Cavell.[34] Solvents were dried over sodium. All other chemicals were used as received.

All glassware used was dried in an oven overnight and treated with a flame when assembled, and the system was purged with dry nitrogen for at least 2 h before charging the chemicals.

Mass spectra were obtained on a du Pont Model 21-491B spectrometer. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer. Proton and fluorine NMR spectra were obtained on a Varian EM-390 spectrometer at 90 and 84.6 MHz, respectively. Phosphorus NMR spectra were obtained at 32.1 MHz on a Varian CFT 20 spectrometer.

Calculations of the trial spectra were carried out using the NMRIT program of Swalen and Reilly.[35] Plots were obtained by using an NMR plot program developed by P. Shevlin at Auburn University. All the coupling constants tried were reduced by a factor of 100 in order to accommodate the parameters to the storage space of the program. Phosphorus was assigned a frequency of +80 000 Hz and fluorine (hydrogen) a frequency of −9000 Hz. Coupling constants estimated from the spectra were adjusted to the best fit between the observed spectra.

$(Me_2N)_2P[B_{10}H_{10}C_2]P(NMe_2)_2$ (II). Bis(dimethylamino)chlorophosphine (143 mmol) was added slowly, under nitrogen, to an ice-bath-cooled slurry of dilithium *o*-carborane (69.0 mmol) in ether. After 1 h, the mixture was refluxed for 20 h and filtered. The residue from evaporation of the filtrate was recrystallized from heptane yielding a white crystalline product (58%). Anal. Calcd: C, 31.6; H, 9.0; N, 14.7. Found: C, 30.9; H, 9.3; N, 14.1.

$Me_2N(F)P[B_{10}H_{10}C_2]P(F)NMe_2$ (IV). In a 150-mL Fischer–Porter[36] tube, a solution of 3.2 mmol of I in 60 mL of *n*-hexane was condensed with 70 mmol of PF_5 and then allowed to warm to room temperature. A white solid was formed. After elimination of excess PF_5, the mixture was heated in an oil bath up to 130 °C, and the white solid disappeared. Immediately the tube was cooled and the volatiles were evaporated in vacuo. The residue was extracted with 70 mL of benzene. The benzene solution was filtered and evaporated to dryness. The solid residue was shaken with 100 mL of *n*-pentane giving a white cloudy solution which was decanted. Evaporation of the pentane gave a white crystalline product (60%). Anal. Calcd: C, 21.8; H, 6.7; N, 8.5. Found: C, 22.6; H, 7.1; N, 8.3.

$FP[B_{10}H_{10}C_2]_2PF$ (III). A 200-mL Fischer–Porter tube was charged with 28 mmol of dilithium *o*-carborane in ethyl ether, and 60 mmol of PF_2Br was condensed into the tube. After 12 h at room temperature, the volatiles were removed, the mixture was filtered, and the residue was shaken with 200 mL of pentane. The white cloudy solution was decanted and evaporated to give the product. The yield was less than 30%.

Acknowledgment. The authors wish to thank the Department of Navy, Sea Systems Command, for partial support of this work. L.M.S.-T. also wishes to thank the Ford Foundation and the University of Concepcion for partial support.

Registry No. I, 22220-85-5; II, 66842-19-1; III, 66842-18-0; IV, 66842-17-9; PF_5, 7647-19-0; PF_2Br, 15597-40-7; $ClP(NMe_2)_2$, 3348-44-5.

References and Notes

(1) O. Stelzer, *Top. Phosphorus Chem.*, **9**, 1 (1977).
(2) W. Levason and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, **14**, 173 (1972).
(3) H. Beall in "Boron Hydride Chemistry", E. Muetterties, Ed., Academic Press, New York, N.Y., 1975, Chapter 9.
(4) R. Alexander and H. Schroeder, *Inorg. Chem.*, **2**, 1107 (1963).
(5) R. Holm and F. Rohrscheid, *J. Organomet. Chem.*, **4**, 335 (1965).
(6) L. Zakharkin and G. Zhigareva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 932 (1965).
(7) W. E. Hill, W. Levason, and C. A. McAuliffe, *Inorg. Chem.*, **13**, 244 (1974).
(8) T. Johnson, and J. Nixon, *J. Chem. Soc. A*, 2518 (1969).
(9) J. Morse and K. Morse, *J. Am. Chem. Soc.*, **95**, 8469 (1973).
(10) (a) S. Brown, K. Crosbie, G. Fraser, and D. W. Sharp, *J. Chem. Soc. A*, 551 (1969); (b) W. Borer and K. Cohn, *Anal. Chim. Acta*, **47**, 355 (1969).
(11) M. G. Thomas, C. W. Schultz, and R. W. Parry, *Inorg. Chem.*, **16**, 994 (1977).
(12) R. Mathis, L. Lafaille, and R. Burgada, *Spectrochim. Acta, Part A*, **30a**, 357 (1974).
(13) G. Reddy and R. Schmutzler, *Inorg. Chem.*, **6**, 823 (1967).
(14) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).
(15) J. Morse, K. Morse, and E. Falardeau, *Inorg. Chem.*, **13**, 2338 (1974); **14**, 132 (1975).
(16) J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, **13**, 364 (1970).
(17) P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).
(18) R. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
(19) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).
(20) E. Finer and R. Harris, *Prog. Nucl. Magn. Reson. Spectrosc.*, **6**, 61 (1971).
(21) D. G. Hendricker, R. E. McCarley, R. W. King, and J. G. Verkade, *Inorg. Chem.*, **5**, 639 (1966).
(22) J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *Inorg. Chem.*, **4**, 228 (1965).
(23) A. Cowley and R. Pinnell, *J. Am. Chem. Soc.*, **87**, 4454 (1965).
(24) J. Van Wazer and J. Letchel, *Top. Phosphorus Chem.*, **5**, 169 (1967).
(25) R. Taylor, R. Keiter, and L. Carey, *Inorg. Chem.*, **13**, 1928 (1974).
(26) G. Mavel, *Annu. Rep. NMR Spectrosc.*, **5B**, 1 (1973).
(27) A. Goya, M. Rosatio, and J. Gilje, *Inorg. Chem.*, **8**, 725 (1969).
(28) R. Maruca, *Inorg. Chem.*, **9**, 1593 (1970).
(29) R. Schaeffer, private communication.
(30) J. Van Wazer et al., *Top. Phosphorus Chem.*, **5**, 169 (1967).
(31) J. G. Verkade, *Coord. Chem. Rev.*, **9**, 1 (1972).
(32) C. Kutal, D. Owen, and L. Todd, *Inorg. Synth.*, **11**, 19 (1968).
(33) H. Noeth and H. J. Vetter, *Chem. Ber.*, **94**, 1505 (1961).
(34) R. Cavell, *J. Chem. Soc.*, 1992 (1964).
(35) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).
(36) A Pyrex thick-walled glass reactor equipped with a Teflon valve obtained from Fischer & Porter, Lab Crest Division, Warminster, Pa.

Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439

Some New Thermochromic Complexes of Ni(II) of the Type $[R_xNH_{4-x}]_2NiCl_4$[1]

JOHN R. FERRARO*[2] and ANNE T. SHERREN[3]

Received February 3, 1978

A new group of thermochromic complexes of Ni(II) of the type $[R_xNH_{4-x}]_2NiCl_4$ have been synthesized, where R is an alkyl or aryl group. These complexes have been prepared from the melt of 2:1 mole ratios of $R_xNH_{3-x}\cdot HCl$ and anhydrous $NiCl_2$. The complexes are brown-yellow to green-yellow at room temperature and turn blue upon heating to the thermochromic temperature (T_c). Magnetic susceptibility, far-infrared spectra, and X-ray powder diffraction patterns indicate that the room-temperature phase is polymeric, containing octahedrally coordinated metal ions with bridging chlorine atoms. The hydrogen bonding from the substituted ammonium cation is important for maintaining the structure. Magnetic susceptibility and absorption and far-infrared spectra indicate that the blue phase involves discrete tetrahedral $NiCl_4^{2-}$ ions. The thermochromism is reversible and the T_c may be controlled by the degree of hydrogen bonding available from the alkyl- or arylammonium group, by the nature and the size of the R group, and by the nature of the halogen atom in the anion. Similarities with the $[R_xNH_{4-x}]_2CuCl_4$ complexes are discussed.

Introduction

Complexes of the type C_2MX_4, where X is a halogen atom, M is a first-row transition element, and C = alkali metal, ammonium ion, or a substituted ammonium ion, are well-known. The compounds with M = Cu(II)[4-8] have been extensively studied, and those of Mn(II)[9-11] and Fe(II)[11,12] have been studied to a lesser extent.

From X-ray studies,[4,6,7,10,11] it has been established that a

0020-1669/78/1317-2498$01.00/0

Table I. Analytical Results for Several $[R_xNH_{4-x}]_2NiCl_4$ Complexes

compd	% found				% theory			
	C	H	N	Cl	C	H	N	Cl
$[CH_3NH_3]_2NiCl_4$	9.1	5.0	10.6	52.5	9.1	4.5	10.6	53.7
$[(CH_3)_2NH_2]_2NiCl_4$	16.4	5.5	9.5	47.2	16.6	5.8	9.5	48.5
$[(CH_3)_3NH]_2NiCl_4$	22.0	6.5	8.5	43.9	22.5	6.2	8.7	44.3
$[C_2H_5NH_3]_2NiCl_4$	16.2	5.4	9.3	48.4	16.4	5.5	9.6	48.5
$[(C_2H_5)_2NH_2]_2NiCl_4$	27.9	7.4	7.9	39.0	27.5	6.9	8.0	40.7
$[(C_2H_5)_3NH]_2NiCl_4$	35.0	8.2	6.9	34.6	35.6	7.9	6.9	35.1
$[i\text{-}C_3H_7NH_3]_2NiCl_4$	22.1	6.4	8.7	43.2	22.5	6.2	8.7	44.3
$[n\text{-}C_3H_7NH_3]_2NiCl_4$	22.8	6.4	8.7	44.0	22.5	6.2	8.7	44.3
$[(C_6H_5CH_2)CH_3NH_2]_2NiCl_4$	42.1	5.5	6.2	31.2	43.2	5.4	6.3	31.9

common type of structure observed for these complexes contains distorted MCl_6 octahedra sharing chlorine atoms on edge and linked into two-dimensional infinite polymeric sheets. When the substituted ammonium is not quaternary, hydrogen bonding between the cation hydrogen and the halogens of the MCl_4^{2-} anion becomes possible. Along with the nature of C and X, the hydrogen bonding plays an important role in determining the properties of the complex, as well as determining the type of structure that is stable in the solid state. For example, $CuCl_4^{2-}$ can exist as isolated planar and flattened tetrahedral ions,[4-8,13-15] depending in part on the degree of hydrogen bonding. Slight chemical modifications can alter the most stable structure. Changes in other conditions, such as temperature (thermochromism)[15,16] and pressure,[17] can also alter the structures of some of the copper complexes.

The reversible process where color changes occur with temperature is termed thermochromism.[18] Two basic types of thermochromism exist. One type deals with a phase transition whereby a change in the coordination geometry around the central ion occurs. The other type is associated with the temperature dependence of the line widths of the electronic transitions. Thermochromism may be discontinuous (abrupt changes of λ vs. T) or continuous (slow change of λ vs. T).[19]

Nickel(II) resembles copper(II) in its ability to form both tetrahedral and planar complexes and a similar but greater tendency to form stable octahedral complexes. Therefore, thermochromic transitions should also occur for Ni(II) systems, based on the possibility of interconversion between the three structural types as the temperature is raised.

Compounds with quaternary amines of the type $(R_4N)_2NiCl_4$, as well as those of type C_2NiCl_4, where C is an alkali metal, are well-known,[20] and the $NiCl_4$ anion is in a distorted T_d environment. However, Ni(II) complexes with partially substituted ammonium cations involving the $NiCl_4^{2-}$ anion remain unreported. This paper concerns itself with the syntheses and properties of a series of new thermochromic Ni(II) complexes of the type $(R_xNH_{4-x})_2NiCl_4$.

Experimental Section

Synthesis. 1. Amine Hydrochlorides. The amine hydrochlorides were synthesized by dissolving the amine in anhydrous ethyl ether. The HCl gas from a lecture bottle was slowly bubbled into the amine solution for several minutes. The precipitate was washed with anhydrous ethyl ether and filtered through a glass frit. The entire procedure took place in a dry N_2 glovebag. The excess ether in the solid was removed in a vacuum oven at room temperature.

2. $[R_xNH_{4-x}]_2NiCl_4$ Complexes. Two moles of the amine hydrochloride and 1 mol of anhydrous nickel chloride were weighed and mixed in a thick-wall (0.3 mm) Pyrex bomb tube (maximum weight of sample about 0.5 g). The tube was connected to a vacuum line (Hg diffusion pump), evacuated for several minutes, and sealed off under vacuum. The tube was then placed in a furnace and heated for several hours at about 10–25 °C above the melting point. The tube was placed in the furnace in a horizontal position during the heating process. Since the reaction seldom went to completion, it was necessary to separate the molten liquid from the unreacted products. This was done by inverting the tube in the furnace and allowing the liquid to drain to the bottom of the tube while the unreacted starting materials adhered on the surface in the upper part of the bomb tube. After cooling, all sampling was accomplished in a drybox. The products isolated from the melt upon cooling were generally brown-yellow or green-yellow and were extemely hygroscopic.

Several problems exist in attempting to make pure phases of the $[R_xNH_{4-x}]_2NiCl_4$ complexes. The reaction seldom goes to completion and one has the problem of separating the product from the unreacted reactants. Vacuum studies have shown that heating can decompose the complex to $R_xNH_{4-x}NiCl_3$ and $R_xNH_{3-x}\cdot HCl$. TGA studies indicate a further decomposition of the compound to anhydrous $NiCl_2$. An additional difficulty involves solid solution of the unreacted amine hydrochloride in the melt of the complex.

Analyses. The compounds were analyzed for carbon, hydrogen, nitrogen, and chlorine. Table I compiles the analytical results, which were obtained from the Argonne National Laboratory analytical group and from Micro-Tech Laboratories, Inc., Skokie, Ill.

Spectral Studies. For the 4000–650-cm^{-1} region, the infrared measurements were made on a Beckman IR-12 with a 6X beam condenser.[21] Samples were loaded in diamond anvil cells (DAC) in a drybox, using a microscope to ensure adequate loading. The method prevented moisture in the air from reacting with the compounds.

The Perkin-Elmer 301 infrared spectrophotometer was used to obtain far-infrared spectra (650–180-cm^{-1}). Both Nujol mull and solid-sample spectra were obtained. The Nujol mull was placed on polyethylene windows, and the solid spectra were obtained using the DAC and associated optics.[22-24]

The Cary 14R spectrophotometer was used to obtain spectra in the visible–near-infrared regions. The spectra were obtained in the solid phase using the DAC interfaced with a beam condensor.[25]

Spectroscopic studies done at high temperatures were made with a heated DAC using a Variac transformer and a chromel–alumel thermocouple (with an ice junction as a reference) to measure temperature.

Determination of Thermochromic Temperatures. The determinations of the thermochromic temperature (T_c) and the melting point were made using a Fisher-Johns melting point apparatus. The apparatus was standardized by checking melting points of several standard solids.

Magnetic Susceptibility Measurements. Magnetic moments were determined by the Gouy method using $CoHg(CNS)_4$ and $Ni(en)_3S_2O_3$ as the standard materials. Some of the moments were checked using a Faraday balance.

Results and Discussion

Table II tabulates the T_c for the complexes synthesized in this study. Also included in the table are several magnetic susceptibility results. There appears to be a qualitative relationship between the number of hydrogen atoms available for hydrogen bonding and the T_c. The greater the number of hydrogen atoms in the substituted ammonium cation, the higher is T_c. Note that if the hydrogen bonding is weak, a tetrahedral blue compound may be isolated (see that $[(n\text{-}C_3H_7)_3NH]_2NiCl_4$ in Table II is a blue liquid at room temperature). Another relationship appears to exist between the nature of the ammonium cation and T_c. Alkyl-substituted ammonium cations show lower values for T_c than aryl-substituted ammonium cations (compare $[(CH_3CH_2)_2NH_2]_2NiCl_4$ and $[(C_6H_5CH_2)CH_3NH_2]_2NiCl_4$). Some relationship may exist depending on the nature of the halogen vs. T_c. For example, $[(C_2H_5)_2NH_2]_2NiCl_4$ shows a T_c at 70 °C, whereas

Table II. Some Physical Properties for $[R_xNH_{4-x}]_2NiCl_4$ Complexes

cation	room-temp color	no. of H atoms for hydrogen bonding	T_c,[a] °C	μ_{eff},[b] μ_B
$(C_2H_5)_4N^+$	blue	0		3.87
$(CH_3)_4N^+$	blue	0		
$(n\text{-}C_3H_7)_3NH^+$	blue (liquid)	1		
$(C_2H_5)_3NH^+$	blue; turns yellow-green on standing	1	104	
$(CH_3)_3NH^+$	brown-yellow	1	70	
$(C_6H_5CH_2)CH_3NH_2^+$	brown-yellow	2	115	
$(C_2H_5)_2NH_2^+$	brown-yellow	2	70	3.44[c] 3.78[d]
$(CH_3)_2NH_2^+$	brown-yellow	2	145	
$i\text{-}C_3H_7NH_3^+$	brown-yellow	3	170	2.93[c]
$n\text{-}C_3H_7NH_3^+$	brown-yellow	3	200	
$C_2H_5NH_3^+$	brown-yellow	3	167	
$CH_3NH_3^+$	brown-yellow	3	>230	2.98[e]

[a] T_c results are given to an accuracy of ±5 °C. [b] Most of these compounds melt 15-30 °C higher than T_c. [c] At 25 °C. [d] At 80 °C. [e] At 19 °C.

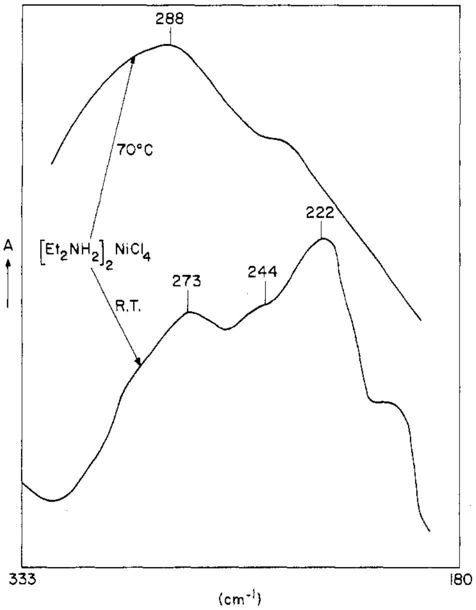

Figure 1. Far-infrared spectra of $[(C_2H_5)_2NH_2]_2NiCl_4$ at room temperature and 70 °C.

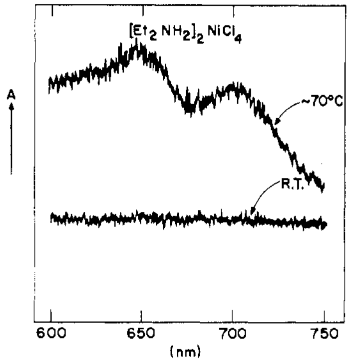

Figure 2. Electronic spectra of $[(C_2H_5)_2NH_2]_2NiCl_4$ at room temperature and 70 °C.

the T_c for $[(C_2H_5)_2NH_2]_2NiBr_4$[26] is about 50 °C. These relationships may be reconciled with the thermal motions of the NH moieties, the organic ammonium cation, and the halogen anion associated with the thermochromism.

The magnetic susceptibilities appear to run in the range of 2.9–3.4 μ_B at 25 °C, for the room-temperature phase isolated from the melt upon cooling. When these compounds are heated to T_c, the materials turn royal blue or blue-green. The complex $[(C_2H_5)_2NH_2]_2NiCl_4$ shows a magnetic moment of 3.78 μ_B at 80 °C.

A. Nature of the Solid Obtained from the Melt. The amorphous solids obtained from the melt syntheses after allowing the melt to cool to room temperature were usually brown-yellow to green-yellow. Single crystals could not be obtained and therefore an X-ray structural analysis was not possible. However, powder diffraction patterns were obtained for some of the solids and compared with patterns of the starting materials and found to be entirely different; but they were similar to other polymeric octahedral complexes (e.g., Mn^{2+}, Cu^{2+}, Fe^{2+}). Electronic, mid-infrared, and far-infrared spectral and magnetic susceptibility measurements were made. Thus, it was possible to make some inferences as to the structure of these materials. Figure 1 shows the far-infrared spectra of $[(C_2H_5)_2NH_2]_2NiCl_4$ at room temperature and at 70 °C. The room-temperature spectrum is typical of an octahedral, polymeric material containing bridging halogens and confirms the interpretation of the powder diffraction patterns. At the thermochromic temperature the spectrum changes and a single absorption occurs at 288 cm⁻¹, which corresponds to a metal–chlorine stretching vibration in a tetrahedral $NiCl_4^{2-}$ ion.[27,28] Figure 2 shows the electronic spectra at room temperature and at 70 °C for $[(C_2H_5)_2NH_2]_2NiCl_4$. It can be observed that a doublet forms at T_c with absorption maxima at 650 and 710 nm, again typical of a tetrahedral $NiCl_4^{2-}$ ion.[28-30] The magnetic susceptibilities for the brown-yellow solids show values typical for polymeric, octahedral Ni(II) complexes.[31-33] These are in the range of 2.9–3.4 μ_B at room temperature, and the value increases to ~3.8 μ_B at T_c (for example, $[C_2H_5)_2NH_2]_2NiCl_4$).

The structure of the polymeric material obtained in these studies is unknown. However, from the spectral and magnetic results obtained, it is postulated that the polymer contains distorted $NiCl_6$ octahedra, with bridging chlorine atoms shared on edge, and hydrogen bonding from the substituted ammonium cations playing an important role. The precise nature of the polymer must await X-ray structural analysis. It is thus proposed that the nature of the melt reaction may proceed as follows:

$$R_xNH_{3-x}\cdot HCl + NiCl_2(\text{anhyd}) \xrightarrow[\text{melting}]{\Delta} \underset{\substack{\text{brown-yellow,}\\ \text{distorted octahedral}\\ \text{polymer at room temp}}}{([R_xNH_{4-x}]_2NiCl_4)_x} \quad (1)$$

It should be noted that the reaction may proceed through a $R_xNH_{4-x}NiCl_3$ phase. In attempting to prepare (*n*-

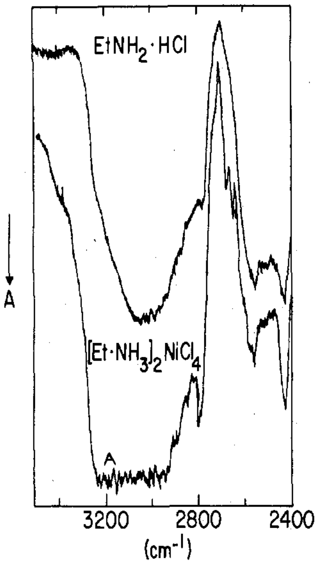

Figure 3. NH stretching vibration region for $C_2H_5NH_2$·HCl and $(C_2H_5NH_3)_2NiCl_4$.

$C_3H_7NH_3)_2NiCl_4$ a salmon-colored phase is indicated at ~140 °C, prior to reaching the thermochromic point, and may indicate an intermediate phase forming. It is not too surprising, then, that X-ray diffraction patterns may show some trichloronickelate species forming as an intermediate phase in (1) or from excess heating of the melt. Only one of the compounds—$[i\text{-}C_3H_7NH_3]_2NiCl_4$—showed a trace of the $NiCl_3^-$ anion in the powder spectrum, so this potential impurity may not be too serious a problem.

B. Nature of Blue Compounds Obtained at T_c. The spectroscopic results as illustrated in Figures 1 and 2 and the magnetic susceptibilities reaching ~3.8 μ_B at T_c are consistent with a T_d geometry occurring around the Ni atoms. Thus tetrahedral $NiCl_4^{2-}$ ions must be formed, similar to the environment of $NiCl_4^{2-}$ ions in $[(C_2H_5)_4N]_2NiCl_4$ and $[(CH_3)_4N]_2NiCl_4$.[27-29] Therefore, reaction 1 may proceed as follows at T_c:

$$\underset{\text{brown-yellow, octahedral}}{([R_xNH_{4-x}]_2NiCl_4)_x} \xrightarrow[T_c]{\Delta} 2(R_xNH_{4-x})^+ + \underset{\text{blue, tetrahedral}}{NiCl_4^{2-}}$$

The mechanism for the thermochromism observed in these complexes involves a change in geometry and coordination numbers from an octahedral (CN = 6) to a tetrahedral (CN = 4) geometry. The possibility that the thermochromism involves a five-coordinate nickel(II) complex can be ruled out on the basis of the experimental results obtained, as well as for stereochemical reasons.[34]

C. Nature of Hydrogen Bonding in Compounds. Information on the nature of the hydrogen bonding in the complexes can be derived from the monitoring of their NH vibrations. Figure 3 illustrates the NH stretching (ν_{NH}) region for $C_2H_5NH_2$·HCl and $(C_2H_5NH_3)_2NiCl_4$ polymer. In the polymer the ν_{NH} vibration shifts toward higher frequency (see A in Figure 3). Simultaneously the NH_2 bending vibration (δ_{NH_2}) at ~1620 cm^{-1} shifts toward lower frequency at ~1580 cm^{-1}. The results indicate that the hydrogen bonding is stronger in the amine hydrochloride than in the $[C_2H_5NH_3]_2NiCl_4$ polymer.

A comparison of the spectra of $(n\text{-}C_3H_7)_3N$·HCl and $[(n\text{-}C_3H_7)_3NH]_2NiCl_4$ (blue liquid—T_d monomer) in the ν_{NH} region is made in Figure 4. The strong absorption in the amine hydrochloride at ~2500 cm^{-1} disappears in the complex, and a new, strong absorption appears at ~3000 cm^{-1}, consistent with weaker hydrogen bonding in the tetrahedral compound, and is further evidence that we are not dealing with a mixture of starting materials.

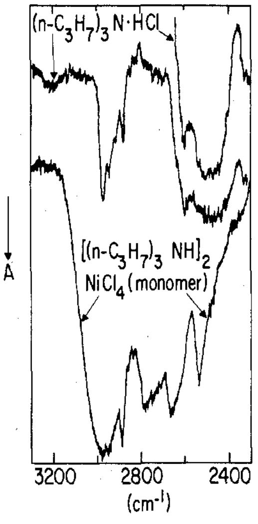

Figure 4. Comparison of the spectra of $(n\text{-}C_3H_7)_3N$·HCl and $[(n\text{-}C_3H_7)_3NH]_2NiCl_4$ monomer in the ν_{NH} region.

That the hydrogen bonding is stronger in the amine hydrochloride than in the complexes is not surprising. It is known that the very strong hydrogen bonding occurs in the amine hydrochlorides.[35-39] The order of hydrogen bonding strength in the amine hydrochlorides proceeds in the order tertiary > secondary > primary.

The weaker hydrogen bonding in the tetrahedral species is expected, as hydrogen bonds in the polymer must be weakened and broken in order for thermochromism to occur. A study[26] of $[(C_2H_5)_2NH_2]_2NiBr_4$ polymer at room temperature and at 70 °C shows that the ν_{NH} stretching vibration shifts toward higher frequency, while the δ_{NH_2} bending vibration shifts toward lower frequency, when T_c is reached, indicative of stronger hydrogen bonding which follows the order

$$R_xNH_{3-x}\cdot HCl > \underset{\text{polymer}}{([R_xNH_{4-x}]_2NiCl_4)_x} > \underset{\text{blue, monomer}}{[R_xNH_{4-x}]_2NiCl_4}$$

These results are consistent with the thermochromic mechanism postulated for these systems.

D. Similarity with Related Copper Complexes. Similarities are noted when the $[R_xNH_{4-x}]_2NiCl_4$ complexes are compared to the related $[R_xNH_{4-x}]_2CuCl_4$ complexes. The preferred geometry around the Cu atom is square planar, when x is 0 or 1. For other values of x, the preferred structure is a distorted T_d or a mixture of square-planar and distorted T_d geometries. In the nickel complexes the favored structure at x = 1 or 2 is the distorted octahedral. For x values of 3 or 4 the preferred orientation becomes T_d. Minor differences between Cu(II) and Ni(II) are probably due to Jahn–Teller effects occurring in the copper complexes, which prevent octahedral configuration for Cu(II).[40]

Presently we are working on the syntheses of the bromine and iodine analogues of these complexes. We are attempting to obtain a single crystal from solution in order to enable us to do X-ray crystal structures of the polymeric chloride compounds.[41] We are also studying the magnetic susceptibilities of the title complexes down to liquid helium temperatures.[42]

Conclusions

1. T_c is a function of R group, degree of hydrogen bonding, and nature of halogen: (a) The larger the R group, the higher is T_c; when R is alkyl, T_c is lower. (b) The greater the amount of hydrogen bonding, the higher is T_c. (c) T_c is lower for Br$^-$ than for Cl$^-$.

2. Compounds at room temperature appear to be polymers of distorted $NiCl_6$ octahedra sharing halogens at corners, containing hydrogen bonding from substituted ammonium groups. These conclusions were reached after considering data from magnetic susceptibility, far-infrared, and visible experiments, as well as powder x-ray patterns. We emphasize that the structure of the polymer can only be firmly established after X-ray structural analysis is completed.

3. The compounds are thermochromic. These conclusions were reached after consideration of the visible, far-infrared, and magnetic susceptibility data. The thermochromism must involve a change in phase in which the coordination geometry around the central nickel atom changes from octahedral to tetrahedral.

4. The thermochromism appears to be discontinuous and is reversible, although in most cases hysteresis plays an important role.

5. The strength of hydrogen bonding appears to follow the order

$$R_xNH_{3-x}\cdot HCl > \underset{\text{polymer}}{([R_xNH_{4-x}]_2NiCl_4)_x} > \underset{\substack{\text{blue,}\\ \text{monomeric}}}{[R_xNH_{4-x}]_2NiCl_4}$$

6. Similarities with related copper complexes are noted.

Acknowledgment. The authors wish to thank Dr. L. J. Basile (ANL), Professor E. Sinn (University of Virginia, Charlottesville, Va.), Professor R. Willett (Washington State University, Pullman, Wash.), and Professor Bruce B. Murray (Wisconsin University, River Falls, Wis.) for valuable discussions. We acknowledge the contributions of Drs. James R. Anderson and L. Allred of Northwestern University for several magnetic susceptibility measurements and Miss Karen Gregoire, who was a participant in the summer 1977 Undergraduate Research Participation Program coordinated by the Argonne Center for Educational Affairs, for her help in the studies of the bromine analogues of these compounds.

Registry No. $[CH_3NH_3]_2NiCl_4$ (polymer), 67114-00-5; $[(CH_3)_2NH_2]_2NiCl_4$ (polymer), 67114-01-6; $[(CH_3)_3NH]_2NiCl_4$ (polymer), 67114-02-7; $[C_2H_5NH_3]_2NiCl_4$ (polymer), 67114-03-8; $[(C_2H_5)_2NH_2]_2NiCl_4$ (polymer), 67114-04-9; $[(C_2H_5)_3NH]_2NiCl_4$ (polymer), 67114-05-0; $[i\text{-}C_3H_7NH_3]_2NiCl_4$ (polymer), 67114-06-1; $[n\text{-}C_3H_7NH_3]_2NiCl_4$ (polymer), 67114-07-2; $[(C_6H_5CH_2)CH_3NH_2]_2NiCl_4$ (polymer), 67114-08-3; $[(C_2H_5)_4N]_2NiCl_4$ (monomer), 5964-71-6; $[(CH_3)_4N]_2NiCl_4$ (monomer), 16594-86-8; $[(n\text{-}C_3H_7)_3NH]_2NiCl_4$ (monomer), 67114-09-4; $[(C_2H_5)_2NH_2]_2NiCl_4$ (monomer), 19581-94-3.

References and Notes

(1) Work performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy.
(2) Author to whom correspondence should be addressed.
(3) Argonne National Laboratory Resident Associate and Professor of Chemistry at North Central College, Naperville, Ill.
(4) R. D. Willett, O. L. Liles, and C. Michelson, *Inorg. Chem.*, **6**, 1885 (1967).
(5) J. P. Steadman and R. D. Willett, *Inorg. Chim. Acta*, **4**, 367 (1970).
(6) D. N. Anderson and R. D. Willett, *Inorg. Chim. Acta*, **8**, 167 (1974).
(7) R. D. Willett, *J. Chem. Phys.*, **41**, 2243 (1964).
(8) R. D. Willett and C. Chow, *Acta Crystallogr., Sect. B*, **30**, 207 (1974).
(9) A. Arend, R. Hoffmann, and F. Waldner, *Solid State Commun.*, **13**, 1629 (1973).
(10) E. R. Peterson and R. D. Willett, *J. Chem. Phys.*, **56**, 1879 (1972).
(11) R. D. Willett and E. F. Reidel, *Chem. Phys.*, **8**, 112 (1975).
(12) M. F. Mostafa and R. D. Willett, *Phys. Rev. B*, **4**, 2213 (1971).
(13) R. L. Harlow, W. J. Wells, G. W. Watt, and S. H. Simonsen, *Inorg. Chem.*, **13**, 2106 (1974).
(14) P. J. Lamotte-Brasseur and G. Van der Bossche, *Acta Crystallogr. Sect A*, **30**, 484 (1974).
(15) J. R. Ferraro, *J. Coord. Chem.*, **5**, 101 (1976), and references therein.
(16) R. D. Willett, J. A. Haugen, J. Lebsack, and J. Morrey, *Inorg. Chem.*, **13**, 2510 (1974).
(17) R. D. Willett, J. R. Ferraro, and M. Choca, *Inorg. Chem.*, **13**, 2919 (1974).
(18) J. H. Day, *Chem. Rev.*, **68**, 649 (1968).
(19) L. Fabbrizzi, M. Micheloni, and P. Paoletti, *Inorg. Chem.*, **13**, 3019 (1974).
(20) G. D. Stucky, J. B. Folkers, and T. J. Kistenmacher, *Acta Crystallogr.*, **23**, 1064 (1967).
(21) L. J. Basile, C. Postmus, and J. R. Ferraro, *Spectrosc. Lett.*, **1**, 189 (1968).
(22) J. R. Ferraro, S. S. Mitra, and C. Postmus, *Inorg. Nucl. Chem. Lett.*, **2**, 269 (1966).
(23) C. Postmus, J. R. Ferraro, and S. S. Mitra, *Inorg. Nucl. Chem. Lett.*, **4**, 55 (1968).
(24) J. R. Ferraro and L. J. Basile, *Appl. Spectrosc.*, **28**, 505 (1974).
(25) G. J. Long, G. Miles, and J. R. Ferraro, *Appl. Spectrosc.*, **28**, 377 (1974).
(26) J. R. Ferraro, A. T. Sherren, and K. Gregoire, unpublished data.
(27) A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).
(28) A. T. Sherren and J. R. Ferraro, *Inorg. Chim. Acta*, **22**, 43 (1977).
(29) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).
(30) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).
(31) C. E. Taylor and A. E. Underhill, *J. Chem. Soc.*, 368 (1969).
(32) P. J. Beadle, M. Goldstein, D. M. L. Goodgame, and R. Grzeskowiak, *Inorg. Chem.*, **8**, 1490 (1969).
(33) J. R. Ferraro and K. C. Davis, *Inorg. Chim. Acta*, **3**, 685 (1969).
(34) L. Sacconi, *Transition Met. Chem.*, **3**, 219 (1968).
(35) B. Chenon and C. Sandorfy, *Can. J. Chem.*, **36**, 1181 (1958).
(36) C. Brissette and C. Sandorfy, *Can. J. Chem.*, **38**, 34 (1960).
(37) R. A. Heacock and L. Marion, *Can. J. Chem.*, **34**, 1782 (1956).
(38) E. A. V. Ebsworth and N. Sheppard, *Spectrochim. Acta*, **13**, 261 (1959).
(39) P. J. Stone, J. C. Craig, and M. W. Thompson, *J. Chem. Soc.*, 52 (1958).
(40) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972.
(41) E. Sinn and J. R. Ferraro, unpublished data.
(42) E. Sinn and J. R. Ferraro, unpublished data.