Preparation and Characterization of Di(tertiary phosphines) with Electronegative Substituents. 1. Symmetrical Derivatives
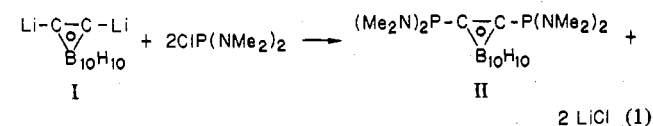
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The o-carborane–phosphino derivatives $RR'P[B_{10}H_{10}C_2]PRR'$ [R = R' = NMe_2 (II); R = NMe_2, R' = F (IV)] and $FP[B_{10}H_{10}C_2]_2PF$ (III) have been prepared and characterized by mass spectrometry and infrared and ^1H, ^{19}F, and ^{31}P NMR spectroscopy. The NMR spectra have been analyzed as $X_nAA'X'_n$ spin systems. Compound IV exists as two diastereomers.

Introduction

The preparation and coordination chemistry of symmetrical di(tertiary phosphines) has been an area of great interest for a number of years. Common backbones used are $-CH=CH-$, $-NR-$, $-(CH_2)_n-$, $-(CH_2)_nO-$, and aromatic ring systems.[1,2] o-Carborane, $B_{10}H_{10}C_2H_2$, is a particularly interesting potential backbone due to its electron-withdrawing power, electron-delocalizing ability, and its large size.[3] Phosphino derivatives of the type $R_2P[B_{10}H_{10}C_2]PR_2$ (R = C_2H_5, C_6H_5) have been prepared as well as some chelate complexes.[4-7] Previously the usual substituents on phosphorus have been phenyl rings and alkyl groups. The presence of highly electronegative groups such as NR_2 or F on phosphorus in di(tertiary phosphines) is rather rare. Fluorophosphines of the type $RN(PF_2)_2$ (R = alkyl) have been prepared and used as ligands forming four-member ring chelates.[8] Morse et al. have reported the fluorophosphine $F_2P(CH_2)_2PF_2$, but it is isolated in very small quantities and is not particularly stable.[9] We report here the preparation and characterization of symmetrical di(tertiary phosphines) with the electronegative substituents $N(CH_3)_2$ and F utilizing o-carborane as the backbone.

Results and Discission

Synthesis. The preparation of $(Me_2N)_2P[B_{10}H_{10}C_2]P-(NMe_2)_2$ was carried out in a manner analogous to that reported by Alexander and Schroeder for the $(C_6H_5)_2P$ derivative[4] (eq 1). Treatment of I with PF_2Br did not lead

$$Li-C\!\!\overbrace{\underset{B_{10}H_{10}}{}}\!\!C-Li + 2ClP(NMe_2)_2 \longrightarrow (Me_2N)_2P-C\!\!\overbrace{\underset{B_{10}H_{10}}{}}\!\!C-P(NMe_2)_2 + 2 LiCl \quad (1)$$

I   II

to the corresponding $F_2P[B_{10}H_{10}C_2]PF_2$ compound but gave the cyclic compound shown in eq 2 in low yield.

$$Li-C\!\!\overbrace{\underset{B_{10}H_{10}}{}}\!\!C-Li + PF_2Br \longrightarrow FP\overbrace{}PF + solids \quad (2)$$

III
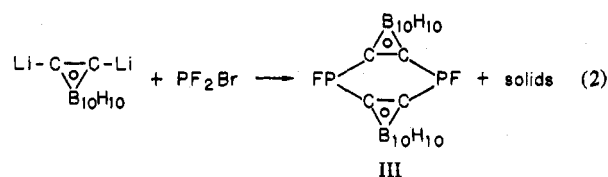
Attempts to prepare the $(PF_2)_2$ derivative by treating II with fluorinating reagents such as $C_6H_5C(O)F$, AsF_3, SbF_5, and SbF_3 were also unsuccessful. Predominantly P–C bond cleavage or unreacted substrates were observed in the reactions. The reaction of I with excess PF_3 gave C–F bond containing products which were not completely characterized and carborane.

When compound II is mixed with a fourfold excess of PF_5 in hexane, a white solid is formed immediately. Pressure

Table I. Mass Spectral Data[a]

m/e	intensity[b] I	II	III	assign[c]
385			100	$FP[B_{10}H_{10}C_2]_2PF$
380	27			$(Me_2N)_2P[B_{10}H_{10}C_2]P(NMe_2)_2$
346			8	$P[B_{10}H_{10}C_2]_2P$
337	47			$(Me_2N)_2P[B_{10}H_{10}C_2]_2$
334			6	$FP[B_{10}H_{10}C_2]_2$
330		30		$Me_2N(F)P[B_{10}H_{10}C_2]P(F)NMe_2$
315			8	$P[B_{10}H_{10}C_2]_2$
311		66		$Me_2NP[B_{10}H_{10}C_2]P(F)NMe_2$
293	35			$Me_2NP[B_{10}H_{10}C_2]PF$
286		59		$Me_2N(F)P[B_{10}H_{10}C_2]PF$
268		10		$HP[B_{10}H_{10}C_2]P(F)NMe_2$
264	24			$Me_2NP[B_{10}H_{10}C_2]P(H)Me$
250	21			$HP[B_{10}H_{10}C_2]P(H)NMe_2$
236		38		$Me_2N(F)P[B_{10}H_{10}C_2]$
218	18			$H[B_{10}H_{10}C_2]PNMe_2$
217		20		$Me_2NP[B_{10}H_{10}C_2]$
192			15	$FP[B_{10}H_{10}C_2]$
120	29			$HP(NMe_2)_2$
119	100			$P(NMe_2)_2$
95		16		$HP(F)NMe_2$
94		100		$FPNMe_2$
76	46			$HPNMe_2$
60	50	17		$HPNCH_2$

[a] Ions with m/e less than 60 are not listed but they are discussed in the text. [b] Relative to the most intense peak in the whole spectrum. [c] Formulas are written suggesting probable ion structure.
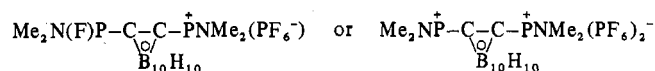
measurements indicate that 2 mol of PF_5/mol of substrate has reacted. This solid is probably an adduct of the type

$$(Me_2N)_2\overset{\uparrow PF_5}{P}-C\!\!\overbrace{\underset{B_{10}H_{10}}{}}\!\!C-\overset{\uparrow PF_5}{P}(NMe_2)_2$$
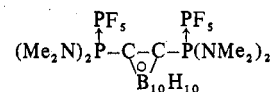
analogous to the adducts observed between some other dialkylaminophosphines and PF_5.[10] The adduct decomposes at 130 °C to give compound IV. Interestingly, the further

$$Me_2N(F)P-C\!\!\overbrace{\underset{B_{10}H_{10}}{}}\!\!C-P(F)NMe_2$$

IV
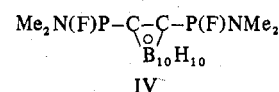
exchange of NMe_2 groups by reaction with PF_5 cannot be carried out. Instead, treatment of IV with PF_5 gives a white solid which clearly shows a PF_6^- ion. While our ^{31}P NMR facilities are not adequate to measure chemical shifts analogous to those observed by Parry for dicoordinate cationic phosphorus,[11] most probably IV reacts further with PF_5 to give

$$Me_2N(F)P-C\!\!\overbrace{\underset{B_{10}H_{10}}{}}\!\!C-\overset{+}{P}NMe_2(PF_6^-) \quad or \quad Me_2\overset{+}{N}P-C\!\!\overbrace{\underset{B_{10}H_{10}}{}}\!\!C-\overset{+}{P}NMe_2(PF_6)_2^-$$

Compound II is stable in air and is not affected by alcohols or water at room temperature. Compounds III and IV are

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Table II. Infrared Spectral Data[a]

compd	N–C str[b]	P–N str	P–F str
II	1270 s	977 s	
	1188 s	965 s	
	1165 ms		
IV	1298 s	988 vs	837 m
	1188 ms		
III			835 vs

[a] In cm^{-1}. Nujol mulls. [b] Abbreviations: str = stretching, s = strong, m = medium, v = very.

not particularly air sensitive but hydrolyze slowly in solution.

Mass Spectra. Table I lists the mass spectral data for the new phosphines. In all cases the parent molecular ion is clearly observed and the m/e is in agreement with the calculated molecular weight. The expected isotopic pattern for 10 boron atoms in the cage is observed for all fragments involving the carborane cage, but the isotopic peaks are not reported here. Interestingly no fragments involving $B_{10}C_2$ cage degradation are observed. In the spectra of II and IV the base peaks are m/e 119 [P(NMe$_2$)$_2$$^+$] and m/e 94 [P(F)NMe$_2$$^+$], respectively, indicating that P–C bond cleavage is facile and that these ions are particularly stable. A peak at m/e 120 for II and one at m/e 95 for IV are assigned to HP(NMe$_2$)$_2$$^+$ and HP(F)-NMe$_2$$^+$, respectively. Most probably they are formed by ion–molecule reactions due to the high concentration of ions formed in the source upon volatilization of the solid.

In spectra for both II and IV, the ions NMe$_2$$^+$, CH$_2NMe^+$, and CH$_2NCH_2$$^+$ are observed in high abundance. The disubstitued phosphorus ions are also highly abundant (see Table I). The predominance of these two types of ions supports the hypothesis that d-shell participation stabilizes the electron deficiency of phosphorus and therefore promotes P–N bond cleavage rather than the formation of phosphonium ions.[10b]

In the fragmentation of compound II, the greater ability of an NMe$_2$ group, compared to the case of fluorine, to stabilize a formal positive charge on phosphorus accounts for the higher abundance of m/e 311 relative to m/e 286. The predominance of this effect in spite of the stronger P–F bond is interesting.

The fragmentation path of III is particularly simple. The only significant fragmentation involves the simultaneous breaking of two P–C bonds to give the m/e 192 ion, $B_{10}C_2H_{10}(PF)^+$.

Infrared Spectra. Table II lists the frequencies assigned to the P–N, P–F, and N–C stretching modes. The assignments have been made by analogy with related systems.[12-15] The typical absorptions of the cage are observed: several strong bands in the 2610–2560-cm^{-1} range (B–H stretching), a strong band in the 738–720-cm^{-1} range (cage deformation), and two to three bands in the 1075–1015-cm^{-1} region (tentatively assigned to B–H deformation modes). The N–C assignments are highly tentative since coupling with the CH$_3$ deformation modes due to the enhancement of the pπ–dπ interaction with increasing substitution is likely.[12,16] The 940–980-cm^{-1} region has been suggested for the P–N stretching in P(NMe$_2$)$_2$ compounds.[12] The rather high P–N frequencies observed here are also a result of p$\pi \rightarrow$ dπ interactions. The high elec-

Figure 1. Proton NMR of (Me$_2$N)$_2$P[B$_{10}$H$_{10}$C$_2$]P(NMe$_2$)$_2$ (sweep width 2 ppm).

tronegativity of the carborane cage favors this interaction. The shift of the P–N frequency to a higher energy in IV can be interpreted in terms of a further enhancement of the pπ–dπ interaction by the more electronegative fluorine atoms.

The N $\rightarrow$ P pπ–dπ interaction should enhance the base strength of the phosphorus atom and concomitantly reduce the basic characteristics of the nitrogen atom. This may account for the considerable P–C cleavage observed (rather than P–N cleavage) as a result of acid attack on the moiety C–P(NMe$_2$)$_2$.

NMR Spectra. Table III lists the ^{1}H, ^{19}F, and ^{31}P NMR parameters of the new phosphines. All three compounds have non-first-order spectra and they are interpreted as X$_n$AA'X'$_n$ spin systems.[17] [For the ^{1}H NMR spectrum of II A = A' = P and X = X' = H (n = 12); for the ^{19}F NMR spectrum of III and IV, A = A' = P, X = X' = F (n = 1).] Harris has developed explicit expressions for the X transitions of the X$_n$AA'X'$_n$ system with $J_{XX'}$ = 0.[18] Observable parameters N and L are the combinations $N = J_{AX} + J_{AX'}$ and $L = J_{AX} - J_{AX'}$.

The ^{1}H NMR spectrum of II is the "deceptively simple" triplet[19] shown in Figure 1 indicating that $|^3J_{PP}| \gg |^3J_{PH} - ^6J_{PH}|$. If it is further assumed that $^6J_{PH}$ = 0, then the separation of the other peaks of the triplet will be equal to $^3J_{PH}$.[18] An estimation of $^3J_{PP}$ was obtained by the line-width procedure.[20-22] In general, this procedure gives minimum values of J_{PP} since many transitions occur very close together to give added width to the central band. However, the $^3J_{PH}$ value and the estimated $^3J_{PP}$ value used as input data for the program were adjusted to obtain a simulated plot that fits heights as well as widths of the peaks with the observed spectrum. There is a slight deviation near the baseline on the high-field side of the triplet. The underlying broad absorptions due to the hydrogen atoms of the carborane cage are responsible for this deviation.[3]

The ^{31}P NMR spectrum appears as a broad singlet. The small magnitude of $^3J_{PH}$ for the spin system X$_{12}$AA'X'$_{12}$ observed here and the broadening of the spectrum due to interaction of the nitrogen quadrupole account for the observed ^{31}P absorption.

The ^{19}F NMR spectrum of IV is shown in Figure 2a. The ^{31}P NMR spectral pattern is identical with that of the fluorine spectrum. Two sets of lines are observed. The lines of each set are denoted by dark and light circles. They are interpreted as the absorptions of two diastereomers, each set of lines being

Table III. ^{1}H, ^{19}F, and ^{31}P NMR Data[a]

compd	δ_{Me}	δ_F	δ_P	$^3J_{PH}$	$^4J_{FH}$	$^1J_{PF}$	$^4J_{PF}$	$^3J_{PP}$
II	2.08 t		97.1 s	±9.9				±73.5
IV	2.76[b] m	115.2 m	147.7 m	~±9.2	~5.1	±991.0	∓46.0	±110.0
	~2.76 m	115.1 m	147.1 m	~±9.2	~5.1	±1030.0	∓14.0	±212.0
III		75.3 m	136.0 m			±1270.0	∓29.0	±60.0

[a] Chemical shifts are in ppm: ^{1}H, downfield Me$_4$Si; ^{19}F, upfield CFCl$_3$; ^{31}P, downfield H$_3$PO$_4$ (80%). Coupling constants are in hertz. Solvent: CDCl$_3$ (II, IV); C$_6$D$_6$ (III). [b] Diastereomers differ by less than 0.01 ppm.
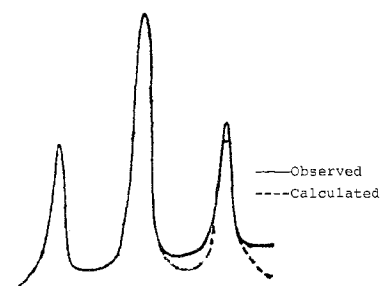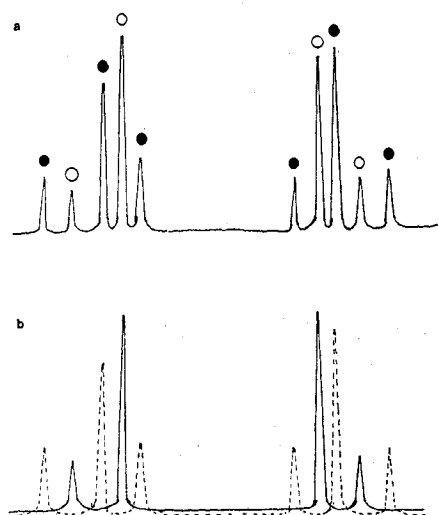
Figure 2. (a) Observed ^{19}F NMR spectrum of $Me_2N(F)P$-$[B_{10}H_{10}C_2]P(F)NMe_2$. (b) Superimposition of the computed ^{19}F NMR spectrum of each diastereomer of $Me_2N(F)P[B_{10}H_{10}C_2]P$-$(F)NMe_2$.
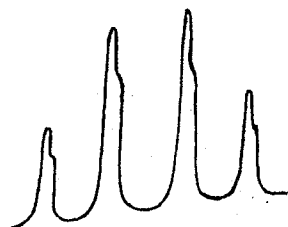
Figure 3. Observed proton NMR spectrum of the diastereomers of $Me_2N(F)P[B_{10}H_{10}C_2]P(F)NMe_2$ (sweep width 1 ppm).

the spectrum of an isomer. Estimates of the $^1J_{PF}$, $^4J_{PF}$, and $^3J_{PP}$ values in each spectrum were obtained by using the Harris formulas.[18] Values were adjusted to give the best fit for each computed spectrum (see Figure 2b). The superposition of the simulated spectra gives an acceptable reproduction of the observed spectrum.

The absolute signs of the coupling constants were not determined. However, if $L > N$, indicating that $(^1J_{PF} - {}^4J_{PF}) > (^1J_{PF} + {}^4J_{PF})$, then the signs of $^1J_{PF}$ and $^4J_{PF}$ are opposite. This is the case for the four-line isomer spectrum of IV and also for the fluorine spectrum of III. In all cases the sign of $^3J_{PP}$ is the same as that of $^1J_{PF}$. Table III lists the coupling constants with their relative signs.

The ^1H NMR spectrum of IV shows four lines giving the appearance of a "quartet". Upon expansion a shoulder appears on each peak (Figure 3). Thus two "quartets" are observed, each resulting from one diastereomer. The $^3J_{PP}$ in both isomers is larger than $^3J_{PH}$ which is known to be less than 20 Hz in all analogous compounds.[16] Thus, a deceptively simple $\sim$1:2:1 triplet is expected for each isomer. A further first-order interaction with the fluorine atom splits each peak of the triplet into a doublet. The similar values for the separation between an outer peak and the central peak of the original triplet and the $^4J_{FH}$ value result in overlapping of lines that gives the final appearance of a "quartet". The isomer in less abundance (about 40% in $CDCl_3$ solution as estimated from the relative heights of the peaks) is upfield to the other one by less than 0.01 ppm. Assuming that $^6J_{PH} = 0$, the $^3J_{PH}$ value in the isomers is about 9.2 Hz, or twice the separation between an outer peak and the next inner peak in the quartet (this would be the separation between the outer peaks in the "original triplet" before interaction with fluorine). The value of $^4J_{FH}$ estimated from the separation between the two inner peaks of the quartet is $\sim$5.1 Hz for both isomers.
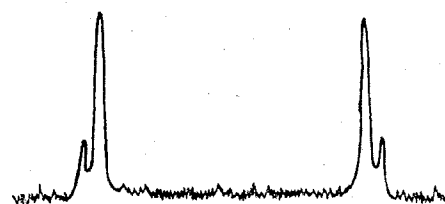

**Figure 4.** Observed ^{19}F NMR spectrum of $FP[B_{10}H_{10}C_2]_2PF$.

The ^{19}F NMR spectrum of III shown in Figure 4 also exhibits a high degree of deception. By using Harris' formulas,[18] estimated values for $^1J_{PF}$, $^4J_{PF}$, and $^3J_{PP}$ were obtained. These values were adjusted until the simulated spectrum superimposed with the observed spectrum.

The ^{31}P NMR spectrum is identical with the fluorine spectrum and does not give additional information about the coupling constants.

The ^1H and ^{31}P chemical shifts seem to be lower than the usual range of known analogous systems,[14,16,26] in particular that of compound III. The deshielding may be attributed in part to the extensive electron-withdrawing ability of the carborane cage.[3] The $^3J_{PH}$, $^4J_{FH}$, and $^1J_{PF}$ are in the expected ranges.[16,27] The magnitude of $^4J_{PF}$ is probably enhanced by the delocalizing character of the carborane cage.[3]

The large magnitude of $^3J_{PP}$ is somewhat surprising. The larger values in IV compared with those in II can be accounted for by an increase in the s character of the phosphorus bonds due to the higher electronegativity of fluorine. The relatively low $^3J_{PP}$ value in III may be partially due to the lower electronegativity of the two carbon atoms bonded to phosphorus although stereochemical effects may be important here.

The chlorinated derivative[4] analogous to compound III has the chlorine atoms in positions cis to the plane formed by the two phosphorus and the two carbon atoms as shown by dipole measurements[28] and an X-ray crystallographic study.[29] With high probability the fluorine atoms in compound III are also occupying the cis position with respect to that plane as shown:
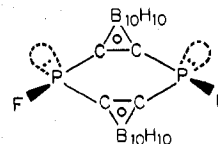
The lone pairs of electrons on phosphorus are also in cis position to the same plane; the geometry of phosphorus is determined by the ring configuration in which it participates. Stereochemical factors[20,26,30,31] (bond angles of substituents on phosphorus, lone-pair–substituent bond angle) may be largely responsible for the relatively low $|^3J_{PP}|$ (60 Hz) and moderately high $|^4J_{PF}|$ (29 Hz) in compound III.

Since both phosphorus atoms in compound IV are chiral centers, meso and racemic diastereomers exist. Because of the highly symmetric carborane cage, these may be represented as shown:

racemic form   meso form
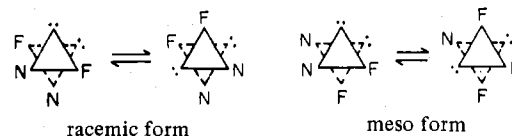
The rather large differences in $^3J_{PP}$, $^1J_{PF}$, and $^4J_{PF}$ between the diastereomers are somewhat surprising. Since no attempt was made to separate the diastereomers, the particular parameters for a given isomer cannot be unequivocally assigned.

Experimental Section

o-Carborane and the lithium derivatives were prepared by methods described in the literature.[4,32] The method used to prepare $ClP(NMe_2)_2$ was that of Noeth and Vetter;[33] PF_2Br was prepared as described by

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%.

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

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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 $R_xNH_{3-x}·HCl$ 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