The Vibrational Spectrum of Tricarbonyl(trichlorostibine)nickel(0), $[Ni(CO)_3(SbCl_3)]$

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The Raman and i.r. spectra of $[Ni(CO)_3(SbCl_3)]$ are reported for the first time. A complete vibrational assignment is made, consistent with C_{3v} molecular symmetry. The wavenumber of the nickel–antimony stretching vibration is *ca.* 230 cm^{-1}.

Although the tetrakis(trihalogenophosphine) compounds of nickel(0) are well characterised, similar compounds have not been reported for antimony and nickel. Reaction between tetracarbonyl nickel and antimony(III) chloride proceeds to the monosubstitution stage only.[1] The compounds $[Ni(CO_3)_3L]$ (L = $SbEt_3$ or $SbPh_3$)[2] and $[Ni(CO)_2LL']$ (L = $SbEt_3$, L' = $SbEt_2Cl$)[3] have been reported.

The vibrational spectra of monosubstituted nickel carbonyl phosphines of type $[Ni(CO)_3(PX_3)]$ have been studied in the ν(C–O) stretching region and it has been concluded that the π bonding in these compounds is very weak.[4–6] Apart from the ν(C–O) stretching frequencies, no vibrational data have been given for any antimony-substituted nickel carbonyls. In the present work the vibrational spectrum of $[Ni(CO)_3(SbCl_3)]$ is reported for the first time.

Experimental

Preparation of $[Ni(CO)_3(SbCl_3)]$.—A modification of the method of Wilkinson[1] was adopted, in which tetracarbonylnickel (5.3 g, 4.0 cm^3) was treated with vacuum-sublimed antimony(III) chloride (7.0 g) in cyclohexane under dry nitrogen and at room temperature according to equation (1). A rather large volume (*ca.* 400 cm^3) of cyclohexane is required because of the low solubility of the antimony(III) chloride. A pale buff precipitate was obtained, which was filtered off under dry nitrogen, washed with cyclohexane, and vacuum-dried. Typical yields were only 30% of theoretical, but attempts to increase the yield by heating the reactants resulted in rapid decomposition to nickel metal (Found: Cl, 28.55; Ni, 15.85; Sb, 33.0. Calc. for $C_3Cl_3NiO_3Sb$: Cl, 28.7; Ni, 15.85; Sb, 32.85%). On standing in the atmosphere, or on heating, decomposition to nickel metal occurs. It was not possible to recrystallise the compound from any solvent with which it did not react.

$$[Ni(CO)_4] + SbCl_3 \rightarrow [Ni(CO)_3(SbCl_3)] + CO \quad (1)$$

Vibrational Spectra.—Because of the insolubility or reactivity of the compound, Raman and i.r. spectra were obtained from the solid state only and polarisation measurements were not made. Raman spectra were excited using the lines at 488.0 and 514.5 nm of an argon-ion laser and a Spex 1401 double monochromator with photon-counting detection. Infrared spectra were obtained from Nujol mulls between caesium halide and Polythene plates using Beckmann IR11 (range 33—800 cm^{-1}) and Perkin-Elmer 521 (range 200—3 000 cm^{-1}) spectrometers. Band positions are accurate to ±2 cm^{-1} and the wavenumbers are given in the Table. The spectra in the ν(Sb–Cl) stretching region were not sharp enough to enable isotopic splitting due to the ^{35}Cl and ^{37}Cl isotopes to be identified.

Results and Discussion

Vibrational Spectra of $[Ni(CO)_3(SbCl_3)]$.—The molecule $[Ni(CO)_3(SbCl_3)]$ may be envisaged in 'eclipsed' or 'staggered' configurations which both conform to the point group C_{3v}. The vibrational activity of $[Ni(CO)_3(SbCl_3)]$ for the molecular point group C_{3v} is as follows: $\Gamma_{vib} = 7A_1 + 2A_2 + 9E$

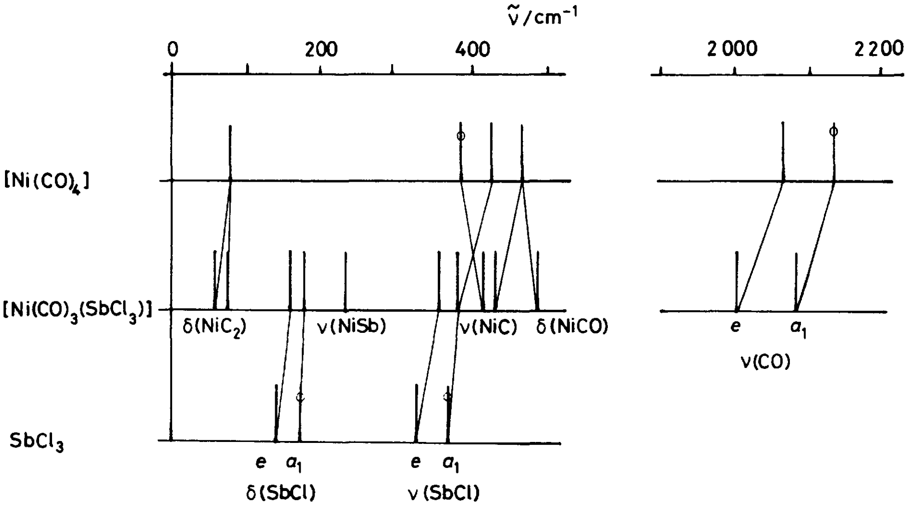

Figure. Correlation diagram for $[Ni(CO)_4]$, $SbCl_3$, and $[Ni(CO)_3(SbCl_3)]$

Table. Wavenumbers and assignments for $[Ni(CO)_3(SbCl_3)]$ (n.o. = not observed)

Symmetry class		Mode and approximate description	$\tilde{\nu}$/cm^{-1}	
			Raman	I.r.
A_1	ν_1	C–O symmetric stretch	2 075ms	2 073m
	ν_2	Ni–C–O symmetric deformation	477m	472w
	ν_3	Ni–C symmetric stretch	424ms	422mw
	ν_4	Sb–Cl symmetric stretch	376m	377m
	ν_5	Ni–Sb stretch	232ms	227ms
	ν_6	$SbCl_3$ symmetric deformation	171m	175mw
	ν_7	NiC_3 symmetric deformation	119mw	115mw
A_2	ν_8	Ni–C–O rock	inactive	inactive
	ν_9	Ni–C–O torsion		
E	ν_{10}	C–O asymmetric stretch	1 992m	1 997m
	ν_{11}	Ni–C–O asymmetric deformation	409mw	404m
	ν_{12}	Ni–C asymmetric stretch	376m,br	377m,br
	ν_{13}	Sb–Cl asymmetric stretch	351m	354s
	ν_{14}	$SbCl_3$ asymmetric deformation	156m	150m
	ν_{15}	NiC_3 asymmetric deformation	74mw	75mw
	ν_{16}	$SbCl_3$ rock	n.o.	n.o.
	ν_{17}	Ni–C–O rock	269mw	272w
	ν_{18}	NiC_3 rock	53mw	60w

(Raman active, $7A_1 + 9E$; i.r. active, $7A_1 + 9E$; inactive in Raman and i.r., $2A_2$).

Assignment. The assignment of the wavenumbers in the Table was made by analogy with the vibrational spectra of tetracarbonylnickel[6–8] and antimony(III) chloride.[9,10] This is especially important where the assignment of the A_1-species modes is complicated by the lack of polarisation data in the Raman spectrum. In the Figure a correlation diagram is shown for the molecules $[Ni(CO)_4]$, $SbCl_3$, and $[Ni(CO)_3(SbCl_3)]$.

Reference to the correlation diagram in the Figure shows that several features of the assignment of the bands in $[Ni(CO)_3(SbCl_3)]$ follow directly from the corresponding features in $[Ni(CO)_4]$ and $SbCl_3$. The ν(C–O) symmetric and asymmetric stretching vibrations, ν_1 and ν_{10}, are assignable to the bands at 2 073 and 1 997 cm^{-1}, respectively, in the i.r. (and at 2 075 and 1 992 cm^{-1} in the Raman spectrum). These compare with 2 067 and 1 996 cm^{-1} for similar vibrations in $[Ni(CO)_3(SbEt_3)]$, 2 066 and 1 988 cm^{-1} in $[Ni(CO)_3(AsEt_3)]$, and 2 127 and 2 057 cm^{-1} in $[Ni(CO)_4]$ itself.

The ν(Ni–C) symmetric and asymmetric stretching frequencies occur at 383 and 422 cm^{-1} in $[Ni(CO)_4]$ and at 373 and 421 cm^{-1}, respectively, in $[Ni(CO)_3(AsEt_3)]$.[3] A state of polarisation is assumed similar to that of the arsenic compound since no polarisation data could be experimentally obtained for $[Ni(CO)_3(SbCl_3)]$. Hence, ν_3 and ν_{12} are assigned to the bands at 422 and 377 cm^{-1} in the i.r. (424 and 376 cm^{-1} in the Raman spectrum). Likewise, the Ni–C–O deformations ν_2 and ν_{11} are assigned to bands at 472 and 404 cm^{-1} in the i.r. (477 and 409 cm^{-1} in the Raman spectrum); these occur at 486 and 429 cm^{-1}, respectively, in the arsenic compound, $[Ni(CO)_3(AsEt_3)]$, and at 462 cm^{-1} in $[Ni(CO)_4]$.

The remaining features of the Ni–C–O part of the molecule to be assigned are the NiC_3 deformations and rocking modes and the Ni–C–O rocking vibration. The Ni–C–O rocking mode, ν_{17}, is assigned to the Raman band at 269 cm^{-1} (272 cm^{-1} in the i.r.). The NiC_3 deformations, ν_7 and ν_{15}, are assigned to the bands at 119 and 74 cm^{-1} in the Raman (115 and 75 cm^{-1} in the i.r.), *cf.* 110 and 70 cm^{-1} in the spectrum of the arsenic compound. One might expect, as in the case of the Ni–C–O vibrations, that the rocking mode ν_{18} has a wavenumber less than the corresponding asymmetric deformation; a weak band at 53 (Raman) and 60 cm^{-1} (i.r.) satisfies this hypothesis and is assigned to ν_{18}.

The vibrational frequencies now remaining to be assigned all belong to the $SbCl_3$ group. The Sb–Cl stretching vibrations, ν_4 and ν_{13}, are assignable to the medium-strong intensity bands at 376 and 351 cm^{-1} in the Raman (377 and 354 cm^{-1} in the i.r.); the bands at 376 cm^{-1} in the Raman and 377 cm^{-1} in the i.r. are asymmetric in appearance and, whilst they have already been assigned to the ν_{12}(Ni–C) stretching vibration it is believed that the ν_4(Sb–Cl) vibration is also in this vicinity. The $SbCl_3$ deformations, ν_6 and ν_{14}, are correspondingly assigned to the medium bands at 171 and 156 cm^{-1} in the Raman (175 and 150 cm^{-1} in the i.r.). The $SbCl_3$ rocking mode is not observed but this could well lie in the vicinity of the NiC_3 deformation, ν_7, and could be masked by it.

Conclusions

It is seen that the vibrational spectrum of the molecule $[Ni(CO)_3(SbCl_3)]$ is consistent with an assignment based on a C_{3v} molecular symmetry. The unique feature of the spectrum is the Ni–Sb stretch at 232 cm^{-1} in the Raman (227 cm^{-1} in the i.r.). This makes an interesting comparison with the Ni–As stretching vibration in the monosubstituted compound $[Ni(CO)_3(AsEt_3)]$ of 207 cm^{-1}.[3] Corresponding data for the monosubstituted compound $[Ni(CO)_3(PX_3)]$ are not available. It would seem, therefore, that vibration for the Ni–Sb bond, occurring at a significantly higher wavenumber than for Ni–As, indicates a stronger bond than for its arsenic analogue.

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