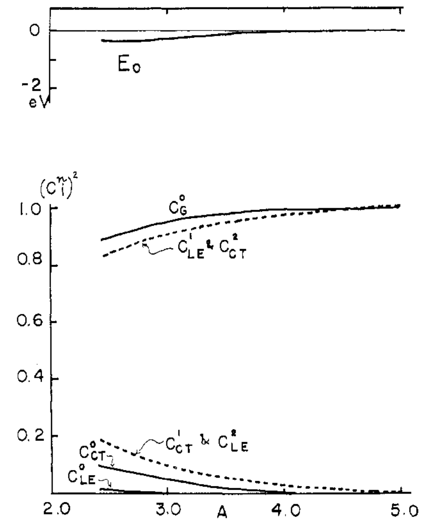


Figure 5.—The R dependence of the wave function of each state and the ground-state stabilization energy due to the interatomic CT interaction: $\psi_0 = C^0{}_{\mathrm{G}}\mathrm{G} + C^0{}_{\mathrm{LE}}\mathrm{LE}_- + C^0{}_{\mathrm{CT}}\mathrm{CT}_-$ for the ground state; $\psi_1 = C^1{}_{\mathrm{LE}}\mathrm{LE}_+ + C^1{}_{\mathrm{CT}}\mathrm{CT}_+$ for the excited state of the band at ~20 kK; $\psi_2 = C^2{}_{\mathrm{LE}}\mathrm{LE}_+ + C^2{}_{\mathrm{CT}}\mathrm{CT}_+$ for the excited state of the band at ~53 kK.

state and the first excited state. This causes the rapid increase of the transition probability for the visible band with the decreasing R, because the moment is large for the transition between the CT− and CT+ configurations. The stabilization energy of the ground state amounts to 5 kcal/mol for Ni(dmg)$_2$. This seems to be one of the reasons for the low solubility of Ni(dmg)$_2$ and also for its particular crystal structure.

From the above-mentioned discussion for the crystal spectra polarized parallel to the c axis, we can conclude that the sharp band at ~20 kK is mainly due to the $3d_{z^2} \rightarrow 4p_z$ transition within a nickel ion and is intensified in the crystal by borrowing the intensity from the interatomic CT excitation. Furthermore, the strong absorption peak in the vacuum ultraviolet region was found to be mainly due to the interatomic CT transition. That is to say, we succeeded in observing the new band characteristic of the interatomic CT interaction in the Ni(dmg)$_2$ and β-Ni(emg)$_2$ crystals. Since the present theoretical results on the crystal spectra depend to some extent on the adopted parameters, too much importance should not be attached to them from the quantitative point of view. Qualitatively, however, the present treatment gives a reasonable interpretation of the observed crystal spectra.

As is seen in Figure 3, the films of Pd(dmg)$_2$ and Pt(dmg)$_2$ show spectra analogous to that of Ni(dmg)$_2$. In the visible region, they have strong bands at 21.5 and 15.1 kK, respectively, which correspond to that at 18.6 kK of Ni(dmg)$_2$. Furthermore, another peak was observed for each complex in the region above 50 kK, corresponding to the 52.5-kK band of Ni(dmg)$_2$, though it is altered to some extent by the central metal ion. The conclusions obtained by the present theoretical calculation for the nickel *vic*-dioximes are considered to be also applicable qualitatively to the crystals of Pd(dmg)$_2$ and Pt(dmg)$_2$.

Acknowledgments.—The authors are greatly indebted to Dr. Koji Kaya of our laboratory for his kind help in measuring the polarized absorption spectra in the vacuum ultraviolet region.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WESTERN ONTARIO, LONDON, CANADA

The Preparation and Hydrogen-1 and Fluorine-19 Nuclear Magnetic Resonance Spectra of Fluoroalkylplatinum(II) and -platinum(IV) Compounds

BY H. C. CLARK* AND J. D. RUDDICK

Received March 11, 1970

Fluoroalkyl halides of the types RI or RCH$_2$I (R = perfluoroalkyl) react with several methylplatinum(II) complexes containing the ligands P(CH$_3$)$_2$C$_6$H$_5$ or As(CH$_3$)$_2$C$_6$H$_5$ to give platinum(IV) complexes whose stereochemistry has been determined by ^{1}H nmr spectroscopy. Long-range H–F coupling has been observed in many of the proton spectra. Fluorine-19 nmr data are given: there is a wide variation in Pt–F coupling constants. Complexes of the type *trans*-PtIR{P(CH$_3$)$_2$C$_6$H$_5$}$_2$ (R = CF$_3$, C$_2$F$_5$, or C$_3$F$_7$) result from the decomposition of some of the platinum(IV) complexes.

Introduction

Alkylplatinum(II) and -platinum(IV) complexes can be prepared using Grignard or lithium reagents,[1,2] but the corresponding fluoroalkyl complexes are not accessible by these routes. Fluoroalkylplatinum(II) complexes have been prepared by oxidative addition of fluoroalkyl iodides to platinum(0) species,[3] and we now report the preparation of some platinum(IV) complexes containing fluoroalkyl groups by oxidative addition of fluoroalkyl iodides to methylplatinum(II) complexes. Some of these compounds can be degraded readily to give fluoroalkylplatinum(II) complexes.

---

* To whom correspondence should be addressed.

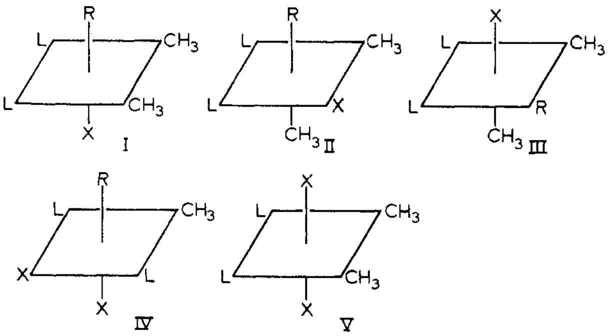
(1) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705, 4020 (1959).

(2) J. D. Ruddick and B. L. Shaw, *Chem. Commun.*, 1135 (1967).

(3) D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc. A*, 164 (1968).

Results and Discussion

The complex *cis*-$Pt(CH_3)_2L_2$ $\{$**1**, L = $As(CH_3)_2C_6H_5$, or **2**, L = $P(CH_3)_2C_6H_5\}$ reacts at room temperature with CF_3I, CF_3CF_2I, $CF_3CF_2CF_2Br$, $CF_3CF_2CF_2I$, or $CF_3(CF_2)_6I$ to give adducts of configuration I (Figure 1). This configuration follows from the ^1H (methyl) resonance patterns in the nmr spectra, which are rather similar to those found[4] for complexes of the type $PtI(CH_3)_3L_2$, configuration I (R = CH_3).



L = $P(CH_3)_2C_6H_5$ or $As(CH_3)_2C_6H_5$; R = fluoroalkyl;
X = Br or I

Figure 1.—Configurations of platinum(IV)–fluoroalkyl derivatives.

In complexes formed from **1** the methyl groups bonded to arsenic give two main resonances, showing that their time-averaged magnetic environment is different. This is because the As–Pt axis does not contain a plane of symmetry,[5] and this makes the two methyl groups attached to a given arsenic atom magnetically nonequivalent. The difference in chemical shift between these two methyl groups increases as the length of the fluoroalkyl group increases. Complexes formed from **2** show similar effects: the methyl groups bonded to phosphorus give two doublets because of coupling with the ^{31}P nucleus. In such cases it was difficult to measure J_{Pt-H} because the satellite peaks were partially obscured by the main resonances.

The ^1H resonance pattern of the methyl groups bonded to platinum in $PtI(CH_3)_2CF_3Q_2$ [Q = $P(CH_3)_2C_6H_5$] is similar to that found[4a,6,7] for complexes of the type *cis*-$Pt(CH_3)_2(PR_3)_2$ and shown[4a] to be characteristic of two methyl groups trans to two $P(CH_3)_2C_6H_5$ ligands in platinum(IV) complexes. However there is some further splitting of the central doublet, presumably due to coupling with the adjacent ^{19}F nuclei. McCleverty and Wilkinson[8] have observed H–F coupling of 0.5 Hz in $C_5H_5Rh(CO)CF_3I$. As the length of the fluorocarbon chain is increased, the resonance pattern of the platinum-bonded methyls undergoes further changes; however, J_{Pt-H} remains essentially constant (Table I).

The ^1H resonance due to the metal-bonded methyls in $PtI(CH_3)_2CF_3A_2$ [A = $As(CH_3)_2C_6H_5$] is a slightly broadened singlet, with satellites showing J_{Pt-H} = 65 Hz which is typical of methyl groups trans to $As(CH_3)_2C_6H_5$ in platinum(IV) complexes.[4b] The corresponding resonance for $PtI(CH_3)_2RA_2$ (R = n-C_3F_7 or n-C_7F_{15}) is a 1:2:1 triplet (J = 1.4 or 1.6 Hz, respectively), which could be caused by coupling with the α-CF_2 group, but $PtI(CH_3)_2C_2F_5A_2$ gives a doublet (J = 1.2 Hz) for this resonance and we are unable to account for this.

Pyrolysis of $PtI(CH_3)_2CF_3Q_2$, configuration I, gives *trans*-$PtI(CF_3)Q_2$ and ethane in high yield. Loss of ethane rather than CF_3CH_3 probably reflects the much greater strength of the Pt–CF_3 bond compared with Pt–CH_3.

The reaction of CF_3CH_2I with **1** gives an adduct to which we assign configuration II (Figure 1). The methyl resonance pattern consists of five singlets and one quartet, with accompanying satellites. Four of the singlets are due to the four nonequivalent methyl groups in the two $As(CH_3)_2C_6H_5$ ligands and the fifth is due to the platinum-bonded methyl group trans to arsenic (the coupling constant to ^{195}Pt of 62 Hz is the magnitude expected[4b] for CH_3 trans to As). The quartet must therefore be assigned to CH_3 trans to CH_2CF_3: the platinum satellites (J = 68 Hz) indicate that this group is directly bonded to Pt. We can only explain the formation of a quartet (J = 1.1 Hz) in terms of coupling between the protons of this methyl group and the three ^{19}F nuclei in the CH_2CF_3 group.

The resonance due to the CH_2 group in the above complex consists of two overlapping quartets (with satellites), showing that the two protons are nonequivalent (this was confirmed by comparison of the 60- and 100-MHz spectra). It is interesting that J_{Pt-H} for one proton is 87 Hz but for the other one it is 89 Hz.

An alternative configuration which would be expected to give six different resonances in the methyl resonance pattern is configuration III. However, we discount this one on the grounds that both metal-bonded CH_3 groups are cis to the CF_3CH_2 group, and it is unlikely that any one of them would undergo long-range H–F coupling.

Compound **1** reacts similarly with $CF_3CF_2CH_2I$ and with $CF_3CF_2CF_2CH_2I$. We again assign configuration II to the adducts, since the methyl resonance patterns are similar to that of the CF_3CH_2I adduct (Table I). The high-field methyl group appears as a 1:2:1 triplet, presumably because there is coupling to the β-CF_2 group only. The resonance due to the CH_2 group was not resolved, presumably because it consists of a large number of relatively weak lines.

In contrast to the above, **2** reacts with CF_3CH_2I, $CF_3CF_2CH_2I$, or $CF_3CF_2CF_2CH_2I$ to give adducts of configuration I; their methyl resonance patterns are closely similar to those of the perfluoroalkyl iodide adducts (Table I). The resonance due to the CH_2 group could not be detected in the proton spectrum of any of these adducts, presumably because it consists of many relatively weak lines.

---

(4) (a) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969); (b) *ibid.*, *A*, 2964 (1969).

(5) B. L. Shaw and A. C. Smithies, *ibid.*, *A*, 2784 (1968), and references therein.

(6) E. O. Greaves, R. Bruce, and P. M. Maitlis, *Chem. Commun.*, 616 (1967).

(7) F. H. Allen and A. Pidcock, *J. Chem. Soc. A*, 2700 (1968).

(8) J. A. McCleverty and G. Wilkinson, *ibid.*, 4200 (1964).

TABLE I

NUCLEAR MAGNETIC RESONANCE DATA[b]

	Methyl[c]							Fluoroalkyl[h]					
Compound[a]	δ_Q[d]	J_{P-H}[e]	J_{Pt-H}[f]	δ_{PtCH_3}[d]	J_{P-H}	J_{Pt-H}	J_{F-H}[g]	δ_F	J_{P-F}	J_{Pt-F}	Description[i]	Assignment[j]	Other coupling constants
$PtI(CH_3)_2CF_3Q_2$	1.66 d	9.0	(10.2)	1.15		57		19.3	14	517	Triplet	α-CF_3	
	1.76 d	9.0	(10.2)										
$PtI(CH_3)_2C_2F_5Q_2$	1.63 d	8.5	(9.5)	1.24		58		69.1	33	273	Triplet	α-CF_2	
	1.87 d	8.5	(9.5)					78.7	. . .	12	Singlet	β-CF_3	
$PtBr(CH_3)_2C_3F_7Q_2$	1.58 d	8.7	(9.5)	1.28		58		66.2	31	260	Octet	α-CF_2	$J_{F\alpha-F\gamma}$ = 14 Hz
	1.81 d	8.7	(9.5)					119.3	. . .	. . .	Singlet	β-CF_2	
								79.3	. . .	21	Triplet	γ-CF_3	$J_{F\alpha-F\gamma}$ = 14 Hz
$PtI(CH_3)_2C_3F_7Q_2$	1.57 d	8.5	(9.5)	1.28		57		66.1	30	260	Octet	α-CF_2	$J_{F\alpha-F\gamma}$ = 14 Hz
	1.80 d	8.5	(9.5)					120.7	. . .	. . .	Singlet	β-CF_2	
								79.8	. . .	22	Triplet	γ-CF_3	$J_{F\alpha-F\gamma}$ = 14.5 Hz
$PtI(CH_3)_2C_7H_{15}Q_2$	1.61 d	8.3	(10)	1.31		57		65.5	?	285	Multiplet	α-CF_2	
	1.84 d	8.3	(10)					*k*					
$PtI(CH_3)_2(CF_3CH_2)Q_2$	1.63 d	8.5	(10.0)	1.24		56		54.1	. . .	100	Triplet	β-CF_3	$J_{H\alpha-F\beta}$ = 15 Hz
	1.74 d	8.5	(10.0)										
$PtI(CH_3)_2(C_2F_5CH_2)Q_2$	1.67 d	8.7	(10.5)	1.34		58		110.4	. . .	48	Triplet	β-CF_2	$J_{H\alpha-F\beta}$ = 25 Hz
	1.77 d	8.7	(9.5)					86.4	. . .	20	Singlet	γ-CF_3	
$PtI(CH_3)_2(C_3F_7CH_2)Q_2$	1.69 d	9.5	(10)	1.35		57.5							
	1.78 d	9.0	(9.5)										
$PtI_2(CH_3)CF_3Q_2$	2.45 t[m]	7.4	(19.3)	1.00 t	5.1	65		17.0	14.5	505	Triplet	α-CF_3	
	2.88 t	8.2	18.8										
$PtI_2(CH_3)C_2F_5Q_2$	2.23 t[m]	(6)	(?)	1.16 t*	5.2	65	1.1	74.2	22	364	Triplet	α-CF_2	
	2.86 t	8.1	19.0					76.1	. . .	. . .	Singlet	β-CF_3	
trans-$PtI(CF_3)Q_2$	2.04 t	7.4	29.5	. . .	. . .	. . .		12.2	20.5	753	Triplet	α-CF_3	
trans-$PtI(C_2F_5)Q_2$	1.95 t	7.2	27	. . .	. . .	. . .		75.7	27.5	445	Triplet	α-CF_2	
								80.5	2.3	54	Triplet	β-CF_3	
trans-$PtI(C_3F_7)Q_2$	1.96 t	7.2	28	. . .	. . .	. . .		72.4	28	442	Octet	α-CF_2	$J_{F\alpha-F\gamma}$ = 11 Hz
								114.8	. . .	105	Singlet	β-CF_2	
								79.6		25	3 triplets	γ-CF_3	$J_{F\alpha-F\gamma}$ = 11 Hz; $J_{F\beta-F\gamma}$ = 2.5 Hz
$PtI(CH_3)_2CF_3A_2$	1.31		6	1.82		65	. . .[n]	17.6		539	Singlet	α-CF_3	
	1.40		6										
$PtI(CH_3)_2C_2F_5A_2$	1.25		6	1.78 d*		64	(1.2)[n]	67.0		277	Singlet	α-CF_2	
	1.43		6					79.3		13.5	Singlet	β-CF_3	
$PtI(CH_3)_2C_3F_7A_2$	1.25		6	1.81 t*		65	1.4[n]	64.3		274	2 quartets	α-CF_2	$J_{F\alpha-F\gamma}$ = 13 Hz; ΔF^{l} = 7 hz
	1.44		6					119.7		. . .	Singlet	β-CF_2	
								79.8		20.5	Triplet	γ-CF_3	$J_{F\alpha-F\gamma}$ = 13 Hz
$PtI(CH_3)_2C_7F_{15}A_2$	1.24		6	1.88 t*		62	1.6[n]	63.9		285	Triplet	α:CF_2	$J_{F\alpha-F\gamma}$ = 20 Hz
	1.45		6					*o*					
$PtI(CH_3)_2(CF_3CH_2)A_2$	1.48		*q*	1.02 q*		68	1.1[p]	53.4		94	Triplet	β-CF_3	$J_{H\alpha-F\beta}$ = 15 Hz
	1.52		*q*	1.39		61							
	1.53		*q*										
	1.63		*q*										
$PtI(CH_3)_2(C_2F_5CH_2)A_2$	1.51		*q*	1.17 t*		69	1.4	107.8		. . .	*r*	β-CF_2	
	1.55		*q*	1.45		61		86.1		19	Singlet	γ-CF_3	
	1.57		*q*										
	1.71		*q*										

$PtI(CH_3)_2(C_3F_7CH_2)A_2$	1.51	*q*	1.19 t*	69	1.2
	1.56	*q*	1.46	61	
	1.58	*q*			
	1.72	*q*			
$PtI_2(CH_3)_2A_2$	{1.46	7.5	2.43	67.5}[n]	

[a] Q = $P(CH_3)_2C_6H_5$; A = $As(CH_3)_2C_6H_5$; all fluoroalkyl groups are straight chains. [b] Solvent $CHCl_3$. Coupling constants in hertz. [c] Measured at 60 MHz. δ in ppm relative to internal TMS. [d] d = doublet; *t* = 1:2:1 triplet, q = 1:3:3:1 quartet. All refer to the central resonance (*i.e.*, not including satellites due to ^{195}Pt). [e] ^2J(P–H) + ^4J(P–H). [f] Values in parentheses are approximate. [g] Coupling constant between ^{19}F nuclei closest to the metal and the Pt-bonded methyl group which has the asterisk. [h] Measured at 94.1 MHz. δ in ppm relative to internal $CFCl_3$. [i] Central resonance, excluding ^{195}Pt satellites. [j] Nomenclature: atoms attached to the carbon next to Pt are called α, *e.g.*, $Pt-CF_2^{\alpha}-CF_2^{\beta}-CF_3^{\gamma}$; $Pt-CH_2^{\alpha}-CF_2^{\beta}-CF_3^{\gamma}$. [k] There are six other resonances, of which the strongest is at lowest field and may be due to CF_3: 81.4, 114.7, 120.7, 122.2, 123.0, 126.5 ppm. [l] See text. Δ*F* is the difference in chemical shift between two slightly nonequivalent ^{19}F nuclei. [m] Broadened peaks. [n] Solvent benzene. [o] There are six other resonances, of which the strongest is at lowest field and may be due to CF_3: 81.3, 115.1, 120.9, 122.2, 122.9, 126.6 ppm. [p] The 100-MHz spectrum in benzene: arsine methyls: 1.15, 1.19, 1.28, 1.33 ppm; Pt methyls: 1.13 q and 1.68 ppm; CH_2 gives two quartet resonances: 3.02 ppm, J_{H-F} = 15 Hz, J_{Pt-H} = 87 Hz; 3.06 ppm, J_{H-F} = 15 Hz, J_{Pt-H} = 89 Hz. [q] Cannot be assigned because the resonances are too close together. [r] See text and Figure 2. Treatment as a simple AB system gives gem J_{F-F} = 258 Hz and Δ*F* = 275 Hz.

TABLE II

Compd[a]	ConfigConfig	Color	Mp, ° C	Mol wt Calcd	Mol wt Found	Analyses, % C Calcd	C Found	H Calcd	H Found	F Calcd	F Found	I Calcd	I Found	Method of prepn	% yield
$PtI(CH_3)_2CF_3Q_2$	I	White	158–159 dec	697	698	32.72	32.35	4.05	3.94	8.17	8.95			A	80
$PtI(CH_3)_2C_2F_5Q_2$	I	White	140–142 dec	747	751	32.14	32.15	3.78	3.65	12.71	12.61			A	87
$PtI(CH_3)_2C_3F_7Q_2$	I	Cream	123–124 dec	797	762	31.63	31.66	3.54	3.63	16.69	17.15			B	70
$PtBr(CH_3)_2C_3F_7Q_2$	I	White	126–127 dec	750	766	33.61	33.38	3.76	3.84	17.72	17.46			B	62
$PtI(CH_3)_2C_7F_{15}Q_2$[b]	I	White	133–134[b] dec	997	945	30.11	29.82	2.83	2.78	28.57	23.74			B	25
$PtI(CH_3)_2(CF_3CH_2)Q_2$	I	White	158–160 dec	711	729	33.77	33.82	4.25	4.22	8.01	8.22			C	75
$PtI(CH_3)_2(C_2F_5CH_2)Q_2$	I	White	123–124 dec	761	754	33.13	35.34	3.97	4.07	12.48	12.18			C	59
$PtI(CH_3)_2(C_3F_7CH_2)Q_2$	I	White	110–113 dec	811	821	32.57	32.53	3.73	3.69	16.39	16.31			C	78
$PtI_2(CH_3)CF_3Q_2$	IV	Red	221–222 dec	809	799	26.72	27.02	3.11	3.13	7.04	7.55				62
$PtI_2(CH_3)C_2F_5Q_2$	IV	Red	183–185 dec	859	845	26.56	26.62	2.93	3.02	11.06	10.71				50
trans-$PtI(CF_3)Q_2$		White	125–127	667	648	30.60	30.90	3.32	3.36	8.54	8.33			(See Experimental Section)	
trans-$PtI(C_2F_5)Q_2$		White	117–118	717	704	30.14	29.92	3.09	3.04	13.24	13.42				48
trans-$PtI(C_3F_7)Q_2$		White	103–105	767	743	29.74	29.96	2.89	2.31	17.33	17.03				35
$PtI(CH_3)_2CF_3A_2$	I	Pale yellow	158–160 dec	785	807	29.06	28.80	3.59	3.64	7.26	7.00			A	97
$PtI(CH_3)_2C_2F_5A_2$	I	Yellow	126–128 dec	835	827	28.76	28.98	3.38	3.57	11.37	11.46			B	66
$PtI(CH_3)_2C_3F_7A_2$	I	Yellow	110–112 dec	885	879	28.49	28.41	3.19	3.33	15.02	15.17			B	63
$PtI(CH_3)_2C_7F_{15}A_2$	I	White	126–128 dec	1085	1075	27.67	28.01	2.60	2.57	26.26	26.69			B	33
$PtI(CH_3)_2(CF_3CH_2)A_2$	II	White	167–168 dec	799	799	30.06	30.03	3.78	3.74	7.13	7.36	15.88	15.59	C	80
$PtI(CH_3)_2(C_2F_5CH_2)A_2$	II	White	164–166 dec	849	854	29.70	29.67	3.56	3.56	11.19	11.39			C	88
$PtI(CH_3)_2(C_3F_7CH_2)A_2$	II	White	132–133 dec	899	874	29.38	29.14	3.36	3.24	14.79	15.20			C	70
$PtI_2(CH_3)_2A_2$	V	Red	*Ca.* 135 isomerizes 168–171 dec	843	861	25.64	25.89	3.35	3.44			30.10	29.44		16

[a] Q = $P(CH_3)_2C_6H_5$; A = $As(CH_3)_2C_6H_5$; all fluoroalkyl groups are straight chains. [b] Not obtained completely pure.

A solution of 1 in diethyl ether reacts with $(CF_3)_2CFI$ to give the iodine adduct $PtI_2(CH_3)_2A_2$, configuration V (Figure 1). The configuration is assigned on the basis of (a) its red color (by analogy with the corresponding yellow chloride and orange bromide[4b]), (b) its methyl resonance pattern, which is similar to that of the corresponding chloride,[4b] and (c) its infrared spectrum, which shows ν(Pt–C) 524 (m) and $\delta_s(CH_3)$ 1209 (s), 1231 cm^{-1} (m).

The reaction of 2 with $(CF_3)_2CFI$ is more complex and the products have not yet been fully characterized.

trans-$PtI(CH_3)Q_2$ reacts with CF_3I at room temperature to give the red complex $PtI_2(CH_3)CF_3Q_2$, configuration IV (Figure 1). The configuration follows from the ^{1}H (methyl) resonance pattern, in which the methyl groups in the phosphines appear as two triplets (plus satellites), indicating[5] trans phosphines with no plane of symmetry containing the P–Pt–P axis. The higher field triplet pattern consists of broader lines than the one at lower field, but the area under each is the same. $PtI_2(CH_3)CF_2Q_2$ is quite stable in solution, but pyrolysis gives *trans*-$PtI(CF_3)Q_2$ and methyl iodide.

trans-$PtI(CH_3)Q_2$ reacts with CF_3CF_2I at room temperature to give initially the red adduct $PtI_2(CH_3)(CF_3CF_2)Q_2$, configuration IV, which has a similar methyl resonance pattern to that of the corresponding CF_3 complex, except that the triplet due to the metal-bonded CH_3 group shows additional triplet fine structure (J = 1.1 Hz), possibly due to coupling with the CF_2 group. Solutions of $PtI_2(CH_3)(CF_3CF_2)Q_2$ slowly decompose at room temperature to give *trans*-$PtI(CF_3CF_2)Q_2$ (and presumably methyl iodide).

The only complex containing fluorocarbon which was isolated from the reaction of $CF_3CF_2CF_2I$ with *trans*-$PtI(CH_3)Q_2$ was *trans*-$PtI(CF_3CF_2CF_2)Q_2$. This was probably formed by decomposition of an unstable Pt(IV) complex of configuration IV.

The preferential loss of CH_3I from complexes of configuration IV again emphasizes the great strength of the perfluoroalkyl–platinum bond compared with the alkyl analogs. There is now much evidence elsewhere that this stability is due to overlap of filled metal d_π orbitals with σ^* orbitals of the fluoroalkyl group.[9]

Discussion of the ^{19}F Nmr Data.—The ^{19}F nmr spectra of transition metal–fluoroalkyl complexes were first analyzed by Pitcher, Buckingham, and Stone.[10] Salient features are a large shift to low field for a CF_2 group bonded directly to a transition metal and strong coupling between α- and γ-fluorine nuclei. Subsequent work[8,11,12] has yielded similar results.

Fluoromethyl Complexes.—Since the CF_3 group is bonded directly to platinum, the ^{19}F resonance is found at low field (Table I), much lower in fact than those for α-CF_2 groups in the other complexes. The coupling constant to platinum is very high, being greater than 500 Hz. McCleverty and Wilkinson have found[8] similar effects in a series of fluoroalkylrhodium complexes.

Fluoroethyl Complexes.—The α-CF_2 group in *trans*-$PtI(CF_3CF_2)Q_2$ is found to couple strongly with ^{195}Pt (J = 445 Hz) and with ^{31}P (J = 27.5 Hz). The β-CF_3 also couples with ^{195}Pt and ^{31}P, but the coupling constants are smaller. We prefer to assign the 2.3-Hz coupling (Table I) to J_{P-F} rather than $J_{F_\alpha-F_\beta}$ because the α-CF_2 resonance shows no indication of further splitting into quartets. In the platinum(IV) complexes, the coupling constants to ^{195}Pt are correspondingly smaller, except for the β-CF_3 group in the complexes $PtI(CH_3)_2(CF_3CH_2)Q_2$, configuration I, and $PtI(CH_3)_2(CF_3CH_2)A_2$, configuration II, which shows a coupling constant to ^{195}Pt of *ca.* 100 Hz. The high value is not surprising however, since the two pairs of fluorines in *trans*-$PtCl(HCF_2CF_2)\{P(C_2H_5)_3\}_2$ have been shown[13] to have J_{Pt-F} of 470 and 106 Hz, and the corresponding coupling constants in *trans*-$PtCl(CH_3CF_2CF_2)\{As(CH_3)_2C_6H_5\}_2$ are[14] 467 and 82 Hz, respectively. Clearly the presence of hydrogen atoms in the fluoroalkyl group has a pronounced effect on the platinum–fluorine coupling constants.

Fluoropropyl Complexes.—Fluorine–fluorine coupling is found in the spectra of these compounds. The α-CF_2 resonance of *trans*-$PtI(CF_3CF_2CF_2)Q_2$ approximates to a 1:3:5:7:7:5:3:1 octet, which can be interpreted in terms of an overlapping triplet of quartets. The triplet is due to coupling with ^{31}P and shows a similar coupling constant (J = 28 Hz) to that found for the α-CF_2 resonance in the corresponding CF_3CF_2 complex; the quartet (J = 11 Hz) is due to coupling with the γ-CF_3 group, and this is confirmed by inspection of the γ-CF_3 resonance, which is a triplet (J = 11 Hz), with each peak split further into triplets (J = 2.5 Hz). We attribute the 2.5-Hz splitting to coupling with the β-CF_2 group, but this could not be confirmed by inspection of the β-CF_2 resonance, since that resonance is a slightly broadened singlet (no doubt there are contributions to the broadness from small coupling with ^{31}P and with the α-CF_2).

$PtI(CH_3)_2(CF_3CF_2CF_2)Q_2$ and the corresponding bromide give a rather similar spectrum (Figure 2) except that no β–γ coupling is observed. $PtI(CH_3)_2$-$CF_3CF_2CF_2)A_2$ gives a similar spectrum for the β-CF_2 and γ-CF_3 resonances, but the α-CF_2 resonance is a quartet as expected when there can be no coupling with ^{31}P. However, close inspection of the quartet shows that each peak is a doublet (separation 7 Hz). We think this must indicate that the two ^{19}F nuclei in the α-CF_2 group are slightly nonequivalent due to some asymmetry in the molecule (possibly caused by the asymmetrical arsine ligands). The resolution of the α-CF_2 resonance of the corresponding phosphine complex

---

[9] H. C. Clark and J. H. Tsai, *J. Organometal. Chem.*, **7**, 515 (1967), and references therein; F. A. Cotton and R. M. Wing, *ibid.*, **9**, 511 (1967), and references therein.

[10] E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, **36**, 124 (1961).

[11] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 26 (1965), and references therein.

[12] P. M. Treichel and G. P. Werber, *J. Organometal. Chem.*, **7**, 157 (1967); A. J. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 3023 (1969).

[13] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, **90**, 2259 (1968).

[14] H. C. Clark and R. J. Puddephatt, unpublished results.

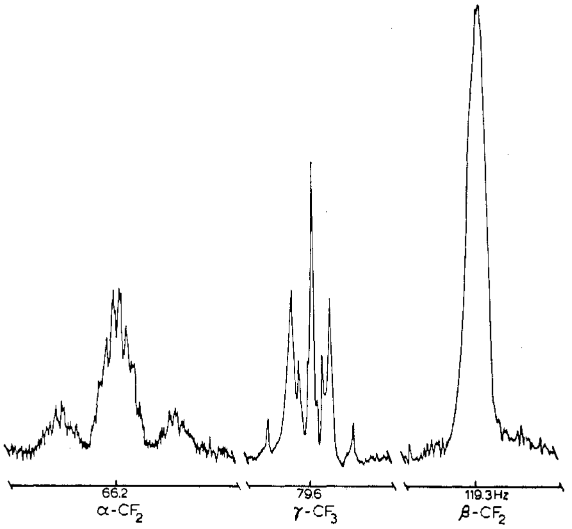


Figure 2.—Fluorine-19 nmr resonances for $PtI(CH_3)_2(C_3F_7)Q_2$' configuration I; not to scale.

was not as good and it is not surprising that a similar nonequivalence of the fluorines was not detected.

$PtI(CH_3)_2(CF_3CF_2CH_2)Q_2$, configuration I, gives a ^{19}F spectrum which consists of (1) a singlet with ^{195}Pt satellites (J = 20 Hz) attributable to the γ-CF_3 group and (2) a 1:6:10:6:1 quintet which we consider to be a triplet (J_{F-H} = 20 Hz) with overlapping ^{195}Pt satellites (J_{Pt-F} 48 Hz) and assign to the β-CF_2 group. $PtI(CH_3)_2(CF_3CF_2CH_2)A_2$, configuration II, gives a much more complicated spectrum (Figure 3) because the four ligands which are bonded to Pt adjacent to the fluorocarbon chain are all different. This makes the two protons in the CH_2 group nonequivalent (they could not be found in the proton spectrum, but the corresponding CF_3CH_2 complex shows this effect in the proton spectrum) and it seems that the asymmetry also affects the fluorine nuclei of the β-CF_2 group so that they give the XY part of an ABXY spectrum. It is not possible to obtain all the coupling constants directly from our spectrum, but if we consider, as a first approximation, that this is an XY spectrum (with each peak split into four), then we find that the difference in chemical shift between the two fluorine nuclei, ΔF is, 275 Hz (2.92 ppm) and the coupling constant between them, gem J_{F-F}, is 258 Hz. There are additional satellite peaks in the spectrum, but they are insufficiently well resolved for us to be able to assign values for J_{Pt-F}.

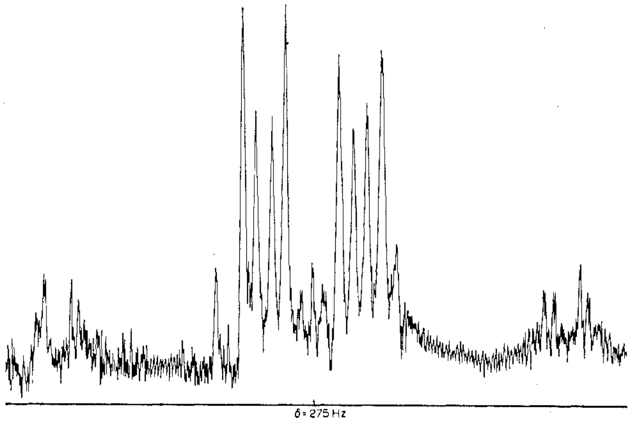


Figure 3.—β-CF_2 resonance of $PtI(CH_3)_2CH_2CF_2CF_3)A_2$, configuration II.

Fluoroheptyl Complexes.—The ^{19}F spectra of the two complexes $PtI(CH_3)_2(C_7F_{15})L_2$ are very similar (Table I). The α-CF_2 resonance is readily assigned because of its ^{195}Pt satellites {J = 285 Hz, close to the value found for other α-CF_2 groups in Pt(IV) complexes}. In the arsine derivative the main α-CF_2 resonance is split into a broadened triplet (J = 20 Hz) and this may be caused by coupling with the γ-CF_2 group. The corresponding resonance in the phosphine derivative was unresolved.

Experimental Section

Microanalyses were carried out by the Schwarzkopf Analytical Laboratory, New York, N. Y. Infrared spectra were recorded as Nujol mulls on a Beckman IR-10 spectrophotometer calibrated against polystyrene film. Molecular weights were measured in benzene solution on a Hitachi Perkin-Elmer instrument, Model 115. Melting points were recorded by capillary methods and are corrected. The 60-MHz nmr spectra were recorded on a Varian Associates A-60 spectrometer. The 100- and 94.1-MHz nmr spectra were recorded on a Varian Associates HA 100 spectrometer. Variable offset for frequency-swept ^{19}F spectra was obtained by replacing the manual oscillator with a variable external oscillator.

Preparation of the Complexes [A = $As(CH_3)_2C_6H_5$; Q = $P(CH_3)_2C_6H_5$; L = A or Q].—The preparation of *cis*-$Pt(CH_3)_2L_2$ and *trans*-$PtI(CH_3)L_2$ is described elsewhere.[4] All other complexes were prepared from these as follows (see Table II). Petroleum ether had a boiling range of 30–60°. Free iodine was removed from C_3F_7I and $C_7F_{15}I$ by shaking them with mercury.

Procedure A.—About 2 ml of the fluoroalkyl halide was condensed onto powdered *cis*-$Pt(CH_3)_2L_2$ (0.5 g) in a 20-ml Pyrex tube. The tube was sealed under vacuum and allowed to warm to room temperature. Colorless crystals formed after 2 days. The excess fluoroalkyl halide was evaporated off and the product was washed with petroleum ether.

Procedure B.—A solution of *cis*-$Pt(CH_3)_2L_2$ (0.5 g) in the fluoroalkyl halide (2 ml) was set aside for 2 days in the dark at room temperature. The excess fluoroalkyl halide was removed under reduced pressure and the resulting oil was allowed to crystallize under petroleum ether or methanol. The $C_7F_{15}I$ adducts were recrystallized from chloroform–petroleum ether.

Procedure C.—Fluoroalkyl iodide (1 ml) was added to a solution of *cis*-$Pt(CH_3)_2L_2$ (0.4 g) in diethyl ether (5 ml) and the mixture was set aside in the dark for 2 days. The CF_3CH_2I adducts precipitated out. In the other cases the solution was evaporated to dryness under reduced pressure and the resulting oil was allowed to crystallize under petroleum ether. Recrystallization, if necessary, was done from chloroform–petroleum ether.

$PtI_2(CH_3)CF_3Q_2$.—Trifluoromethyl iodide (3 ml) was condensed onto *trans*-$PtI(CH_3)Q_2$ (0.20 g) in a 20-ml Pyrex tube which was sealed under vacuum. The red solution was set aside at room temperature for 3 days and red needles were formed. The excess CF_3I was evaporated off and the residue was recrystallized from chloroform–petroleum ether or dichloromethane–methanol.

$PtI_2(CH_3)(CF_3CF_2)Q_2$.—A similar procedure was used, but the product did not precipitate from the reaction mixture. The red solution was evaporated to dryness to give an oil which was crystallized from chloroform–methanol.

trans-**$PtI(CF_3CF_2)Q_2$.**—A similar procedure was used, but with a reaction time of 1 month. The initially red solution became colorless and evaporation of the excess CF_3CF_2I gave an oil which crystallized under methanol.

***trans*-PtI($CF_3CF_2CF_2I$)Q_2.**—$CF_3CF_2CF_2I$ (2 ml) was added to *trans*-PtI(CH_3)Q_2 (0.18 g); the mixture was set aside in the dark for 1 day and then evaporated to dryness and extracted with petroleum ether containing *ca.* 5% chloroform. The red residue did not contain fluorine. The extracts were evaporated to dryness and allowed to crystallize under methanol.

Pyrolysis of PtI(CH_3)$_2$$CF_3$$Q_2$.—The complex (0.49 g) was heated at 180° under vacuum. The evolved gas was shown to be mainly ethane by its infrared spectrum. The residue was recrystallized from methanol to give *trans*-PtI(CF_3)Q_2 as white plates (0.40 g).

Pyrolysis of PtI_2(CH_3)$CF_3$$Q_2$.—The complex (0.32 g) was heated to 225° under vacuum. The evolved gas was shown to be mainly methyl iodide by its infrared spectrum. The residue was recrystallized from methanol to give *trans*-PtI(CF_3)Q_2 (0.22 g).

Reaction of *cis*-Pt(CH_3)$_2$$L_2$ with (CF_3)$_2$CFI.—To a solution of *cis*-Pt(CH_3)$_2$$A_2$ (0.31 g) in diethyl ether (6 ml) was added (CF_3)$_2$CFI (0.5 ml) which had been previously purified by shaking with mercury and distillation. The mixture was set aside in the dark for 2 days and gave a red precipitate of the iodine adduct PtI_2(CH_3)$_2$$A_2$, configuration V. A sample of (CF_3)$_2$CFI which was kept next to the reaction vessel did not undergo any decomposition to free iodine during this period of time.

A similar experiment using *cis*-Pt(CH_3)$_2$$Q_2$ gave a mixture of products which have not yet been fully characterized.

Other Reactions.—CH_3CF_2Cl or CF_3Br did not react with *cis*-Pt(CH_3)$_2$$Q_2$ using procedure A; however addition of 1% ferric chloride and diethyl ether catalyzed the reaction of CF_3Br and a product was obtained which had the ^1H and ^{19}F nmr spectra expected for PtBr(CH_3)$_2$$CF_3$$Q_2$. A satisfactory elemental analysis could not be obtained, however.

CF_2=CFBr reacted with *cis*-Pt(CH_3)$_2$$Q_2$, using procedure A, to give *trans*-PtBr(CH_3)Q_2.

trans-PtI(CH_3)Q_2 was recovered unchanged from a solution in CF_3CH_2I after 12 days in the dark at room temperature.

Acknowledgments.—We gratefully acknowledge the work done by Dr. B. K. Hunter and Miss Linda Ball to produce the ^{19}F nmr spectra. We thank the National Research Council, Ottawa, for financial support, and Johnson, Matthey Co. for the loan of platinum compounds.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CASE WESTERN RESERVE UNIVERSITY, CLEVELAND, OHIO 44106

The Circular Dichroism of Tetradentate Schiff Base Chelates of Oxovanadium(IV)

BY RICHARD L. FARMER AND F. L. URBACH*

Received January 19, 1970

The circular dichroism (CD) and electronic absorption spectra of some oxovanadium(IV) complexes with tetradentate Schiff bases derived from (*S*)-(+)-propane-1,2-diamine and (*SS*)-(+)-cyclohexane-1,2-diamine have been measured in several solvents. On the basis of the CD data, both the preferred conformation of the central chelate ring and the absolute configuration of the flattened tetrahedral array of ligand donor atoms about the oxovanadium(IV) ion have been assigned. Improved band resolution occurs in the CD spectra compared to the absorption spectra, and tentative band assignments have been made.

Introduction

Previous studies have established the utility of circular dichroism (CD) measurements for determining the preferred chelate ring conformation and donor atom configuration of tetradentate copper(II),[1] nickel(II),[2,3] and zinc(II)[4] complexes with optically active Schiff base ligands. In this paper, the results of these prior investigations are applied to elucidate the stereochemical details of several analogous square-pyramidal[5,6] oxovanadium(IV) chelates. The circular dichroism spectrum of a similar oxovanadium(IV) complex, VO(acac)$_2$(−)pn,[7] has been published, but no attempt was made to interpret the data in terms of a particular stereochemical model.

The electronic structures of oxovanadium(IV) complexes have been the subject of many investigations,[8,9] and several recent reports[10–12] have dealt specifically with the absorption spectra of complexes of the type reported here. The application of circular dichroism measurements to these complexes offers the possibility of revealing more detailed band splittings than are obtained from absorption spectra. This advantage of CD, which arises because of the signed bands, narrower band widths, and differences in selection rules, is sometimes limited by the adverse effects of overlapping bands of opposite sign.[13] By a careful comparison of the absorption and CD spectra of a series of related complexes in several solvents, the ambiguities caused by band overlap can be minimized and additional spectral information may be obtained.

---

* To whom correspondence should be addressed.

(1) R. S. Downing and F. L. Urbach, *J. Amer. Chem. Soc.*, **91**, 5977 (1969).

(2) R. S. Downing and F. L. Urbach, *ibid.*, **90**, 5344 (1968).

(3) R. S. Downing and F. L. Urbach, *ibid.*, in press.

(4) B. Bosnich, *ibid.*, **90**, 627 (1968).

(5) L. J. Boucher, D. E. Bruins, T. F. Yen, and D. L. Weaver, *Chem. Commun.*, 363 (1969).

(6) D. Bruins and D. L. Weaver, *Inorg. Chem.*, **9**, 130 (1970).

(7) K. M. Jones and E. Larsen, *Acta Chem. Scand.*, **19**, 1210 (1965).

(8) J. Selbin, *Chem. Rev.*, **65**, 153 (1965).

(9) J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).

(10) L. J. Boucher, E. C. Tyman, and T. F. Yen, *Inorg. Chem.*, **7**, 731 (1968).

(11) L. J. Boucher and T. F. Yen, *ibid.*, **7**, 2665 (1968).

(12) L. J. Boucher and T. F. Yen, *ibid.*, **8**, 689 (1969).

(13) R. D. Gillard in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Wiley-Interscience, New York, N. Y., 1968, Chapter 5.