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Gaseous Complexes of Nickel Chloride with Indium Chloride

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Received February 25, 1977 AIC70141Z

The reactions $NiCl_2(s) + nInCl_3(g) = NiCl_2(InCl_3)_n(g)$ ($n = 1, 2$) have been studied by optical spectroscopy and by quenching and analyzing the equilibrated gas phase [for $n = 1$, $\Delta H°_{298} = 22.4$ kcal mol^{-1} and $\Delta S°_{298} = 15.7$ eu; for $n = 2$, $\Delta H°_{298} = -12.3$ kcal mol^{-1} and $\Delta S°_{298} = -24.3$ eu]. In $NiIn_2Cl_8(g)$ a tetrahedral $NiCl_4$ center is indicated by the relative stabilities of the series $NiCl_2(InCl_3)_n(g)$ and $CoCl_2(InCl_3)_n(g)$. The optical spectra, however, are in favor of an octahedral $NiCl_6$ chromophore.

There are very few examples illustrating the first step of the formation of gaseous complexes according to

$$MCl_2(s) + LCl_3(g) = MLCl_5(g) \tag{1}$$

(where M = alkaline earth metal, first-row transition metal; L = Al, Ga, In, Fe), while the overall reaction

$$MCl_2(s) + 2LCl_3(g) = ML_2Cl_8(g) \tag{2}$$

has been studied extensively.[1,5] The only systems where both equilibria 1 and 2 have been investigated are $CoCl_2/InCl_3$[2] and $CuCl_2/GaCl_3$.[3] From general stability trends,[4] the system $NiCl_2/InCl_3$ seemed to be particularly well suited to study reaction 1, and it was hoped that a complete set of equilibrium constants and optical spectra in the systems $NiCl_2/InCl_3$ and $CoCl_2/InCl_3$[2] would allow one to correlate stability and structure of these complexes.

Experimental Section

Experimental and computational techniques used in this investigation have been described in ref 2, 4, and 6. Experimental details about the samples used for optical spectroscopy are given in Table I, and those for the quenching experiments in Table II.

Results

If $NiCl_2$ is heated with and without $InCl_3$, the gas-phase spectra are very similar but, at any given temperature, the $NiCl_2/InCl_3$ sample has a much higher absorption than the $NiCl_2$ sample (Figure 1). A similar observation has been made in the system $CoCl_2/InCl_3$ where the spectra of $CoCl_2(g)$ and $CoInCl_5(g)$ differ mainly in their molar absorptivities.[2] As the spectrum of $NiAl_2Cl_8(g)$[8] is very different from that of the $NiCl_2/InCl_3$ gas phase, the latter is most probably due to $NiInCl_5(g)$.

Owing to the similar spectra of $NiCl_2(g)$ and $NiInCl_5(g)$, the vapor pressure and the molar absorptivity of nickel chloride have to be known before the formation of $NiInCl_5(g)$ can be investigated by optical spectroscopy. Literature values for the vapor pressure of $NiCl_2$ vary appreciably.[7,9,10] To choose an appropriate one, we measured the absorption of $NiCl_2(g)$ in equilibrium with $NiCl_2(s)$ as a function of temperature (Table I, sample 6). In good agreement with Kubaschewski[7] and Schäfer[10] we obtained eq 3.

$$\log [p_{NiCl_2} (\text{atm})] = 10.13 (\pm 0.3) - [12420 (\pm 313)]/T \tag{3}$$ [11]

With increasing temperature, the absorption of spectrophotometric cells containing $NiCl_2$ alone, or $NiCl_2$ plus $InCl_3$, rises (Figure 1) until all the $NiCl_2$ and $InCl_3$ have evaporated. From the maximum of absorption (A_{max} at T_{max}, Table I), the analysis of the content of the cell (Ni, atomic absorption; In, EDTA titration), its volume and optical path length, the molar absorptivities ϵ of $NiCl_2(g)$ and $NiInCl_5(g)$ can be calculated.[4] In calculating $\epsilon_{NiInCl_5(g)}$ at 20.9×10^3 cm^{-1} the absorption due to the vapor pressure of $NiCl_2(g)$ is computed and subtracted from the measured maximum absorption. Values for the molar absorptivities are given in Tables I and III.

Table I. Samples for VIS Spectroscopy

Sample[a]	Vol, cm^3	Amt, mg		A_{max}	T_{max}, °C	ϵ[b]
		$InCl_3$	$NiCl_2$			
1	30.47	138.20	4.55	2.55	795	268
2	33.02	78.35	4.89	2.35	820	321
3	32.65	190.66	4.15	2.41	780	290
4	32.06	189.56	1.68	1.05	720	281
5	~32	674.6	Excess			
6	38.95		9.20	2.13	865	117[12]

[a] Optical path length is 10 cm for all samples. [b] ϵ at 20.9×10^3 cm^{-1} (in M^{-1} cm^{-1}).

Table II. Samples for Quenching Experiments (550 °C)

Vol, cm^3	Amt, mg		p, atm			$K_{c,2}$, atm^{-1}
	$NiCl_2$	$InCl_3$	$NiInCl_5$	$NiIn_2Cl_8$	In_2Cl_6	
102.9	2.770	1932	2.17×10^{-3}	1.19×10^{-2}	4.43	13.89×10^{-3}
87.9	1.354	975	1.65×10^{-3}	6.38×10^{-3}	2.54	13.01×10^{-3}

Table III. Molar Absorptivities

	MCl_2-(g)	MIn-Cl_5(g)	MIn_2-Cl_8(g)	Ref
M = Co; $\epsilon_{\sim 1.5\ \mu m^{-1}}$[a]	54	85	158	2, 12
M = Ni; $\epsilon_{\sim 2.1\ \mu m^{-1}}$[a]	117	290	88[b]	12

[a] Molar absorptivities at ν_{max} (in M^{-1} cm^{-1}). [b] $NiAl_2Cl_8(g)$.[8]

As long as there is solid $NiCl_2$ but no solid $InCl_3$ in the optical cells, eq 4 and 5 hold, where n is the number of moles

$$n_{NiInCl_5} = (A_{tot} - A_{NiCl_2(g)})V_{cell}/\epsilon_{NiInCl_5}l_{cell} \tag{4}$$

$$p_{InCl_3,\text{ tot}} = p_{InCl_3} + 2p_{In_2Cl_6} + p_{NiInCl_5} \tag{5}$$

and V the volume of the spectrophotometric cell with optical path length l. In combining eq 4 and 5 with K_{diss}, the dissociation constant of $In_2Cl_6(g)$,[13] eq 6, and with the law of ideal

$$K_{diss} = \frac{p_{InCl_3}{}^2}{p_{In_2Cl_6}} = \frac{p_m{}^2}{p_d} \tag{6}$$

$$\log [K_{diss} (\text{atm})] = 6.9562 - 6313/T$$

gases, Beer's law, and eq 3, p_{InCl_3} and p_{NiInCl_5} ($=p_{c,m}$) can be calculated.[2,4] With a graph of log $p_{c,m}$ vs. log p_m, the stoichiometry of $NiInCl_5(g)$ is confirmed:[4] Ni:In = 1:1 (±0.25).[11] For the formation of $NiInCl_5(g)$ according to reaction 1, we obtain

$$\log K_{c,1} = \log \frac{p_{c,1}}{p_m} = 3.04 (\pm 0.13) - [4670 (\pm 130)]/T \tag{7}$$ [11]

In sample 5 (Table I), the conditions to observe the spectrum of $NiIn_2Cl_8(g)$ are as favorable as we can achieve, $p_{InCl_3,tot} \simeq 5.5$ atm at 550 °C in equilibrium with $NiCl_2(s)$, but the

Table IV. Enthalpies and Entropies of Reaction in the Systems $CoCl_2/InCl_3$ and $NiCl_2/InCl_3$

		M = Co			M = Ni		
Reaction	ΔC_p(estd), cal K^{-1} mol^{-1}	ΔH°_{298}, kcal mol^{-1}	ΔS°_{298}, eu	Ref	ΔH°_{298}, kcal mol^{-1}	ΔS°_{298}, eu	Ref
$MCl_2(s) = MCl_2(g)$	−4.5	59.5	52.0	7, 16	59.1	51.7	10
$2MCl_2(g) = M_2Cl_4(g)$	2	−36.5	−32.0	14, 15	−34.6	−32.0	15
$MCl_2(s) + InCl_3(g) = MInCl_5(g)$	−1.5	19.6	16.3	2	22.4	15.7	
$MCl_2(s) + 2InCl_3(g) = MIn_2Cl_8(g)$	2.5	−19.3	−25.6	2, 5	−12.3	−24.3	
$MCl_2(g) + InCl_3(g) = MInCl_5(g)$	3	−38.9	−35.2	2	−37.5	−35.9	
$MInCl_5(g) + InCl_3(g) = MIn_2Cl_8(g)$	4	−39.2	−41.2	2	−34.5	−39.8	

[a] Estimated errors: ΔH, ±2 kcal mol^{-1}; ΔS, ±2 eu.

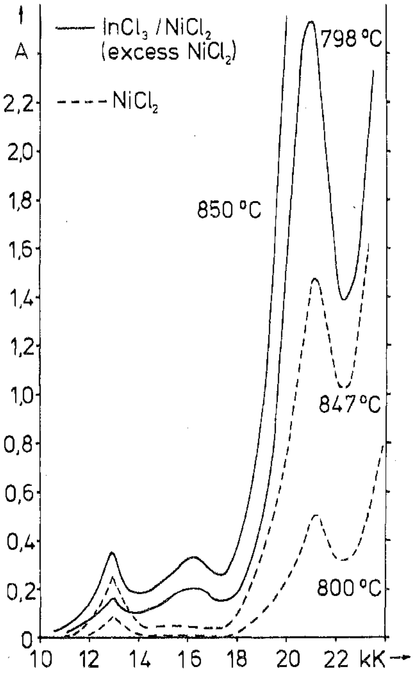

Figure 1. Spectra of $NiCl_2(g)$ (peak at 21.1×10^3 cm^{-1}) and $NiInCl_5(g)$ (peak at 20.9×10^3 cm^{-1}) at ~800 and ~850 °C.

absorption in the visible region does not exceed 0.15. This result can be used to estimate an upper limit for the molar absorptivity of $NiIn_2Cl_8(g)$, $\epsilon_{NiIn_2Cl_8(g)} < 100$ M^{-1} cm^{-1}, but it should be kept in mind that the spectra of $NiInCl_5(g)$ and $NiIn_2Cl_8(g)$ certainly overlap. The quenched gas phase of sample 5 contains more nickel than can be accounted for by $NiCl_2(g)$ and $NiInCl_5(g)$, indicating that $NiIn_2Cl_8(g)$ is formed. From two quenching experiments in special ampules[6] (Table II) we find at 550 °C

$$K_{c,2} = \frac{p_{NiIn_2Cl_8}}{p_{InCl_3}{}^2} = \frac{p_{c,2}}{p_m{}^2} = [13.45\ (\pm 0.62)] \times 10^{-3}\ atm^{-1}$$

$\Delta S_T = -22$ eu is a reasonable estimate for reaction 2.[1,4] If we use this to calculate the temperature dependence of $K_{c,2}$ from its value at 550 °C, we obtain

$$\log\,[K_{c,2}\,(atm)] = -4.78 + 2395/T \qquad (8)$$

With eq 3, 7, and 8, the molar absorptivities of $NiCl_2(g)$ and $NiInCl_5(g)$, and the assumption that $NiIn_2Cl_8(g)$ does not contribute to the absorption, the temperature dependence of the absorption of samples 1–4 (Table I) can be calculated. The calculated curves fit the experimental points extremely well. This fit is most critical for sample 4 (Figure 2) where the temperature of maximum absorption, T_{max}, is rather low and therefore the amount of $NiIn_2Cl_8(g)$ is relatively high. We consider the agreement between computed curve and experimental points (allowing for 2% error in the nickel analysis) a valid proof that eq 7 and 8 are reasonable.

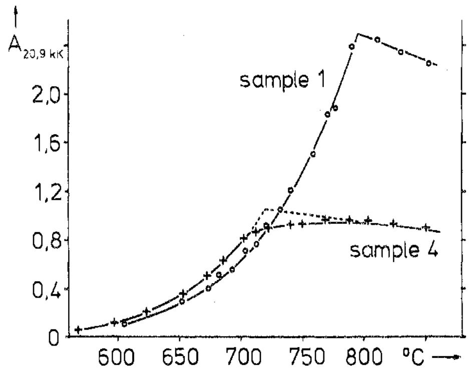

Figure 2. Temperature dependence of the absorption due to formation and decomposition of gaseous $NiCl_2/InCl_3$ complexes: ○, +, experimental points; —, curve calculated considering $NiCl_2(g)$, $NiInCl_5(g)$, and $NiIn_2Cl_8(g)$; ---, curve calculated considering $NiCl_2(g)$ and $NiInCl_5(g)$.

To further check eq 7 and 8, transpiration experiments have been performed at 528 °C. In evaluating these experiments, two equilibrium constants have to be simultaneously calculated from one set of data,[2] and therefore the limits of error in the result are large. Nevertheless, the mutual agreement[17] of the equilibrium constants from optical and from entrainment experiments is considered a confirmation of the more precise result obtained by VIS spectroscopy. $K_{c,1}$: at 528 °C (entrainment), $[1.7\ (\pm 1.4)] \times 10^{-3}$;[11] eq 7, 1.6×10^{-3}. $K_{c,2}$: at 528 °C (entrainment), $[8.4\ (\pm 59)] \times 10^{-3}$ atm^{-1};[11] eq 8, 1.6×10^{-2} atm^{-1}.

Figure 3 summarizes the results by showing the equilibrium pressures in the $NiCl_2/InCl_3$ system.

Discussion

Our result that nickel complexes are less stable than cobalt complexes in the cases $MInCl_5(g)$ and $MIn_2Cl_8(g)$ is in line with previous observations in the MCl_2/Al_2Cl_6 and MCl_2/Fe_2Cl_6 systems.[5] If ligand field stabilization is important in $ML_2Cl_8(g)$, the observed stability trend would indicate tetrahedral rather than octahedral coordination around M. But, while the absorption spectra of $CoL_2Cl_8(g)$ are consistent with a tetrahedral $CoCl_4$ chromophore,[4] this is not the case for $NiAl_2Cl_8(g)$,[8] which seems to tend toward an octahedral $NiCl_6$ center. Although we were not able to measure the spectrum of $NiIn_2Cl_8(g)$, it is safe to assume[2,4,6] that it resembles closely the spectrum of $NiAl_2Cl_8(g)$. We may therefore compare the molar absorptivities of the 21×10^3 cm^{-1} band given in Table III. The observed trend is consistent with loss of the center of symmetry of the chromophore in going from linear $NiCl_2(g)$ to trigonal $NiInCl_5(g)$[2] and appearing again in octahedral $NiAl_2Cl_8(g)$. In the analogous series of cobalt complexes, the intensity of the 15×10^3 cm^{-1} band increases (Table III). This favors the hypothesis that $CoIn_2Cl_8(g)$ has no center of symmetry, which is consistent with a tetrahedral $CoCl_4$ chromophore.

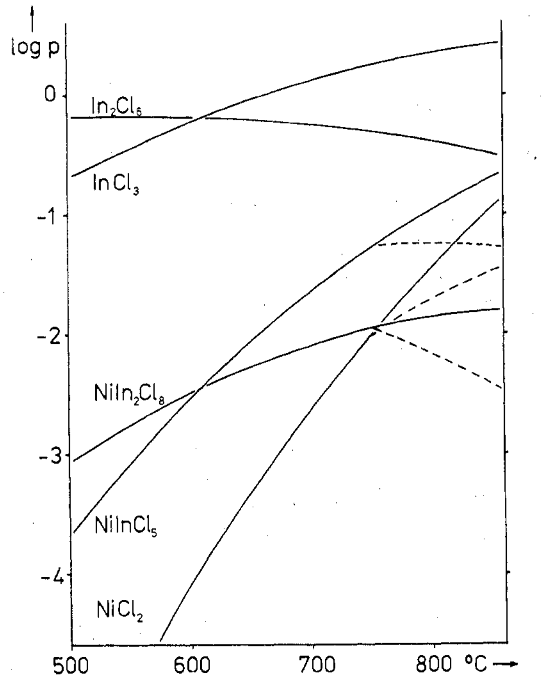

Figure 3. Partial pressures in an ampule containing 1 mol of $InCl_3$/22.4 L: —, excess $NiCl_2$; ---, 0.02 mol of $NiCl_2$/22.4 L.

For comparison, thermodynamic data related to the formation of gaseous complexes in the $NiCl_2/InCl_3$ and in the $CoCl_2/InCl_3$ systems are collected in Table IV. Within the limits of error, the enthalpies of adding the first and second $InCl_3(g)$ to $NiCl_2(g)$ are the same,[2] -36 ± 2 kcal mol^{-1}, but they are significantly less negative than for the addition of $InCl_3(g)$ to $CoCl_2(g)$. The same sequence of stability is observed in the dimerization of $CoCl_2(g)$[14] and $NiCl_2(g)$[15] (Table IV), but there the coordination is the same for both metals while here it appears to be different for $CoIn_2Cl_8(g)$ and $NiIn_2Cl_8(g)$. We have no proposition for reconciling the low stability of $NiL_2Cl_8(g)$ with its apparently octahedral $NiCl_6$ center.

Acknowledgment. This project has been supported by the Swiss National Science Foundation (Grant 2.359-0.75).

Registry No. $NiIn_2Cl_8$, 63950-50-5; $NiInCl_5$, 63950-49-2; $NiCl_2$, 7718-54-9; $InCl_3$, 10025-82-8; In_2Cl_6, 21563-01-9.

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Microwave Spectrum, Structure, Dipole Moment, and Quadrupole Coupling Constants of Iminosulfur Oxydifluoride

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Received March 25, 1977 AIC70228K

The microwave spectra of $HNSOF_2$, $DNSOF_2$, $H^{15}NSOF_2$, and $HN^{34}SOF_2$ have been measured. The molecule has a plane of symmetry containing the H, N, S, and O atoms and the hydrogen atom is trans to the oxygen atom. The following structural parameters have been determined from a least-squares analysis of the observed moments of inertia: $d(NS) = 1.466 \pm 0.003$ Å, $d(SO) = 1.420 \pm 0.005$ Å, $d(SF) = 1.549 \pm 0.002$ Å, $d(NH) = 1.023 \pm 0.007$ Å, $\angle NSO = 119.5 \pm 0.2°$, $\angle NSF = 112.9 \pm 0.1°$, $\angle FSF = 93.7 \pm 0.1°$, and $\angle HNS = 115.5 \pm 0.5°$. The values for the dipole moments obtained from Stark splittings are: $HNSOF_2$, $\mu_a = \pm 0.65 \pm 0.01$ D, $\mu_b = \pm 2.343 \pm 0.005$ D, $\mu_T = 2.43 \pm 0.01$ D; $DNSOF_2$, $\mu_a = \pm 0.45 \pm 0.05$ D, $\mu_b = \pm 2.44 \pm 0.01$ D, $\mu_T = 2.48 \pm 0.03$ D. The ^{14}N quadrupole coupling constants are: $HNSOF_2$, $\chi_{aa} = 0.46 \pm 0.02$ MHz, $\chi_{bb} = 1.75 \pm 0.02$ MHz, $\chi_{cc} = -2.21 \pm 0.005$ MHz. These data are discussed in terms of the bonding and compared with similar molecules.

Introduction

Iminosulfur oxydifluoride, HN=S(O)F_2, was first prepared by Parshall et al.[2] from NH_3 and SOF_4 in ether in the presence of NaF. It belongs to the class of sulfur–nitrogen compounds which have been of increasing interest to chemists in recent years and many studies on chemical and physical properties, bonding, and structure have been performed[3] particularly on the acyclic compounds. On the other hand, very few sulfur–nitrogen compounds have been studied by microwave spectroscopy: NSF,[4] NSF_3,[5] *cis*-HNSO,[6] and NS.[7]

Two of the most interesting questions regarding $HNSOF_2$ are the following: (a) the conformation of this molecule (four possible conformations are shown in Figure 1); (b) the detailed structure, particularly the determination of the N–S bond length, which should provide some insight on the bonding.

Microwave spectroscopy is an excellent tool for studying such problems. In the present work, the microwave spectra of $HNSOF_2$, $DNSOF_2$, $H^{15}NSOF_2$, and $HN^{34}SOF_2$ have been assigned and the structure, dipole moment, and nuclear quadrupole constants were determined.

Experimental Section

Synthesis.[32] The initial sample of the normal species $HNSOF_2$, as well as a sample of SOF_4 used in the synthesis of the ^{15}N species,