TABLE V

DISTORTIONS OF $Ni(CN)_2X_3$ COMPLEXES FROM A TRIGONAL-BIPYRAMIDAL GEOMETRY

	X			
	CN^-	$P(C_6H_5)(OC_2H_5)_2$	$P(C_6H_5)(CH_3)_2$	Trigonal bipyramid
		Angle,[a] deg		
X_1-Ni-X_2	107.4 (5)	113.0 (2)	116.8 (1)	120
X_1-Ni-X_3	111.5 (5)	113.5 (2)	116.2 (1)	120
X_2-Ni-X_3	141.2 (5)	133.5 (2)	127.0 (1)	120
C_1-Ni-C_2	172.8 (5)	170.8 (8)	176.5 (4)	180
X_1-Ni-C_1	92.3 (5)	93.4 (5)	92.4 (3)	90
X_1-Ni-C_2	94.4 (5)	95.7 (6)	91.1 (3)	90
X_2-Ni-C_1	89.3 (5)	89.8 (6)	88.6 (3)	90
X_2-Ni-C_2	91.3 (5)	88.7 (5)	90.0 (3)	90
X_3-Ni-C_1	89.5 (4)	87.4 (5)	87.8 (3)	90
X_3-Ni-C_2	85.6 (4)	87.0 (5)	90.5 (3)	90
		Distance, Å		
Ni-X_1	1.992 (14)	2.289 (5)	2.261 (3)	
Ni-X_2	1.913 (13)	2.205 (6)	2.223 (3)	
Ni-X_3	1.902 (13)	2.189 (6)	2.223 (3)	

[a] The three X ligands lie in the equatorial plane, with Ni-X_1 being the longest bond in each case.

mated. However, the distortions of the molecule remain highly significant.

The derived bond distances can be corrected for the effects of thermal motion,[11] the most reasonable assumption appearing to be that of a "riding" model. The calculated bond lengths increase slightly; for example, the Ni-P_3 distance increases from 2.223 to 2.231 Å, but the relative differences in bond lengths remain essentially the same.

The variation in Ni-P bond lengths is similar to that cited in the preceding paper, but less extreme: the values of 2.223, 2.223, and 2.261 Å can be compared with those of 2.189, 2.205, and 2.289 Å in $Ni(CN)_2(P(C_6H_5)(OC_2H_5)_2)_3$. The average Ni-C distance of 1.85 Å, however, is closer to the axial Ni-C bond length in $Ni(CN)_5^{3-}$ of 1.84 Å than to the 1.88 Å in $Ni(CN)_2(P(C_6H_5)(OC_2H_5)_2)_3$. This seems to be a consequence of the more idealized geometry: the C-P nonbonded interactions in the two $Ni(CN)_2(PR_3)_3$ complexes are approximately the same, but the less distorted trigonal bipyramid permits shorter Ni-C bonds while keeping the same C-P interactions.

At this time the trends away from an idealized trigonal-bipyramidal configuration toward a tetragonal-pyramidal configuration displayed in Table V are difficult to interpret. Thus although the basic properties of various phosphines have been determined by indirect means,[12] there appears to be no definitive information on where one might place CN^- in this scheme. If indeed one is seeing the effects of decreasing σ donation in approaching the tetragonal pyramid, then one could conclude that CN^- has decreased σ-donation character over the phosphite ligand. In fact, comparative studies of $Ni(CN)_2(PR_3)_3$ systems may provide a sensitive and direct measure of such donating properties. Nevertheless, there are obvious steric factors in these systems: steric factors must be the reason that the compound $Ni(CN)_2(P(C_6H_5)_3)_3$ is not formed, since $P(C_6H_5)_3$ is less basic than $P(C_6H_5)(CH_3)_2$ but more basic than $P(C_6H_5)(OC_2H_5)_3$.

Further chemical and structural studies are in progress which may provide additional insight into the factors involved in the determination of the distortions of related five-coordinate complexes of Ni(II).

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Preparation and Spectral Studies of a Series of Rhodium(III)-Acetonitrile Complexes

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A series of rhodium(III)-acetonitrile complexes of the general formula $RhCl_m(CH_3CN)_n^{3-m}$ have been prepared and characterized by their visible, infrared (4000–70 cm^{-1}), and proton nmr spectra. The preparation of the *trans*-$RhCl_4(CH_3CN)_2^-$ is reported for the first time. The configurations of the two geometrical isomers of the complex $RhCl_3(CH_3CN)_3$ are elucidated on the basis of their proton nmr spectra. The visible and far-infrared spectra of these rhodium(III) acetonitrile complexes are quite similar to those exhibited by the analogous rhodium(III) pyridine complexes, thus indicating the considerable strength of acetonitrile as a ligand for second-row transition metals.

Introduction

The reactions between transition metal halides and various nitriles and the characterization of the resulting metal complexes have attracted a great deal of attention.[1] However, there is relatively little known about nitrile complexes of rhodium(III), although Lebedinskii and Fedorov[2] have reported the synthesis of the species

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(1) R. A. Walton, *Quart. Rev.* (London), **19**, 126 (1965), and the references quoted therein.

(2) V. V. Lebedinskii and I. A. Fedorov, *Ann. Inst. Platine* (U.S.S.R.), **12**, 87 (1935).

$RhCl_5(CH_3CN)^{2-}$ and the geometrical isomers of $RhCl_3(CH_3CN)_3$ have been investigated.[3-5] In the present study we have synthesized the *trans*-$RhCl_4(CH_3CN)_2^-$ species and have perfected simple methods for the direct preparation of *cis*- and *trans*-$RhCl_3(CH_3CN)_3$. The conversion of the *cis*-$RhCl_3(CH_3CN)_3$ to the *trans* isomer has also been effected by refluxing in acetonitrile, thus indicating that the latter is the thermodynamically favored isomer.

These species, in addition to $RhCl_5(CH_3CN)^{2-}$, have been characterized in some detail by studying their visible, infrared (with special emphasis on the far-infrared region), and proton nmr spectra. The spectral properties of this series of compounds more closely resemble those reported for the analogous pyridine series[6] than those of the corresponding rhodium(III)–aquo complexes.[7] This is a somewhat surprising result in view of the relative ligand strengths of pyridine, water, and acetonitrile when coordinated to various first-row transition metals and it implies that acetonitrile behaves as a relatively strong ligand when reacting with second-row transition metals. This effect becomes more pronounced in the acetonitrile complexes of platinum, a third-row transition element, where the platinum–acetonitrile bond appears to be exceptionally strong.[8]

Experimental Section

Preparation of Tetraethylammonium Tetrachlorodiacetonitrilerhodate(III).—$[(C_2H_5)_4N][RhCl_4(CH_3CN)_2]$ was obtained from a 1:1 by volume acetonitrile–water solution by the addition of equimolar amounts of tetraethylammonium chloride and rhodium trichloride (trihydrate). The compound precipitated out as orange plates. It was washed with ethanol and ether and dried under vacuum over P_2O_5.

Anal. Calcd for $C_{12}H_{30}N_3RhCl_4$: C, 31.54; H, 5.73; N, 9.19; Rh, 22.52; Cl, 31.03. Found: C, 32.18; H, 6.01; N, 9.27; Rh, 23.11; Cl, 30.66.

The cesium salt of $RhCl_4(CH_3CN)_2^-$ was prepared in an analogous manner.

Preparation of the Pentachloroacetonitrilerhodate(III) Salts.—The cesium, ammonium, and tetramethylammonium pentachloroacetonitrilerhodate(III) complexes were prepared by the method of Lebedinskii and Fedorov. $Na_3[RhCl_6]$ was dissolved in a 1:1 mixture of CH_3CN and H_2O and warmed slightly until the solution appeared pale orange. After cooling, a stoichiometric amount of the appropriate halide salt, dissolved in a minimum amount of water, was added and the desirable compound precipitated immediately. Addition of absolute ethanol to the filtrate produced more compound. The sodium salt (desirable because of its greater solubility) was obtained by extracting the complex gradually from the aqueous layer with acetonitrile and precipitating with ether. All of the salts were washed first with absolute ethanol and then with ether and were dried under vacuum over P_2O_5. The salts vary from brown to orange-brown depending on the cation. In all cases the presence of the $RhCl_5(CH_3CN)^{2-}$ species was verified by its visible and infrared spectra.

Preparation of *trans*-Trichlorotriacetonitrilerhodium(III).—The *trans*-$RhCl_3(CH_3CN)_3$ complex was prepared by a slightly different method than the one reported originally by Johnson and Walton.[3] It was found that this compound could be prepared much easier from an ethanol–acetonitrile solution in the following way. $RhCl_3 \cdot 3H_2O$ (1.0 g, 4.0 mmol) was dissolved in 20 ml of anhydrous ethanol and 10 ml of CH_3CN was added. The solution was refluxed for 4 hr at which time a yellow precipitate was obtained. The filtrate was treated with a large portion of ether to obtain more yellow precipitate; total yield, 0.9570 g (72%). Upon recrystallization from acetonitrile a small amount of a pale orange, insoluble portion was recovered which, on the basis of its visible and infrared spectra, its elemental analysis, and qualitative test for the ammonium ion, was formulated as $[NH_4][RhCl_4(CH_3CN)_2]$. *Anal.* Calcd for $[NH_4][RhCl_4(CH_3CN)_2]$ C, 13.92; H, 2.92; N, 12.17. Found: C, 14.68; H, 3.41; N, 11.95. The desired compound, *trans*-$RhCl_3(CH_3CN)_3$, was recovered from the acetonitrile by evaporation of the solvent in a rotary evaporator or by slow precipitation with ether. It was washed with two portions of ether and dried under vacuum over P_2O_5.

Anal. Calcd for $C_6H_9N_3RhCl_3$: C, 21.68; H, 2.73; N, 12.64. Found: C, 21.81; H, 2.91; N, 12.31.

trans-$RhCl_3(CH_3CN)_3$ was also prepared by refluxing the corresponding *cis* compound (see preparation given below) for 12 hr in acetonitrile. Isolation of the *trans* product was accomplished by slow precipitation with cold ether. Recrystallization could be carried out in acetonitrile as above.

Preparation of *cis*-Trichlorotriacetonitrilerhodium(III).—The *cis*-$RhCl_3(CH_3CN)_3$ was prepared and identified as reported previously.[5] A sample of 0.34 g (1.0 mmol) of $RhCl_3 \cdot 3H_2O$ was dissolved in 50 ml of acetonitrile and the solution was brought to boiling. The reaction mixture was allowed to stand and some product appeared in the cool solution. The remainder of the product was recovered by evaporating the solvent in a rotary evaporator. Both fractions gave identical infrared and proton nmr spectra. The final product was recovered from a fresh acetonitrile solution by the addition of ether. It was washed with ether and dried under vacuum over P_2O_5 (yield 80%).

Anal. Calcd for $C_6H_9N_3RhCl_3$: C, 21.68; H, 2.73; N, 12.64; Cl, 31.99. Found: C, 22.88; H, 2.71; N, 13.08; Cl, 31.76.

Visible, Infrared, and Proton Nmr Spectra.—All visible spectra were obtained on a Perkin-Elmer Model 450 spectrophotometer. The infrared spectra in the 4000–650-cm^{-1} region were taken on a Beckman Model IR-5A spectrophotometer and those in the 500–70-cm^{-1} region were recorded on a Beckman Model IR-11 spectrophotometer. All proton nmr spectra were obtained on a Varian Model A-60 high-resolution spectrometer at 60 Mc.

Analyses.—C, H, N, and Cl elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Rhodium analyses were carried out by reducing to the metal using a standard hydrogen reduction technique.

Results and Discussion

Visible Absorption Spectra.—The visible absorption spectra of this series of rhodium(III)–acetonitrile complexes are given in Table I. There is no general trend established as additional acetonitrile ligands are substituted for chloride as was the case for the analogous aquo complexes.[7] However, the spectra reported here are very similar to those reported for the corresponding pyridine complexes as summarized by Gillard and Wilkinson.[6] The assignments of the transitions were made with the aid of previous reports.[6,9]

Infrared Spectra.—Nitriles are known to coordinate almost exclusively through the "lone pair" of electrons that is localized on the nitrogen.[1] With only one

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(8) J. R. O'Brien, G. E. Glass, and W. L. Reynolds, *ibid.*, **7** 1964 (1968).

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TABLE I

VISIBLE ABSORPTION SPECTRA OF RHODIUM(III) ACETONITRILE COMPLEXES

Complex	Absorption max, mμ	ε	Assignment	Conditions
$Cs_2[RhCl_5(CH_3CN)]$	462	. . .	$^1A_{1g} \rightarrow {}^1T_{1g}$	Reflectance
	382	. . .	$\rightarrow {}^1T_{2g}$	
	464	144	$\rightarrow {}^1T_{1g}$	Aqueous solution
	380	102	$\rightarrow {}^1T_{2g}$	
$(NH_4)_2[RhCl_5(CH_3CN)]$	465	147	$\rightarrow {}^1T_{1g}$	1:1 CH_3CN–H_2O solution
	382	100	$\rightarrow {}^1T_{2g}$	
trans-$[(C_2H_5)_4N][RhCl_4(CH_3CN)_2]$	490	59	$\rightarrow {}^1T_{1g}$	CH_3NO_2 solution
	423	146	$\rightarrow {}^1T_{2g}$	
	486	55	$\rightarrow {}^1T_{1g}$	Aqueous solution
	418	130	$\rightarrow {}^1T_{2g}$	
cis-$RhCl_3(CH_3CN)_3$	410	. . .	$\rightarrow {}^1T_{1g}$	Reflectance
	408	123	$\rightarrow {}^1T_{1g}$	Aqueous solution
trans-$RhCl_3(CH_3CN)_3$[a]	433	105	$\rightarrow {}^1T_{1g}$	CH_3NO_2 solution

[a] Reference 3 reported 430 (100) and 371 (109) mμ in CH_3NO_2. Ultraviolet cutoff for CH_3NO_2 in 1-cm cells is 380 mμ.

TABLE II

SOME IR STRETCHING FREQUENCIES OF RHODIUM(III)–ACETONITRILE COMPLEXES[a]

Compound	ν(C≡N), cm^{-1}	ν(C—C), cm^{-1}
$Cs_2[RhCl_5(CH_3CN)]$	2304	951
$(NH_4)_2[RhCl_5(CH_3CN)]$	2304	960
trans-$[(C_2H_5)_4N][RhCl_4(CH_3CN)_2]$	2320	960
cis-$RhCl_3(CH_3CN)_3$	2310	952
trans-$RhCl_3(CH_3CN)_3$[b]	2304	953

[a] Spectra were obtained on KBr pellets. [b] Reference 3 reported values of 2305 and 955 cm^{-1}, respectively.

exception[10] it is known that when nitriles are coordinated through the "lone pair" they show an unusual increase in the infrared stretching frequency of the C≡N donor group. In fact, in acetonitrile complexes there is an increase in the frequencies assigned to the ν_2(C≡N str), ν_4(C—C str), and ν_8(C—C≡N bend) modes of vibration as well as the frequencies of some combinations and overtones of the ligand.[11,12]

TABLE III

FAR-INFRARED SPECTRA OF ACETONITRILE COMPLEXES OF Rh(III)[a]

Compound	Symmetry	ν(Rh–Cl) ir-active modes	Rh–Cl str, cm^{-1}	Other bands, cm^{-1}
$Cs_2[RhCl_5(CH_3CN)]$	C_{4v}	$a_1 + 2e$	343 s, 328 s, 295 sh	429 w, 235 m, 181 m
trans-$[(C_2H_5)_4N][RhCl_4(CH_3CN)_2]$	D_{4h}	$2e_u$	338 s, 300 sh	459 m, 251 s, 173 m–s
cis-$RhCl_3(CH_3CN)_3$	C_{3v}	$a_1 + e$	356 s, 346 s	456 w, 432 m, 415 w
trans-$RhCl_3(CH_3CN)_3$[b]	C_{2v}	$2a_1 + b_1$	356 s, 350 s, 300 sh	456 m, 430 vw, 254 m, 201 w, 159 w

[a] Samples were run as Nujol mulls and band positions were reproducible to ±2 cm^{-1}. [b] Reference 3 reported the following bands (cm^{-1}): 450 m–s, 427 sh, 350 s, 340 s, 300 sh, 248 s, 230 sh.

In the region between 4000 and 600 cm^{-1} the absorption bands of most interest for any of the complexes studied are those due to the C≡N stretching mode. In Table II the values of ν(C≡N) and ν(C—C) for this series of rhodium–acetonitrile complexes are shown. The position and character of this C≡N band have been used as criteria for evaluating certain properties of nitrile complexes, including structure. However, it has been pointed out by Beattie[13] that the assignment of structure on the basis of the splitting of the C≡N band observed for solid compounds can be misleading because of the contribution from lattice effects.

The far-infrared spectra of these complexes should provide significant structural information and/or lend support for the structural assignments made. Table III lists the complexes studied, the symmetry, and infrared-active modes expected from a simple application of group theory to the octahedral structure, and the bands can be assigned with some confidence by comparison with other complexes of the type $RhCl_3L_3$.[3,14–17] In all cases the predicted number of Rh–Cl stretching vibrations was observed. The assignment of the remaining bands is more difficult. For example, the *cis*-$RhCl_3(CH_3CN)_3$ should exhibit two Rh–$NCCH_3$ stretching frequencies and the corresponding *trans* complex should exhibit three such vibrations. In addition, the *trans*-$RhCl_3(CH_3CN)_3$ and *trans*-$[(C_2H_5)_4N][RhCl_4(CH_3CN)_2]$ complexes should have an N–Rh–N bending mode which would be absent in *cis*-$RhCl_3(CH_3CN)_3$ and $Cs_2[RhCl_5(CH_3CN)]$. According to Nakamoto,[18] this bending vibration should appear below 300 cm^{-1}. Thus the 252-cm^{-1} band in *trans*-$[(C_2H_5)_4N][RhCl_4(CH_3CN)_2]$ and the 254-cm^{-1} band in *trans*-$RhCl_3(CH_3CN)_3$ can be assigned to this mode. Acetonitrile, furthermore, has a C—C≡N bending

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vibration ν_8(E), which is expected to appear between 420 and 380 cm^{-1} by comparison with other acetonitrile complexes.[11] The assignment of metal–nitrogen stretching frequencies in nitrile complexes is a matter of great uncertainty, and reports of such bands for various metals range between 550 and 80 cm^{-1}.[4] We were unable to detect any definite absorption bands below 150 cm^{-1}. However, all of the compounds under investigation contained bands above 420 cm^{-1} which would be considered high for the C—C≡N bending mode (Figure 1). Therefore by comparing the spectra of all of the complexes studied here, it is reasonable to assign the 456-cm^{-1} band in the trisubstituted compounds, the 457-cm^{-1} band in the disubstituted compound, and the 429-cm^{-1} band in the monosubstituted compound to one of the Rh–N stretching modes. Nevertheless this should be considered as a tentative assignment. The other unassigned bands in Table III may arise from Rh–Cl bending modes, to be expected below 200 cm^{-1}. The spectra observed and the assignment of the Rh–Cl stretching vibrations point out the utility of the far-infrared spectra as an aid in the structural assignment of complexes of the type reported here.

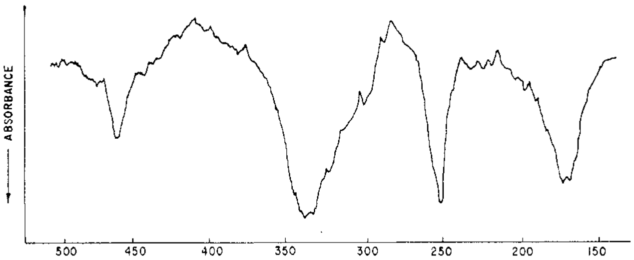

Figure 1.—Far-ir spectrum for *trans*-$[(C_2H_5)_4N][RhCl_4(CH_3CN)_2]$. See Table III.

Nuclear Magnetic Resonance Spectra.—There is no report of a systematic study of the proton nmr spectra of coordinated nitriles, although some work has been done on the spectra of the paramagnetic nitrile complexes of the first-row transition metals,[19–21] platinum blue,[22] and the acetonitrile adducts of the boron trihalides.[23] A rapid, unambiguous method for assigning possible geometrical isomeric forms, such as *cis*-$RhCl_3(CH_3CN)_3$ and *trans*-$RhCl_3(CH_3CN)_3$, can be formulated using the proton nmr spectra of the complexes. Free acetonitrile exhibits a singlet due to the methyl protons at δ 2.00 ppm. The compound $Na_2[RhCl_5(CH_3CN)]$ also shows a singlet but at 2.60 ppm in D_2O (see Table IV). The single peak indicates the absence of long-range coupling of the methyl protons with the rhodium atom ($I = {}^1/_2$).

The trisubstituted chloro complexes, $RhCl_3(CH_3CN)_3$, proved to be most interesting. The *cis* isomer should contain three equivalent acetonitrile molecules and give a single nmr peak for the methyl protons at a chemical shift value comparable to that of the monosubstituted complex. The *trans* isomer, on the other hand, should have two equivalent acetonitrile molecules bonded *trans* to each other and a unique nitrile bonded *trans* to a chloride. In fact, the proton nmr spectra of these isomers should be the basis of the definitive assignment of the *cis–trans* configuration. The *cis* isomer does indeed exhibit a single peak at 2.60 ppm in CD_3CN and the *trans* isomer exhibits two peaks, at 2.64 and 2.59 ppm in CD_3CN in the ratio of 2:1. The spectrum of the *trans* complex had to be obtained in CD_3CN in order to avoid the rapid aquation that occurred in D_2O. This aquation was evident by the appearance of a free acetonitrile signal at 2.00 ppm and the simultaneous reduction in intensity of the 2.64-ppm peak.

Table IV

Proton Nmr Data for Rhodium(III)–Acetonitrile Complexes

Compound	Chem shift δ	Solvent	Standard
CH_3CN	2.00 s[a]	. . .	TMS
$Na_2[RhCl_5(CH_3CN)]$	2.60 s	D_2O	HDO
$[(C_2H_5)_4N][RhCl_4(CH_3CN)_2]$ (*trans* isomer)	2.59 s 3.18 q 1.18 t	D_2O	HDO
trans-$RhCl_3(CH_3CN)_3$	2.59 s 2.64 s	CD_3CN	TMS
cis-$RhCl_3(CH_3CN)_3$	2.60 s	CD_3CN	TMS

[a] Abbreviations: s, singlet; q, quartet; t, triplet.

For the disubstituted complex $[(C_2H_5)_4N][RhCl_4(CH_3CN)_2]$, little structural information could be obtained from its proton nmr spectrum, as one would expect a single acetonitrile methyl signal for both the *cis* and *trans* configurations since the two acetonitrile molecules would be equivalent to each other in either case. Nevertheless the spectrum of $[(C_2H_5)_4N][RhCl_4(CH_3CN)_2]$ demonstrated the use of proton nmr as a tool for determining the stoichiometry of coordination compounds which contain quaternary ammonium cations. This can be achieved by comparative integration of the protons of the quaternary ammonium cation and the nitrile protons. Since there are only a limited number of structural possibilities, the final formula can be easily deduced. In the $[(C_2H_5)_4N][RhCl_4(CH_3CN)_2]$ case, the ratio for the protons of the acetonitrile singlet to the methylene quartet was 3:4. Also the ratio of the acetonitrile singlet to the methyl proton triplet was found to be 1:2. These ratios substantiate the stoichiometry of the dinitrile complex.

The confirmation by nmr of the structure assignments made for the *cis–trans* isomers of $RhCl_3(CH_3CN)_3$ on the basis of their far-infrared spectra is gratifying. This agreement provides confidence for the assignment made for *trans*-$RhCl_4(CH_3CN)_2^-$ as well as for future assignments that may be made on the basis of far-infrared spectra for complexes not amenable to nmr studies.

Acknowledgments.—Partial support for the pur-

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chase of the Varian A-60 nmr instrument was provided by the National Science Foundation under Grant No. GP-3674. We are also indebted to Tulane University for use of the Beckman IR-11 provided partially by funds from National Science Foundation Grant No. 28709.

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Spectroscopic Investigations of Dimethylberyllium Vapors

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Variable-temperature infrared spectra of saturated and unsaturated vapors of dimethylberyllium have been recorded. Band assignments have been made in comparison with published spectra for $M(CH_3)_2$ compounds (M = zinc, cadmium, or mercury). The spectrum of the unsaturated vapor is consistent with a monomer with a linear C–Be–C skeleton. Band assignments are confirmed from analysis of the infrared spectrum of the deuterated analog. Mass spectral measurements confirm the presence of monomers only. Hyperconjugation effects are employed to explain the large beryllium–carbon bond strength and the unexpected stability of the monomer.

Introduction

Vapor pressure and vapor density measurements[1] of saturated vapors of dimethylberyllium have indicated an equilibrium mixture of monomers, dimers, and trimers. It was calculated that the vapor consists of 41% monomer, 44% dimer, and 14% trimer at 180° with corresponding percentages of 27, 50, and 23 at 160°.

Infrared spectra of both saturated and unsaturated vapors have been reported[2] and interpreted in comparison with the vapor density results. For the monomer (unsaturated vapor) $\delta(CH_3)$ was assigned at 1262 cm^{-1} and methyl rocking modes were at 1086, 1032, and 816 cm^{-1}. The spectrum of the saturated vapor was more complex, consistent with the presence of polymeric structures in addition to the monomer. When the saturated vapor was heated, however, the spectra revealed unpredictable changes. Numerous new bands appeared which, in contrast to the vapor density results, implies that some new species is formed. The spectra were not fully discussed or interpreted.

We decided to measure the variable-temperature gas-phase infrared spectra of both saturated and unsaturated vapors of deuterated and undeuterated dimethylberyllium. We intended to characterize the vapors of dimethylberyllium better by making assignments of bands in the infrared spectra for each species present in the vapor.

Experimental Section

All sample preparations were carried out in an inert-atmosphere enclosure equipped with an air circulation system for removal of trace amounts of water and oxygen.[3]

Synthesis of Compounds.—Dimethylberyllium was synthesized by the reaction of beryllium metal (200 mesh powder obtained from Alfa Inorganics, Inc.) and dimethylmercury (obtained from Eastman Organic Chemicals and used without further purification). The beryllium powder was heated to 400° under vacuum to remove traces of adsorbed moisture. An equimolar quantity of dimethylmercury was combined with the activated beryllium metal in an ampoule which was sealed and subsequently heated to 120° in an oil bath. After 3 days, the ampoule was opened in the inert-atmosphere enclosure. Samples were sublimed at 100° immediately prior to use.

A Grignard method was utilized for the synthesis of $(CD_3)_2Be$. Because of the difficulty of removing trace amounts of diethyl ether from dimethylberyllium, dimethyl sulfide was utilized as the solvent.[4] The Grignard reagent was synthesized by dropwise addition of methyl-d_3 iodide (obtained as 98% d_3 from Stohler Isotope Chemical Corp. and used without further purification) dissolved in dimethyl sulfide to magnesium metal in dimethyl sulfide. The resultant exothermic reaction proceeded smoothly until all of the iodide had been added. Solid beryllium chloride (obtained from Alfa Inorganics, Inc., and used without further purification) was added to the flask containing the Grignard reagent and brought to reflux. After 4 hr excess solvent was removed under vacuum. The resultant solid was transferred to the inert-atmosphere enclosure and sublimed several times to ensure complete removal of coordinated dimethyl sulfide.[5]

For purposes of characterizing the symmetrical methyl deformation of a terminal methyl group bonded to beryllium, the trimethylamine adducts were synthesized. Excess, dry trimethylamine was vacuum transferred directly into the infrared cell containing either dimethylberyllium or dimethyl-d_6-beryllium and excess amine removed under vacuum while the cell was cooled to approximately 0°. The melting point of the undeuterated adduct was 36° compared to the reported melting point of 36°.[6] Gas-phase spectra of the adducts were recorded at room temperature.

Construction of Infrared Cell.—During the course of this investigation it was observed that dimethylberyllium vapors react with most common gasketing materials, especially silicone rubber. For this reason a commercial variable-temperature chamber could not be used. A cell was therefore constructed from thick-walled, Pyrex tubing, 6 cm in length. A vacuum stopcock was joined to the center of the tube and the ends were ground smooth

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[1] G. E. Coates, F. Glockling, and N. D. Huck, *J. Chem. Soc.*, 4496 (1952).

[2] G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 1, Methuen and Co., Ltd., London, 1967, p 106.

[3] T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

[4] G. Bähr and K. H. Thiele, *Chem. Ber.*, **90**, 1578 (1957).

[5] Contrary to earlier reports we have observed complex formation between dimethylberyllium and dimethyl sulfide.

[6] G. E. Coates and N. D. Huck, *J. Chem. Soc.*, 4501 (1952).