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Electronic, Counterion and Medium Effects on the Bonding Mode of the Selenocyanate Ion in *trans*-Hydridoselenocyanatotetrakispiperidineiridium(III) Complexes*

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The results of infrared spectral studies of the complexes trans-*[Ir(pip)$_4$(H)CNSe] Y (pip = piperidine; CNSe$^-$ = selenocyanate ion, bonding mode unspecified; Y = NCSe$^-$, B(C$_6$H$_5$)$_4^-$, and ClO$_4^-$), both in the solid state and in solution, have shown them to be ideal systems for the investigation of ambidentate ligand bonding mode controls. The greater stability of the N-bound selenocyanate, with SeCN$^-$ as the counterion, both in the solid state and in solution (irrespective of solvent dielectric), serves to further confirm the existence of antisymbiosis in an octahedral complex of a class (b) metal involving a strong* trans-*director (H$^-$) with no π-bonding capability. The greater stability of the Se-bound selenocyanate, with B(C$_6$H$_5$)$_4^-$ as the counterion, in the solid state is a clear-cut example of counterion bonding mode control. The selenocyanato–tetraphenylborate complex was found to be subject to a KBr-assisted isomerization in the solid state, and all three complexes were observed to undergo a heterogeneous KBr-catalyzed ionization of the coordinated SeCN$^-$ ion in DMSO solution, when studied in KBr cells. In CH$_2$Cl$_2$ solution, where minimal KBr catalysis is observed, hydride transfer to the solvent, with a concomitant loss of NCSe$^-$ to give a five-coordinate intermediate, which recombines with NCSe$^-$ to form* trans-*[Ir(pip)$_4$(SeCN)$_2$]$^+$, occurs instead over an extended time period. The νCN frequency of the non-coordinated NCSe$^-$ is very sensitive to the solvent dielectric, suggesting the existence of H-bonding to the amine proton of the piperidine ligands in the low dielectric solvents. The complexes* trans-*[Ir(pip)$_4$(H)X] ClO$_4$ (X = NCS$^-$, CN$^-$) were included in the study, for purposes of comparison. The νIr–H frequency exhibited by the cyanide complex was found to be very low, due to the strong* trans-*influence of the cyanide group.*

Introduction

The overwhelming majority of the systems used to study symbiosis [1] and antisymbiosis [2] have been, respectively, octahedral complexes of class (a) metals and square planar or linear complexes of class (b) metals [3–5]. Recently, Weddle, *et al.* [6] observed antisymbiotic behavior in the class (b) octahedral system, *trans*-[Ir(pip)$_4$(H)CNS] Y, where pip = piperidine, Y = SCN$^-$ and B(C$_6$H$_5$)$_4^-$, and CNS indicates the presence of the thiocyanate ion without specifying its bonding mode. Weddle, *et al.* [6] also found the thiocyanate's bonding mode in this complex to be sensitive to both counterion and medium control. The use of the *trans* hydride ligand established, for the first time, the antisymbiotic behaviour of an ambidentate ligand *trans* to a strong *trans* director which possesses no π-bonding capability.

In the present study, we sought to extend this investigation to include the analogous selenocyanate complex, with several different counterions in various media, in the hope of further establishing the existence of antisymbiosis in octahedral complexes of class (b) metals. The corresponding perchlorate salts of *trans*-[Ir(pip)$_4$(H)X]$^+$, where X = NCS$^-$ and CN$^-$, were included in the study for comparison purposes.

Experimental

Preparation of Complexes

The *trans*-[Ir(pip)$_4$(H)NCX] XCN (X = S, Se) complexes used in this study as starting materials were prepared according to methods previously reported by Birnbaum [7, 8].

Trans-*hydridoselenocyanatotetrakispiperidineiridium(III) tetraphenylborate*

Trans-[Ir(pip)$_4$(H)NCSe] SeCN (0.759 g, 1.02 mmol) was dissolved in 80 ml of CH$_2$Cl$_2$ and filtered through a fine-porosity frit. Sodium tetraphenylborate (0.546 g, 1.60 mmol) in 60 ml of ethanol was

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TABLE I. Analytical Data for the *trans*-[Ir(pip)$_4$(H)X] Y Complexes.

X	Y	% Calcd.			% Found		
		C	H	N	C	H	N
$NCSe^-$	$NCSe^-$	35.5	6.1	11.3	35.5	6.0	11.0
$SeCN^-$	$B(C_6H_5)_4^-$	56.4	6.8	7.3	56.4	6.7	7.5
$NCSe^-$	ClO_4^-	34.2	6.1	9.5	34.4	5.9	9.5
NCS^-	ClO_4^-	36.5	6.5	10.1	36.5	6.7	9.9
CN^-	ClO_4^-	38.3	6.8	10.6	38.6	6.7	10.5

also filtered and the two filtrates were combined. Evaporation to dryness of the resultant solution left a residue which was vigorously stirred in 100 ml of distilled water for 20 min and separated by filtration. Thorough washing with 10 ml portions of distilled water, followed by drying *in vacuo* at room temperature left the crude pale yellow product in 88% yield.

The crude product was purified by dissolving 1.82 g (1.90 mmol) of it in 150 ml of CH_2Cl_2, followed by addition of 50 ml of absolute ethanol containing 0.223 g (0.652 mmol) $NaB(C_6H_5)_4$, according to the procedure outlined above. This resulted in an 82% yield of pure [Ir(pip)$_4$(H)SeCN]B(C$_6$H$_5$)$_4$. The complex was diamagnetic, decomposed without melting at 166 °C and yielded the following X-ray powder diffraction data, 8 most intense lines: *d* (A) (I/I$_o$): 14.97 (0.60), 13.18 (0.80), 8.42 (1.00), 7.19 (0.70), 6.55 (0.60), 4.87 (0.40), 4.14 (0.70), 3.90 (0.60).

Trans-*hydridoisothiocyanatotetrakispiperidineiridium(III) perchlorate*

Trans-hydridoisothiocyanatotetrakispiperidineiridium(III) thiocyanate [8] (1.49 g, 2.30 mmol) was dissolved in *ca.* 135 ml of absolute methanol, and the resultant solution filtered through a fine-porosity scintered glass frit. To the filtrate were added 50 ml of water and then *ca.* 200 ml of saturated aqueous potassium perchlorate. The yellow precipitate which formed immediately was digested for 45 min, separated by filtration, washed with several portions of water, and vacuum desiccated at room temperature. The dried product (1.26 g, 1.82 mmol, 79%) had a canary yellow color, was diamagnetic, and upon being heated, gradually decomposed without melting. X-ray powder diffraction data, 8 most intense lines: *d* (A) (I/I$_o$): 9.82 (1.00), 8.50 (0.20), 7.08 (0.20), 6.12 (0.80), 5.20 (0.40), 4.84 (0.30), 4.14 (0.50), 3.79 (0.40).

Trans-*hydridoisoselenocyanatotetrakispiperidineiridium(III) perchlorate*

Trans-hydridoisoselenocyanatotetrakispiperidineiridium(III) selenocyanate [8] (0.749 g, 1.01 mmol) was dissolved in 71 ml of methylene dichloride, and the resultant solution filtered through a fine-porosity scintered glass frit. Sodium perchlorate (1.25 g, 10.2 mmol) was dissolved in 50 ml of absolute methanol, and this solution was similarly filtered. The methylene dichloride and methanol filtrates were combined, and evaporated to dryness *in vacuo* at room temperature. The resultant non-volatile material was thoroughly washed with several portions of water and vacuum desiccated at room temperature. The dried product (0.671 g, 0.909 mmol, 90%) was a canary yellow, diamagnetic solid that, upon being heated, gradually decomposed without melting. X–ray powder diffraction data, 8 most intense lines: *d* (A) (I/I$_o$): 9.71 (1.00), 8.15 (1.00), 6.96 (0.90), 6.41 (0.60), 5.47 (0.60), 4.72 (0.90), 3.83 (0.80) 3.12 (0.70).

Trans-*hydridocyanotetrakispiperidineiridium(III) perchlorate*

A suspension of ammonium hexachloroiridate(IV) (2.28 g, 5.17 mmol) in piperidine (19 ml. 190 mmol) was refluxed and the ensuing piperidine-insoluble material treated with water (40 ml), as described previously [9]. To the resultant aqueous filtrate was added potassium cyanide (1 g, 15 mmol, dissolved in water, 10 ml). This reaction mixture was allowed to stand for 45 min and was then filtered. The addition to the filtrate of saturated aqueous potassium perchlorate (50 ml) produced an immediate pale yellow precipitate. After a 60 min digestion period, the precipitate was separated by filtration, washed with several portions of water containing a trace of potassium perchlorate, and vacuum desiccated at room temperature. The dried product (0.794 g, 23%) had a canary yellow color, was diamagnetic, and upon being heated, gradually decomposed without melting. We were unable to obtain a satisfactory X-ray powder pattern for the complex.

The analytical data obtained for the compounds used in this study are shown in Table I.

Physical Measurements

The magnetic susceptibility and X-ray diffraction instruments have been described elsewhere [9]. Infrared spectra of the selenocyanate and thiocyanate complexes were recorded on a Perkin–Elmer model

TABLE II. Initial νCN Stretching Frequencies and Integrated Absorption Intensities for *trans*-$[\mathrm{Ir(pip)_4(H)X}]$Y Complexes.

Medium or Solvent	νCN (cm^{-1}) for X = CNS^{-}			νCN (cm^{-1}) for X = $CNSe^{-}$			νCN (cm^{-1}) for X = CN^{-}
	Y = NCS^{-}[6]	$B(C_6H_5)_4^{-}$[6]	ClO_4^{-}	$NCSe^{-}$	$B(C_6H_5)_4^{-}$	ClO_4^{-}	ClO_4^{-}
Nujol Mull	2090 (N) 2045 (ionic)	2104 (S)	2081 (N)	2087 (N) 2049 (ionic)	2099 (Se)	2072 (N)	2114
KBr disk	2087 (N) 2045 (ionic)	2087 (N)	2085 (N)[a]	2087 (N) 2050 (ionic)	2086 (N)	2090 (N) 2075 (?) }[d]	2117
CH_2Cl_2[b]	2087 (N) 2046 (ionic)	2104 sh(S) 2087 (N)	2090 (N)	2089 (N) 2060 (ionic)	2088 (N)	2090 (N)	2124[c]
DMSO[b]	2087 (N) 2057 (ionic)	2087 (N)	2091 (N)	2092 (N) 2075 (ionic) }[d]	2090 (N)	2093 (N)	–
	νCN Integrated Absorption Intensities $\times 10^{-4}$ (M^{-1} cm^{-2})			νCN Integrated Absorption Intensities $\times 10^{-4}$ (M^{-1} cm^{-2})			
CH_2Cl_2	13.0 (N) 12.5 (ionic)	–	6.3 (N)	–	7.6 (N)	11.3 (N)	
DMSO	6.4 (N) 4.0 (ionic)	–	9.9 (N)	–	6.3 (N)	6.0 (N)	

[a] Solid state intensity ratio = 2.1. [b] Measured in CaF_2 solution cells. [c] Measured in $CHCl_2CHCl_2$ solution. [d] Doublet.

180 double-beam, grating spectrophotometer. Survey spectra (4000–400 cm^{-1}) and expanded abscissa spectra (2200–2000 cm^{-1}) were measured for each compound. Solid state samples were examined both as Nujol mulls suspended between KBr plates and as KBr disks. Solution spectra in CH_2Cl_2 and DMSO were recorded using matched CaF_2 (1.135 mm) and KBr (1.098 mm) cells. The infrared spectra of the cyanide complex were obtained by means of a Perkin–Elmer model 283 spectrophotometer. Integrated absorption intensities for the νCN bands in the infrared solution spectra (10 X expanded abscissa) were determined by Ramsay's method of direct integration [10]. Solid state integrated intensity ratios were measured relative to a salicylic acid internal standard according to the procedure of Hassel and Burmeister [11]. When samples were monitored with time, they were left in their cells until the measurements were completed. Proton nmr spectra of solutions of the complexes in d^6-DMSO were recorded using Perkin–Elmer model R-12B and Bruker HFX-90 spectrometers, employing TMS as an internal standard. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, N.Y. 11377.

Results and Discussion

The initial ir results for the complexes under consideration in this study, as well as those previously reported by Weddle, *et al.* [6], are shown in Table II, and were derived from spectra which were recorded less than 30 min after the samples were prepared.

From the position of the νCN bands and the magnitude of their integrated absorption intensities, it can be seen that, regardless of medium or counterion, the coordinated pseudohalide ions exhibit nitrogen bonding almost exclusively in these compounds. The only instances were S or Se bonding is present to a significant degree occur in the solid state when the large tetraphenylborate counterion is used. The steric interaction of this ion with the large S or Se uncoordinated end in the N-bound isomer is apparently large enough to promote S or Se bonding in the solid state. This behavior is analogous to that previously observed [12] for the $[\mathrm{Pd(Et_4dien)CNX}]$Y complexes (X = S, Se; Y = NCX^{-}, $B(C_6H_5)_4^{-}$). The overwhelming preference for N-bonding in these systems in spite of the soft Ir(III) central metal ion (compare with $[\mathrm{Ir(SCN)_6}]^{3-}$, for example [13]) demonstrates the antisymbiotic effect of the soft, *trans* hydride ligand.

An alternative explanation for why N-bonding is favored in these systems is the possibility that the steric requirements of the equatorial piperidines are large enough to crowd the sixth coordination site and thereby promote N-bonding. A Fisher–Hirschfelder–Taylor space filling molecular model of an octahedral complex having four equatorial piperidine ligands shows that at least one of the conformers of the piperidine rings presents no appreciable steric hindrance to the S or Se bound isomers.

The solid state ir results in Table II exhibit some interesting variations. For both tetraphenylborate salts, the Nujol mull spectra gave νCN frequencies which fall in the S or Se bound regions [14]. Alternatively, when these same salts were run as KBr

TABLE III. νCN Frequencies for DMSO Solutions of *trans*-[Ir(pip)$_4$(H)X] Y Complexes.

X	Y	Cells	Initial νCN (cm^{-1})	Changes with Time
NCSe$^-$	ClO$_4^-$	CaF$_2$	2093	None
NCSe$^-$	ClO$_4^-$	KBr	2120 w, 2093, 2072	Peak at 2093 dominant initially but became a shoulder after 30 min.
NCSe$^-$ (KBr doped)	ClO$_4^-$	CaF$_2$	2091	Gradual increase in intensity of a weak shoulder at 2072 (35 min), with no further change for 26 hr.
NCSe$^-$	B(C$_6$H$_5$)$_4^-$	CaF$_2$	2090	Slow growth of a shoulder at 2117 and a weak peak at 2071 after 67 hr.
NCSe$^-$	B(C$_6$H$_5$)$_4^-$	KBr	2092 sh, 2070	Shoulder at 2092 diasppeared after 30 min.
NCSe$^-$ (with stoichiometric NaClO$_4$)	(B(C$_6$H$_5$)$_4^-$	KBr	2073	No change after 26 hr.
NCSe$^-$ (with stoichiometric NaClO$_4$ and KBr)	B(C$_6$H$_5$)$_4^-$	CaF$_2$	2090, 2072 sh	Shoulder at 2072 grew to medium intensity after 45 min, then stayed constant for 50 hr.
NCSe$^-$	NCSe$^-$	CaF$_2$	2092, 2075	Peak at 2092 disappeared after 15 days, with the appearance of a medium intensity peak at 2125.
NCS$^-$	ClO$_4^-$	CaF$_2$	2091	Weak shoulder at 2060 appeared after 20 hr, then stayed constant for 5 days.

disks νCN was shifted to ~2087 cm^{-1}, which can safely be assigned as being due to the N-bound isomers. Weddle *et al.* [6] have explained this result for the thiocyanate–tetraphenylborate salt by proposing a KBr-assisted solid state isomerization. To exclude the possibility of a pressure induced isomerization, they measured the ir spectrum of the thiocyanate–tetraphenylborate compound as a cold-pressed polyethylene disk and obtained a value for νCN comparable to the value observed for the Nujol mull. The observation of this same phenomenon in the selenocyanate–tetraphenylborate analogue lends further credence to some sort of KBr-assisted pathway.

The selenocyanate–tetraphenylborate and perchlorate salts proved not to be amenable to measurements of solid state νCN integrated absorption intensity ratios. Addition of the salicylic acid internal standard apparently facilitated a side reaction whereby the hydride ligand reacted with the acidic proton of the salicylic acid to liberate H$_2$. This side reaction resulted in the appearance of anomalous low wavenumber shoulders as well as shifts in νCN. This problem was not observed with the analogous thiocyanate salts, presumably due to the lower reactivity of these compounds as a result of the thiocyanate ligand's having a weaker *trans*-effect than selenocyanate. The same reactivity trend (increasing reactivity with increasing *trans*-effect of the *trans* ligand) has previously been noted for the reaction of octahedral Ir(III) hydride complexes with dilute mineral acids [15].

The solid state spectra of the selenocyanate–perchlorate salt produced some perplexing results. Measured as a Nujol mull, it exhibited the lowest N-bound νCN frequency of any compound investigated in this study (2072 cm^{-1}). This peak can be confidently assigned as being due to an N-bound selenocyanate, since it is far too low for Se-bonding, and is more than 20 cm^{-1} higher than that exhibited by ionic selenocyanate in Nujol. Nujol mull spectra of the cyanide-, thiocyanate- and selenocyanate–perchlorate salts were recorded in the ClO$_4^-$ region (1300–900 cm^{-1}) and gave strong, broad peaks centered at 1100 cm^{-1} as well as medium intensity peaks at 935 cm^{-1}. These bands correlate well with previously determined ir frequencies for ionic perchlorate [16].

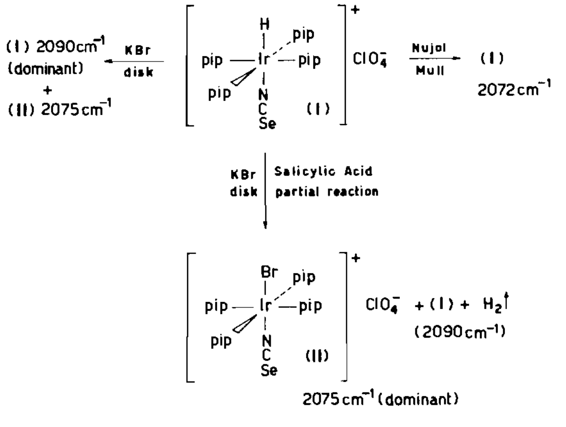
When run as a KBr disk, the selenocyanate perchlorate complex gave a doublet of peaks at 2090 cm^{-1} and 2075 cm^{-1}, with the 2090 cm^{-1} peak being slightly more intense. Upon the addition of salicylic acid, the KBr disk spectrum showed the same two peaks except that now the 2075 cm^{-1} peak was definitely the more dominant. Our rationale for these results is diagrammed below.

The N-bound selenocyanate–perchlorate salt (I), exhibits a single νCN peak at 2072 cm^{-1} when measured as a Nujol mull. When measured as a KBr disk, either with or without added salicylic acid, the νCN peak for compound (I) is shifted up to 2090 cm^{-1}, in good accord with other N-bound selenocyanates when recorded as KBr disks. In addition, whenever KBr is present, a second peak at 2075 cm^{-1} appears which we have attributed to the νCN of the perchlorate salt(II) in which the hydride ligand has

TABLE IV. νCN Frequencies (cm^{-1}) for CH_2Cl_2 Solutions of *trans*-[Ir(pip)$_4$(H)X] Y Complexes.

Time	X = NCSe$^-$ [a] Y = ClO_4^-	X = NCSe$^-$ [b] Y = $B(C_6H_5)_4^-$	X = NCSe$^-$ [a] Y = NCSe$^-$	X = NCS$^-$ [a] Y = ClO_4^-
Initial	2090	2088	2089 s, 2060 m	2090
1 hr	2090	2088	2119 vw, 2089 s, 2060 m	2090
2.5 hr	2090	2088, 2062 vw	2119 vw, 2089 s, 2060 m	2090
5 hr	2121 w, 2090 s, 2058 vw	2088, 2060 sh	2119 vw, 2089 s, 2060 m	2090
7 hr	2121 w, 2090 s, 2058 vw	2088, 2060 sh	2119 w, 2089[c], 2060[c]	2090
21 hr	2121 m, 2090 s, 2058 m	2125 w, 2088 m, 2060 w	2118 s, 2089 vw, 2058 s	2125 vw, 2090 s
2 days	2121 m[d], 2090 s, 2058 m[d]	2125 w, 2088 m, 2060 w	2118 m, 2058 m[e]	2125 vw, 2090 s
3 days	2121 m, 2090 m, 2055 m	2125 w, 2088 m, 2060 w	f	2125 vw, 2090 s
	——— dec. int. ———→			
6 days	f	2121 w, 2089 vw, 2060 vw	f	2125 vw, 2090 s, 2050 vw
9 days	f	2121 w	f	2120 sh, 2090 s, 2050 w
38 days	f	f	f	2120 m, 2090 s[g], 2049 vw[g,e]

[a] CaF_2 solution cells. [b] KBr solution cells. [c] Equal intensity. [d] Increased intensity. [e] H-bound (see text); νIr–H peak has slowly decreased in intensity. [f] Not recorded. [g] Decreased intensity.



been replaced by a bromide. Since salicylic acid facilitates the loss of hydride, it promotes the formation of the bromo species resulting in a dominant 2075 cm^{-1} peak. In the absence of salicylic acid, the bromide substitution reaction proceeds to a lesser extent and the 2090 cm^{-1} peak of compound (I) is more intense.

The most tentative point in this argument is our suggestion that νCN for this compound undergoes an eighteen cm^{-1} shift to higher wavenumber when run as a KBr disk as opposed to a Nujol mull. It is somewhat comforting to observe the same kind of higher wavenumber shift in the analogous thiocyanate–perchlorate salt, although it is of a much smaller magnitude.

A way of averting this problem is to assign the 2075 cm^{-1} peak of the KBr disk spectrum to the νCN of compound (I). This would result in a shift of only three wavenumbers (2072 cm^{-1} *vs.* 2075 cm^{-1}) with a change in medium. We are then faced with the more formidable problem of explaining the variation in relative intensities of the 2090 cm^{-1} and 2075 cm^{-1} peaks. It is apparent that KBr must be present in order for the 2090 cm^{-1} peak to appear. Conceivably this new peak could result from isomerization to the Se bound isomer, or some sort of bromide substitution leading to either the loss of coordinated selenocyanate with the formation of the *trans*-hydrido-bromo complex, or loss of hydride to give compound(II). The first two possibilities appear unlikely since KBr has been shown to cause isomerization to the N-bound isomer in the tetraphenylborate salts, and the presence of ionic NCSe$^-$ has not been observed in the ir spectra. Thus, according to this alternative explanation, the 2090 cm^{-1} peak would be assigned to compound(II) which means that its intensity should be enhanced by the addition of a hydride-scavenger (salicylic acid). The observation that the presence of salicylic acid served to enhance the 2075 cm^{-1} peak instead led to our assignment of the 2075 cm^{-1} peak as being due to compound (II) and the 2090 cm^{-1} peak being due to compound (I).

The results obtained from the DMSO and CH_2Cl_2 solution spectra are shown in Tables III and IV, respectively. These solvents were chosen because of their large difference in dielectric constant (CH_2Cl_2 = 9.08, DMSO = 46.7), which would presumably permit the elucidation of any solvent effect. The behaviour of the νCN bands, when measured in solution using CaF_2 cells, appears to be much more straightforward than in the solid state. Exclusive of the thiocyanate–tetraphenylborate compound, the N-bound isomer is generally the more stable isomer in these solvents. As previously explained by Weddle *et al.* [6] the initial 2104 cm^{-1} S-bound shoulder in the CH_2Cl_2 spectrum (see Table II) of the thiocyanate–tetraphenylborate salt, which disappears with time, is due to a slower rate of isomerization of the S-bound isomer in the solvent of lower ionicity. It is interesting to note that, for the selenocyanate analogue, we observed no evidence of Se-bonding in solution, in accordance with the generally greater reactivity of the selenocyanates.

An 11–12 cm^{-1} shift to higher wavenumbers is observed for the νCN bands of the ionic SCN^- and $SeCN^-$ in changing the solvent from CH_2Cl_2 to DMSO (see Table II). The lower value for the ionic νCN frequency in CH_2Cl_2 is due to the fact that this solvent is poorer at insulating ions in solution and thereby allows a significant amount of hydrogen-bonding between the free XCN^- ion and the N–H residue of piperidine. The higher dielectric DMSO prevents the H-bonding for the most part, leaving a more truely "free" pseudohalide ion.

As was the case in the solid state, the presence of KBr proved to have a significant effect on the solution ir results. It can be seen from the data in Table III that the selenocyanate–perchlorate salt exhibits essentially the same initial νCN values in DMSO solution, with or without added KBr, when measured in CaF_2 cells. In the KBr-doped sample, a weak shoulder due to ionic $SeCN^-$ appeared after 35 min, which showed no further change in intensity. However, when the same salt was monitored in KBr cells, the initial spectrum exhibited a doublet at 2093 and 2072 cm^{-1}, with the latter becoming dominant after 30 min, as the former diminished to a weak shoulder.

Similar results were obtained for the selenocyanate–tetraphenylborate salt which, when examined in KBr cells, gave a strong peak at 2070 cm^{-1} with complete loss of the 2092 cm^{-1} shoulder after 30 min. In CaF_2 cells, only the 2090 cm^{-1} peak was observed. The addition of stoichiometric $NaClO_4$ had no significant effect, while the addition of KBr to a sample which was monitored in CaF_2 cells caused the appearance of a 2072 cm^{-1} shoulder which grew to medium intensity after 45 min, and then remained constant.

From these data, we have concluded that the use of KBr solution cells with DMSO solutions of the selenocyanate-perchlorate or tetraphenylborate salts *heterogeneously* catalyzes the appearance of a ~2072 cm^{-1} ionic peak and a ~2120 cm^{-1} weak shoulder, which will be discussed later, as well as diminution of the ~2090 cm^{-1} N-bound peak. It is also apparent that dissolved KBr produces the same effect, but to a much-diminished extent, which is to say that, in this system, KBr is a much better heterogeneous than homogeneous catalyst.

It was generally found that the νCN bands exhibited a substantial time-dependence in solution but not in the solid state. When dissolved in CH_2Cl_2, all four salts appeared to undergo the same kind of transformations with varying time-dependencies. Typically, in CH_2Cl_2 (see Table IV), the initial N-bound peak was gradually joined by shoulders at ~2120 and ~2055 cm^{-1} which grew in intensity as the main N-bound peak decreased, and with long enough time,

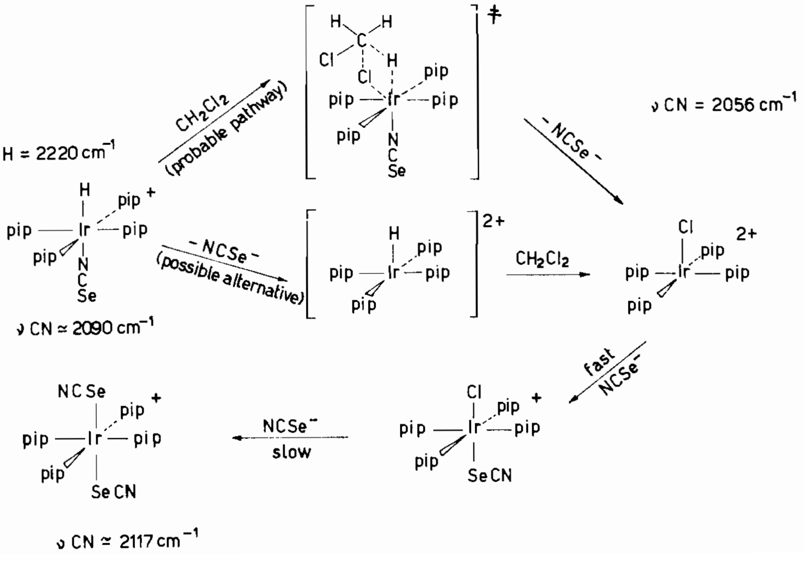


TABLE V. νIr–H and Hydride Chemical Shift Values for *trans*-[Ir(pip)$_4$(H)X] Y Complexes.

X	Y	νIr–H (cm^{-1})	δ^c (ppm)
$NCSe^-$	$NCSe^-$	2214^a, 2195^b	−26.90
$SeCN^-$	$B(C_6H_5)_4^-$	2209^a	−26.90
$NCSe^-$	ClO_4^-	2179^a	−26.20
NCS^-	NCS^-	$2215^{a,d}$	-25.73^d, -25.82^d
SCN^-	$B(C_6H_5)_4^-$	$2215^{a,e,d}$	-26.07^d
NCS^-	ClO_4^-	2188^b	−26.20
CN^-	ClO_4^-	2021^a, 2025^e	f

[a]Nujol Mull. [b]CH_2Cl_2 Solution. [c]d^6-DMSO solution, δ measured upfield relative to TMS standard. [d]Reference 6. [e]KBr disk. [f]Not observed.

vanished. With extended times, the ~2055 cm^{-1} (ionic) peak also began decreasing in intensity as the ~2120 cm^{-1} peak continued to grow. The results shown in Table IV, as well as the observations of a slow decrease in intensity of the νIr–H bands for the thiocyanate–perchlorate and selenocyanate–selenocyanate salts at 2188 cm^{-1} and ~2195 cm^{-1} respectively, closely parallel the time-dependencies found for the thiocyanate–thiocyanate and tetraphenylborate salts by Weddle, *et al.* [6]. They attributed these observations to a slow hydride transfer to the solvent, followed by the subsequent formation of the *trans*-[Ir(pip)$_4$(SCN)$_2$]$^+$ cation, giving the ~2120 cm^{-1} peak, similar to that of the known *trans*-[Pt(NH$_3$)$_4$-(SCN)$_2$]$^{+2}$ cation at 2122 cm^{-1}. We have found that the formation of the analogous *trans*-[Ir(pip)$_4$-(SeCN)$_2$]$^+$ cation also occurs.

A mechanism for these rearrangements which accounts for all of the observed spectral changes is illustrated below.

Hydride transfer to chlorinated hydrocarbons to give the chloro-substituted product is a known general reaction of transition metal hydrides [17, 18] but we have no clear-cut proof for the formation of the five-coordinate chloride intermediate. There is some question concerning whether the coordinated selenocyanate dissociates before or after solvent attack. Initial selenocyanate ionization, followed by chloride substitution would lead to the same five-coordinate intermediate. Although the existence of seven-coordinate Ir(III) complexes is not without precedent [19, 20] the steric requirements of the equatorial piperidines could make an initial *cis*-attack of CH_2Cl_2 energetically unfavorable, or, assuming the formation of the seven-coordinate activated complex, encourage the loss of selenocyanate. In the final analysis, whether selenocyanate dissociation is caused by steric hindrance or the strong *trans*-influence of the hydride ligand is a moot point, and we are left with the fact that in CH_2Cl_2, and to a lesser degree in DMSO, both the hydride and selenocyanate ligands undergo some sort of dissociation from the six-coordinate N-bound species, presumably to leave a five-coordinate intermediate.

Without exception, the presence of ionic selenocyanate was detected much sooner than that of ionic thiocyanate. Indeed, in the case of the thiocyanate–tetraphenylborate salt, ionic thiocyanate was never observed during some sixty-five days of monitoring [6]. We have interpreted the relatively rapid observation of ionic $SeCN^-$ as an indication that it is being generated faster than it is being consumed. The detection of ionic SCN^- only at extended times implies that it is generated slower than it is consumed. Since $SeCN^-$ is a better nucleophile than SCN^-, the consumption of SCN^- is, most likely, no more rapid than that of $SeCN^-$, which means that the slower rate of formation of [Ir(pip)$_4$(SCN)$_2$]$^+$, relative to that of [Ir(pip)$_4$(SeCN)$_2$]$^+$, is a result of the slower generation of ionic SCN^-. This result implies that the isothiocyanate ligand is more firmly bound to Ir(III) in *trans*-[Ir(pip)$_4$(H)(NCS)]$^+$ than is the isoselenocyanate ligand in *trans*-[Ir(pip)$_4$(H)NCSe]$^+$. The slow generation of SCN^- is also evidenced by the fact that in the thiocyanate–perchlorate salt, the ~2125 cm^{-1} shoulder of the bis-thiocyanato complex appears much sooner than the 2050 cm^{-1} shoulder. Apparently the bis-thiocyanato complex is being formed before any detectable accumulation of ionic SCN^-.

The data in Table IV show that the bis-pseudohalide complex forms most rapidly in the case of the selenocyanato–selenocyanate salt. This is to be expected since not only is this salt the only one of those shown which contains a stoichiometric amount of pseudohalide necessary for formation of the bis-pseudohalide product, but also, the presence of twice as much $SeCN^-$ pushes the $SeCN^-$ recombination steps toward completion. It is interesting to note that the most rapid formation of [Ir(pip)$_4$(SeCN)$_2$]$^+$, which initially involves selenocyanate ionization, is observed for a salt which contains selenocyanate counterions in solution. If the initial ionization step were a simple one-step self-ionization, the presence of

$SeCN^-$ counterions in solution should retard this process. Alternatively, if ionization is prompted by the *cis*-attack of CH_2Cl_2 to give a seven-coordinate activated complex, followed by a steric expulsion of $SeCN^-$, the presence of $SeCN^-$ in solution would not be expected to have a significant effect since the equilibrium is already shifted well to the right by the steric strain of the seven-coordinate intermediate.

The spectral changes observed in CH_2Cl_2 were apparently independent of the type of solution cells used. As was seen earlier in Table III, the use of KBr cells for the DMSO solution samples had a pronounced effect. In contrast to the known, general reactivity mentioned above for transition metal hydrides towards chlorinated hydrocarbons, there does not appear to have been an investigation of the reactivity of transition metal hydrides towards DMSO. We attribute the difference in KBr dependence between the CH_2Cl_2 and DMSO solutions as most probably being due to a more facile hydride transfer to the solvent in CH_2Cl_2 than in DMSO. Apparently the *cis*-attack of CH_2Cl_2 with the subsequent loss of NCX^- supercedes the ionizing effect of KBr observed in DMSO. The presence of weak bands at ~2120 cm^{-1} in some of the DMSO solutions indicates the possible formation of a small amount of the bis-pseudohalide species, but further study would be required to verify this since νIr-H was not monitored for the DMSO solutions.

Table V shows the νIr–H frequencies and hydride chemical shift values for all of the compounds studied. The hydride resonances were generally found to be broad, low intensity peaks. The presence of a doublet hydride resonance, as reported by Weddle *et al.* [6] for the thiocyanate complexes could not be confidently confirmed for the selenocyanates due to the broadness of the peaks. It can be seen from Table V that, for a given triatomic pseudohalide ligand, the perchlorate salt exhibits the lowest νIr–H value. This phenomenon most probably is a reflection of hydrogen bonding interactions between the hydride atoms and the ClO_4^- counterions. In the case of the cyanide–perchlorate complex, however, the extremely low νIr–H values must be due primarily to the strong *trans*-influence of the CN^- ligand. Unusually low νIr–H values have similarly been observed for other octahedral Ir(III) complexes in which a hydride is *trans* to a strong *trans*-effect ligand: for example, $[Ir(P(C_2H_5)_2C_6H_5)_2(CO)(H)Cl_2]$ [21] (νIr–H = 2008 cm^{-1}, H *trans* to CO); and *mer*-$[Ir(P(C_2H_5)_2C_6H_5)_3(Cl)H_2]$ [22] (νIr–H = 2026 cm^{-1} for hydride *trans* to phosphine, 2162 cm^{-1} for hydride *trans* to chloride).

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