ligand of large trans influence such as phenyl, and less attention has been given to the variations within the halide and pseudohalide ligand series. Since the fluorinated alkoxides form a class of pseudohalides, we have attempted to assess the significance of their trans influence on the barrier to thioether inversion, and a close comparison to the two halides studied by Abel ($PtCl_2$, PtI_2)[39] has been made. However, it was first necessary to establish the position of PFP^{2-} in the trans-influence series.

Trans Influence of the Perfluoropinacolato Ligand. Our previous studies on fluorinated alkoxides have shown, on the basis of measurements on nickel(II) complexes, that PFP^{2-} shows a ligand field strength comparable to that of SCN^- and slightly above the halides in the spectrochemical series.[3] The availability of the complexes synthesized in the present work now enables us, using NMR probes, to relate the trans influence of PFP^{2-} to that of the

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Table IV. NMR Data on Some Phosphine Complexes[a]

		cis complex			
	phosphine	Pt(PFP)	$PtCl_2$	$PtBr_2$	PtI_2
$\Delta\delta$	PMe_3	29.7	37.4	38.2[b]	36.0[b]
	PMe_2Ph	24.5	31.1	31.1	28.9
	$PMePh_2$	19.3	25.6	38.0	35.4[c]
	PPh_3	11.4	19.7[d]		
^1J(Pt,P), Hz	PMe_3	3414	3481	3426[e]	3300[e]
	PMe_2Ph	3490	3550	3506	3374
	$PMePh_2$	3578	3621	3576	3435
	PPh_3	3669	3678[d]		
^3J(Pt,H), Hz	PMe_3	32.9	35.6[b]	36.1[b]	36.1[b]
	PMe_2Ph	31.4	35[f]	35.5[f]	~37[f]

[a] Unless otherwise indicated, data on dihalide complexes are taken from ref 43. [b] Reference 42. [c] A value of 22.9 ppm has also been reported.[44] [d] Reference 45. [e] Reference 46. [f] Reference 47.

halides and other common ligands. No previous attempts to estimate the trans influence of a fluorinated alkoxy ligand have been reported.

Following established usage,[41,42] we use the term *trans influence* to describe the ability of a ligand to weaken a trans-disposed bond in the ground state of the complex, while the term *trans effect* is applied to kinetic phenomena. (In the particular case of a symmetrical bidentate ligand such as PFP^{2-} in a square-planar complex, it is of course impossible to distinguish between effects resulting from cis and trans substitution, but precedent suggests that the ligand in the trans site is of greater importance.) Because of the availability of a wide range of reference compounds, and the convenience of observation of the ^{31}P resonance, the series of phosphine complexes constitutes the best means of evaluating the trans-influence of the PFP^{2-} ligand. Data on the coordination shifts, $\Delta\delta$, of the phosphine complexes are given in Table IV, together with the ^1J(Pt,P) and ^3J(Pt,H) coupling constant values.

The coordination shift values are at a maximum in the trimethylphosphine complexes, $Pt(PFP)(PMe_3)_2$ and $PtX_2(PMe_3)_2$. They generally decrease as phenyl groups are substituted for methyl in the phosphine, in accordance with the concept that $\Delta\delta$ is greater in phosphines that are stronger σ-donors,[48] although there are apparent anomalies in complexes where $PMePh_2$ is present in conjunction with the largest halides, Br^- and I^-. In complexes with all four phosphines studied, the coordination shift in the PFP^{2-} derivative is 6–7 ppm less than in the Cl^- analogue, suggesting that PFP^{2-} has a definitely greater trans influence than Cl^-.

In the methylphosphine complexes of PtPFP, the position of the CH_3 resonance is in each case about 0.2 ppm to high field of that in the $PtCl_2$ analogues, representing a smaller coordination shift and a greater trans influence for PFP^{2-}.

The coupling constants ^1J(Pt,P) for PtPFP and the dihalides show a regular increase in each series of complexes as the introduction of phenyl groups increases the π-acceptor character of the ligand. We therefore follow the precedent of previous workers[49,50] in using ^1J(Pt,P) as the best criterion of trans influence, and it is clear from the data that PFP^{2-} is in the pseudohalide class, with a trans influence marginally greater than that of Br^-. A comprehensive rating of ligands has been made[49] by measurement of ^1J(Pt,P) in complexes *cis*-$PtX_2(P\text{-}n\text{-}Bu_3)_2$, and the order of increasing trans influence has been found to be $ONO_2^- < Cl^- < Br^- < N_3^- \approx NCO^- < I^- < SCN^- < NO_2^-$.

The value of ^1J(Pt,P) in P-*n*-Bu_3 complexes is generally ~20 Hz greater than in the PMe_3 analogues, which would suggest ~3440 Hz in $Pt(PFP)(P\text{-}n\text{-}Bu_3)_2$. The values for $X^- = Br^-, N_3^-$, and NCO^- are respectively 3477, 3409, and 3396 Hz, giving placement of PFP^{2-} between Br^- and N_3^-.

An extensive comparison of trans influences has been made by Appleton and Bennet[50] using the series of bis(phosphine) complexes $[-P(Ph)_2CH_2CH_2P(Ph)_2-]Pt(CH_3)X$. On the basis of the value of ^1J(Pt,P) trans to X, their ordering includes the following ligands: $ONO_2^- < Cl^- < CH_3COO^- < I^- < NCO^- < p\text{-}CH_3OC_6H_4O^- < SCN^- < OH^- < NO_2^-$.

This series is of particular relevance to the present work because of its inclusion of the hydroxide ion, which clearly has a trans influence that is stronger than that of the halide or thiocyanate ions and hence, by implication, stronger than that of fluorinated alkoxide.

An alternate, less satisfactory, measure of the trans influence in phosphine complexes is the value of ^3J(Pt,H) when methyl groups are attached to phosphorus. This coupling is, of course, much smaller than direct Pt–P coupling, and spectra are complicated by H–P and P–P coupling effects. Data for $PtX_2(PMe_3)_2$ and $PtX_2(PMe_2Ph)_2$ complexes show little differentiation between the halides on this criterion, with ^3J(Pt,H) being 35.6–36.1 Hz in the former[42] and 35–37 Hz in the latter.[47] In each case, PFP^{2-} shows a significantly stronger trans influence (i.e., a decrease in the coupling constant) with ^3J(Pt,H) values in the analogous complexes of 32.9 and 31.4 Hz, respectively. Another ligand bonding to Pt through oxygen, $acac^-$, shows a very similar value of 32.2 Hz in the complex $Pt(acac)Cl(Me_2PPh)$.[47]

In complexes **7**, **8**, **10**, and **11**, where a CH_3–S–Pt linkage is present in conjunction with PFP^{2-}, an estimate of the trans influence of the latter may be made from the value of ^3J(Pt,H) in the methyl protons. In both **7** (SMe_2) and **8** (MeSEt), ^3J(Pt,H) is 44.0 Hz, significantly less than the 49.0 Hz reported for *cis*-$PtCl_2(SMe_2)_2$[11] and the 49.5 Hz we find in *cis*-$PtCl_2(MeSEt)_2$. In the DTH complex, **10**, the coupling constant varies according to temperature, solvent, and ligand conformation in the range 46.4–48.3 Hz (Table II); the value for $PtCl_2(DTH)$ is 47 Hz.[24] In the Me_2SO complex, **11**, ^3J(Pt,H) is 20.5 Hz, whereas the value in *cis*-$PtCl_2(Me_2SO)_2$ is 23 Hz.[27] These figures are in general agreement with the results obtained on the phosphine complexes, showing PFP^{2-} to have a stronger trans influence than Cl^-, leading to smaller values of ^3J(Pt,H) in *trans*-S-CH_3 ligands in comparable situations.

Conclusions. From this large body of results on complexes where PFP^{2-} is coordinated trans to phosphines or thioethers on Pt^{2+}, we can place the static trans influence of the fluorinated alkoxy group relative to two other important series of ligands. First, among ligands bonding to platinum(II) through oxygen, the order of increasing trans influence corresponds to the order of increasing basicity of the groups: $ONO_2^- < CH_3COO^- \approx -C(CF_3)_2O^- < p\text{-}CH_3OC_6H_4O^- < OH^-$. Second, in comparison to the halide series, the trans influence of PFP^{2-} is significantly greater than that of Cl^-. In situations where a differentiation between the halide ions can be made, it is very similar to Br^- and weaker than I^-.

At the same time, our experiments on the thioether complexes have shown that PFP^{2-} is *less* effective than Cl^- in reducing the barrier to inversion at a trans sulfur atom. It is important to recognize that this is a completely independent result. Thioether inversion is a dynamic phenomenon whose rate is being measured, and differences found between PFP^{2-} and halide complexes are due to the *trans effect* of these ligands. We now have a clear case where there is an inversion of the relative positions of two ligands in the trans-effect and the trans-influence series. We suggest that this difference, although at first sight surprising, is in fact in agreement with the difference that might be expected between Pt–O and Pt–Cl bonds in nondelocalized systems on the assumption that the Pt–O bond has the greater degree of ionic character.

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Inorg. Chem. **1985**, *24*, 1065–1069 **1065**

We rationalize these observations in the following way: The rate of thioether inversion will be enhanced by stabilization of the intermediate, and this will be favored by a greater charge density on the metal atom to which the thioether is coordinated. In early discussion of this problem, Haake and Turley[51] had proposed a lone pair displacement mechanism for inversion at platinum in a square-planar complex. More recently, Abel and co-workers[52] have provided a more satisfactory approach in which they apply classical treatments of pyramidal inversion[53,54] to inversion at sulfur. The inversion process is assumed to proceed through an intermediate involving a planar, three-coordinate sulfur atom with sp^2 hybridization and a lone pair of electrons accommodated in a p orbital perpendicular to the bonding plane. This model leads to the conclusion that the barrier to inversion should be *raised* by the presence of more electronegative substituents X in $X\text{-}SR_2$ but *lowered* by an increased degree of π overlap between X and S in the transition state. Thus, in both ways the more strongly electron-withdrawing groups trans to coordinated sulfur would be expected to raise the barrier to inversion. (Variations between ligands are, however, still small in comparison with the large reduction in $\Delta G^{\ddagger}$ occurring when a sulfur-containing ligand is coordinated to a metal atom.) Our results therefore suggest that the fluorinated alkoxy group is *more strongly electron withdrawing* than Cl^-.

The concept of a more strongly electron-withdrawing group implies a higher degree of *ionic* character to the bond, which seems at first sight to be incompatible with an observation of greater trans influence. However, we suggest that it would be an oversimplification to infer from the higher trans-influence of alkoxide over chloride a greater degree of covalency in the Pt–O over the Pt–Cl bond. Rather, it is due to an inductive electron-withdrawing effect by the ligand, which robs the trans ligand of electron density from its σ orbital and thus leads to smaller values of the coupling constants. Concentration on the covalent interactions of ligands in discussions of the trans influence has perhaps been overemphasized, and we would suggest that other factors are involved. This is particularly the case when the ligands in question bond to the metal through atoms of significantly different character. First-row donors, such as oxygen and nitrogen, are hard to compare with second-row and later elements (P, S, Cl^-, Br^-, I^-) that possess π-acceptor character.

In virtually all bonding situations, bond effects are dependent on both the electronegativities of the linked atoms ("ionic character") and effective orbital overlap between them ("covalent character"). Within the series of ligands bonding through oxygen, the increasing trans influence parallels the increasing basicity of the ligand and the associated increase in the covalent character of the metal–ligand bond. Overlap is more significant than electronegativity change in this group. Similarly, within the halide series, the order of increasing trans influence runs $Cl^- < Br^- < I^-$; this is the converse of the increase in electronegativity but corresponds to the increase in the covalent character of the metal–halide bond. In contrast, the greater trans influence of $-C(CF_3)_2O^-$, OH^-, and N_3^- relative to Cl^- may then be attributed to their greater electronegativity, leading to the withdrawal of electron density from the metal σ orbitals.

The generalized order of trans influence usually presented[28] is therefore a composite of these two effects, and hence it is not surprising that many small inversions of the sequence are observed when different metal complexes are used to establish a comparative trans influence.

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X-ray Structure of a Ternary Metal Complex: Copper(II)–Inosine 5′-Monophosphate–Imidazole. Metal Binding to the N(7) Atom of the Nucleotide in a Mixed-Ligand System Containing an Aromatic Amine

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A ternary metal–nucleotide complex, $Na_2[Cu(5'\text{-}IMP)_2(im)_{0.8}(H_2O)_{1.2}(H_2O)_2]\cdot 12.4H_2O$, has been prepared and its structure analyzed by X-ray diffraction (5′-IMP = inosine 5′-monophosphate; im = imidazole). The complex crystallizes in space group $C222_1$ with $a = 8.733$ (4) Å, $b = 23.213$ (5) Å, $c = 21.489$ (6) Å, and $Z = 4$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares technique on the basis of 2008 observed reflections to a final R value of 0.087. Symmetry-related 5′-IMP anions coordinate in cis geometry through the N(7) atoms of the bases. The other cis positions of the coordination plane are statistically occupied by nitrogen atoms of disordered im groups and water oxygens with occupancies 0.4 and 0.6, respectively. Water oxygens in axial positions complete the octahedral coordination of Cu(II). The complex is isostructural with *cis*-$[Pt(5'\text{-}IMP)_2(NH_3)_2]^{2-}$, a model proposed for Pt(II) binding to DNA. The base binding observed in the present case is different from the typical "phosphate only" binding shown from earlier studies on metal–nucleotide complexes containing various other π-aromatic amines.

Introduction

During the past few years interaction of metal ions with nucleic acid constituents has been a field of active research.[1] This activity is motivated, in large part, by the well-recognized role of metal ions in the biochemistry of nucleic acids[2] and by the speculation that the antineoplastic agents, notably *cis*-$[Pt(NH_3)_2Cl_2]$, exhibit their activity by binding to DNA.[3] Metal–nucleotide complexes containing heteroaromatic N bases are of special interest since

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