CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS 78712

The Thermal Decomposition of *cis*- and *trans*-Dichlorotetraamminecobalt(III) Chloride

BY GEORGE W. WATT AND DAVID A. BUTLER

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The thermal decomposition of *trans*-dichlorotetraamminecobalt(III) chloride has been shown to involve *trans–cis* isomerization in the solid state. Evidence bearing upon possible precursors of cobalt(II) chloride is presented and discussed.

It was shown previously[1] that, at low heating rates, $[Co(NH_3)_6]Cl_3$ is converted quantitatively to $[Co(NH_3)_5Cl]Cl_2$ which at higher temperatures decomposes to $CoCl_2$ in a manner closely similar to the decomposition of *trans*-$[Co(NH_3)_4Cl_2]Cl$. We report here a comparative study of the thermal decomposition of the latter complex and its *cis* isomer.

Experimental Section

trans-Dichlorotetraamminecobalt(III) chloride was prepared by the procedure of Jørgensen[2] (*Anal.* Calcd for $[CO(NH_3)_4Cl_2]$-Cl: Co, 25.2. Found: Co, 25.2), *cis*-$[Co(NH_3)_4Cl_2]Cl\cdot 0.5H_2O$ as described by Werner[2] (*Anal.* Calcd for $[Co(NH_3)_4Cl_2]Cl\cdot 0.5H_2O$: Co, 24.3. Found: Co, 24.0), and $(NH_4)_2CoCl_4$ by the method of Fogel, *et al.*[3] (*Anal.* Calcd for $(NH_4)_2CoCl_4$: Co, 24.9. Found: Co, 25.0). The infrared spectrum of the latter salt consists of the bands (cm^{-1}): 316 s, 350 sh, 436 vw, 1005 s, 1023 sh, 1107 m, 1407 vs, 1604 m, 1760 m, b, 3040 s, 3220 vs, b, 3410 s.

Samples were heated as described elsewhere[1] at a rate of 0.5–1.0°/min; samples were quenched at temperatures dictated in most cases by color and/or phase changes (Tables I and II). All measurements made on these samples employed the methods described earlier.[1] X-Ray diffraction data are given in Tables III and IV, infrared spectral data in Tables V and VI, and the differential thermal analysis data in Figure 1. The stoichiometry of the decomposition and the role of NH_4Cl volatilization have already been established.[1]

Discussion

Collectively, the X-ray diffraction data and infrared spectral data presented here lead to the conclusion that *trans*-$[Co(NH_3)_4Cl_2]Cl$ is thermally converted to the *cis* isomer in the solid state but that this isomerization is accompanied by some decomposition.

We consider first the X-ray diffraction data which, unfortunately, are of limited utility for two reasons. First, the data for the two isomers (25°, Tables III and IV) are closely similar. Second, the features that are different involve only lines of low intensity.

Despite the visual observations recorded in Table I, the essentially constant cobalt content (Table I) and the X-ray diffraction data for 25, 150, and 180° (Table III) show that the *cis* compound does not undergo appreciable decomposition up to 180°. The only significant evidence is the increased intensity in the line corresponding to $d = 3.44$ A; this increases further in the 220° product and persists in all subsequent ones. Still further evidence for lack of decomposition is the absence of lines attributable to NH_4Cl, a known[1] product of decomposition. The three most intense lines (A) for NH_4Cl (relative intensities in parentheses) are: 2.74 (1.0), 3.87 (0.2), and 1.58 (0.2).[4] For the *trans* isomer there was no visible evidence of change until a temperature of 210° was reached and the cobalt content did not change significantly; accordingly, samples over the range 25–210° were not examined.

Inspection of the X-ray data for the product obtained by heating the *trans* isomer to 210° shows markedly better correspondence to those for the *cis* as opposed to the *trans* compound. The 210° product and the *cis* isomer have 12 lines in reasonably good agreement, and all of the discrepancies are found in lines of low intensity. Thus, the 210° product includes three *d* spacings (4.39, 3.03, and 2.67 A) not found for the pure *cis* isomer. These low-intensity lines must be attributed to nonextensive decomposition, and they cannot be attributed to ammonium chloride.[4] Also, four *d* spacings from the pattern for the *cis* isomer (4.60, 3.71, 2.15, and 2.02 A) are not among the data for the 210° product. Accordingly, it must be concluded that, although strongly indicative of *trans–cis* isomerization, these data alone are not conclusive.

Support however is found in the infrared spectrum of the 210° product which is compared with those of the two isomers in Figure 2. That decomposition accompanies isomerization is indicated by the band at 1405 cm^{-1} which is not present in the spectrum of either isomer. That decomposition is not extensive is indicated by the low intensity of the NH_4^+ band at 1400 cm^{-1}. Otherwise, the spectral data are indicative of isomerization although they do not preclude the possibility that some unconverted *trans* isomer may be present at 210°.

There are numerous examples of *cis–trans* isomerization and racemization of octahedral complexes involving polydentate ligands in solution, but only isolated cases wherein these processes occur in the solid state.[5] We are not aware of any case of *trans–cis* isomerization of an octahedral complex involving only monodentate ligands in the solid state. Mechanisms proposed for isomerization in solution usually invoke participation

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(1) G. W. Watt, *Inorg. Chem.*, **3**, 325 (1964).

(2) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 14, Longmans Green and Co., New York, N. Y., 1935, p 668.

(3) N. Fogel, C. Lin, C. Ford, and W. Grindstaff, *Inorg. Chem.*, **3**, 720 (1964).

(4) ASTM Index of X-Ray diffraction patterns.

TABLE I
DECOMPOSITION OF
cis-DICHLOROTETRAAMMINECOBALT(III) CHLORIDE

Temp, °C	Properties[a]	% Co
25	Violet solid	24.0
150	Gray-violet solid	23.7
180	Blue-violet solid	24.2
220	Blue-violet solid	24.3
260	Light blue solid	24.9
270	Light blue solid	26.4
279[b]	Dark blue liquid	27.5

[a] Before quenching. [b] Incipient melting.

TABLE II
DECOMPOSITION OF
trans-DICHLOROTETRAAMMINECOBALT(III) CHLORIDE

Temp, °C	Properties[a]	% Co
25	Dark green solid	25.2
210	Gray-blue solid	25.4
245	Bright blue solid	25.6
255	Bright blue solid	...
274[b]	Light blue solid	28.1
283	Dark blue liquid	29.8
300	Dark blue liquid	30.0
335	Dark blue liquid	31.5

[a] Before quenching. [b] Incipient melting.

TABLE III
X-RAY DIFFRACTION DATA FOR
cis-DICHLOROTETRAAMMINECOBALT(III) CHLORIDE AND
ITS THERMAL DECOMPOSITION PRODUCTS

25°		150°		180°		220°	
d,Å	I/I_0	d,Å	I/I_0	d,Å	I/I_0	d,Å	I/I_0
5.7	1.00	5.6	1.00	5.6	1.00	5.6	1.00
5.1	0.05	5.1	0.05	5.1	0.05	5.0	0.05
4.60	0.10	4.58	0.15	4.65	0.10	4.70	0.01
4.11	0.10	4.13	0.10	4.10	0.01	4.33	0.05
3.88	0.05	3.92	0.05	3.83	0.01	4.06	0.01
3.71	0.10	3.66	0.15	3.62	0.15	3.88	0.20
3.62	0.10	3.59	0.15	3.44	0.30	3.45	0.50
3.48	0.10	3.31	0.20	3.24	0.10	3.26	0.20
3.28	0.10	3.27	0.15	2.76	0.10	3.01	0.20
2.79	0.10	2.76	0.05	2.56	0.30	2.77	0.20
2.56	0.10	2.56	0.15	2.37	0.15	2.58	0.40
2.39	0.05	2.37	0.10	2.15	0.15	2.36	0.05
2.15	0.10	2.11	0.10	2.02	0.10	2.03	0.20
2.02	0.05	2.01	0.05	1.95	0.10	1.96	0.20
1.94	0.01	1.94	0.05	1.85	0.15	1.86	0.10
1.85	0.10	1.85	0.10				

260°		270°		279°	
d,Å	I/I_0	d,Å	I/I_0	d,Å	I/I_0
5.6	1.00	5.5	1.00	5.6	0.50
5.2	0.30	5.2	1.00	5.3	1.00
3.90	0.10	4.27	0.05	4.70	0.01
3.48	0.50	3.92	0.05	4.38	0.10
3.00	0.10	3.47	0.60	3.95	0.05
2.78	0.20	3.11	0.01	3.75	0.05
2.56	0.30	2.96	0.20	3.49	0.50
2.37	0.05	2.83	0.01	3.01	0.30
2.30	0.01	2.75	0.30	2.76	0.30
2.04	0.05	2.56	0.30	2.57	0.30
1.96	0.10	2.35	0.10	2.37	0.10
1.86	0.10	2.02	0.05	2.28	0.01
		1.95	0.10	1.87	0.10
		1.85	0.10		

TABLE IV
X-RAY DIFFRACTION DATA FOR
trans-DICHLOROTETRAAMMINECOBALT(III) CHLORIDE AND
ITS THERMAL DECOMPOSITION PRODUCTS

25°		210°		245°		255°	
d,Å	I/I_0	d,Å	I/I_0	d,Å	I/I_0	d,Å	I/I_0
5.7	1.00	5.5	1.00	5.6	1.00	5.6	1.00
5.2	0.01	5.0	0.50	5.3	0.50	5.2	0.50
4.57	0.20	4.39	0.01	4.37	0.02	4.35	0.10
4.19	0.01	4.05	0.10	4.02	0.20	4.05	0.05
3.81	0.20	3.91	0.10	3.75	0.10	3.91	0.05
3.62	0.50	3.63	0.10	3.49	0.50	3.77	0.05
3.29	0.02	3.46	0.10	3.29	0.05	3.49	0.50
2.85	0.20	3.29	0.05	3.05	0.05	3.35	0.03
2.72	0.01	3.03	0.10	2.97	0.05	3.26	0.03
2.38	0.05	2.78	0.10	2.80	0.05	3.03	0.05
2.13	0.10	2.67	0.05	2.74	0.05	2.86	0.01
2.06	0.01	2.58	0.10	2.66	0.01	2.78	0.05
2.00	0.05	2.38	0.01	2.59	0.50	2.67	0.02
1.91	0.02	1.97	0.02	2.38	0.02	2.58	0.50
1.85	0.05	1.86	0.02	1.96	0.02	2.37	0.02
1.82	0.01			1.86	0.02	1.96	0.03
						1.86	0.05

274°		283°		300°		335°	
d,Å	I/I_0	d,Å	I/I_0	d,Å	I/I_0	d,Å	I/I_0
5.2	1.00	5.1	0.50	5.1	0.50	6.0	1.00
4.55	0.01	4.55	0.01	4.55	0.05	5.3	0.01
4.27	0.05	3.59	0.10	3.62	0.05	4.70	0.01
3.91	0.05	3.28	0.05	3.31	0.01	3.26	0.10
3.67	0.05	3.21	0.05	3.11	0.10	2.98	0.10
3.45	0.05	3.10	0.10	2.99	0.10	2.81	0.20
3.20	0.01	2.98	0.10	2.77	1.00	2.74	0.40
3.09	0.01	2.76	1.00	2.59	0.05	2.68	0.50
3.00	0.30	2.58	0.01	2.27	0.10	2.28	0.10
2.73	0.30	2.49	0.01	2.00	0.05	2.16	0.10
2.53	0.20	2.37	0.01			2.11	0.10
2.34	0.01	2.27	0.15			1.99	0.10
1.99	0.05	1.94	0.05			1.75	0.10
1.93	0.05	1.88	0.05			1.70	0.10
						1.66	0.10

TABLE V
INFRARED SPECTRAL DATA (CM^{-1}) FOR
cis-DICHLOROTETRAAMMINECOBALT(III) CHLORIDE
AND ITS DECOMPOSITION PRODUCTS

25°C.	289 s	-	330 s	355 m	-	-	490 w,b	-	850 m,b
150°C.	290 s	-	330 s	356 m	436 vw	464 vw	490 w,b	-	847 m,b
180°C.	290 s	-	328 s	356 m	438 vw	468 vw	490 w,b	-	847 m,b
220°C.	290 s	303 s	332 s	350 m	438 vw	468 w	491 m	500 m	847 m,b
260°C.	288 s	307 s	329 s	-	439 vw	488 w	491 m	500 m	847 m,b
270°C.	289 s	307 s	327 s	-	439 vw	466 w	491 m	500 m	845 m,b
279°C.	288 s	307 s	325 s	-	438 vw	467 w	490 m	499 m	838 m,b

25°C.	1288 s	1302 s	1312 s	-	-	1600 m,b	3180 s	3290 s
150°C.	1287 s	1302 sh	1312 s	-	-	1600 m,b	3180 s	3290 s
180°C.	1288 s	-	1312 s	-	1410 w	1600 m,b	3180 s	3290 s
220°C.	1280 s	-	1313 s	-	1407 m	1600 m,b	3180 s	3290 s
260°C.	1278 s	-	1311 s	1319 sh	1412 m,b	1600 m,b	3180 s	3290 s
270°C.	1277 m	-	1311 s	1319 sh	1410 s	1600 m,b	3200 s	3280 s
279°C.	1278 m	-	1314 s	1320 sh	1410 s,b	1600 m,b	3200 s	3280 s

TABLE VI
INFRARED SPECTRAL DATA (CM^{-1}) FOR
trans-DICHLOROTETRAAMMINECOBALT(III) CHLORIDE
AND ITS DECOMPOSITION PRODUCTS

25°C.	298 s	-	-	358 s	-	-	-	502 m	550 m	-	790,820 m,b
210°C.	288 s	-	329 s	350 s	-	466 w	490 m	499 m	-	-	850 m,b
245°C.	285 s	305 s	326 s	-	438 w	466 w	490 m	499 m	-	-	850 m,b
255°C.	288 s	306 s	327 s	-	438 w	466 w	490 m	499 m	-	-	848 m,b
274°C.	289 m	306 s	321 s	-	468 vw	466 vw	469 m	-	-	-	828 m,b
283°C.	-	312 s	-	-	438 vw,vb	-	-	-	-	840 s,b	-
300°C.	-	312 s	-	-	438 vw,vb	-	-	-	-	640 s,b	-
335°C.	-	312 s	-	-	438 vw,vb	-	-	-	-	640 s,b	-

25°C.	1282 s	1299 s	1310 s	-	-	1600 m,b	-	3160 s	3270 s	-
210°C.	-	-	1311 s	1317 sh	1405 m	1600 m,b	-	3200 s	3300 s	-
245°C.	1277 w	-	1311 s	1317 sh	1412 m	1600 m,b	-	3200 s	3280 s	-
255°C.	1278 w	-	1312 s	1317 sh	1410 s	1600 m,b	-	3200 s	3290 s	-
274°C.	1277 w	-	1315 s	1325 s	1410 s	1600 m,b	-	3180 s	3280 s	-
283°C.	1250 w	-	1313 vw	-	1410 s	1600 m,b	3050 s	3200 s	3250 s	3320 s
300°C.	1250 w	-	1313 vw	-	1410 s	1600 m,b	3050 s	3200 s	3250 s	3320 s

of solvent molecules or ions derived therefrom.[5] In the present case it is suggested that isomerization might result from simple intermolecular ligand exchange.

The data of Figure 1 show that, following isomeriza-

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(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 241–302, and references therein.

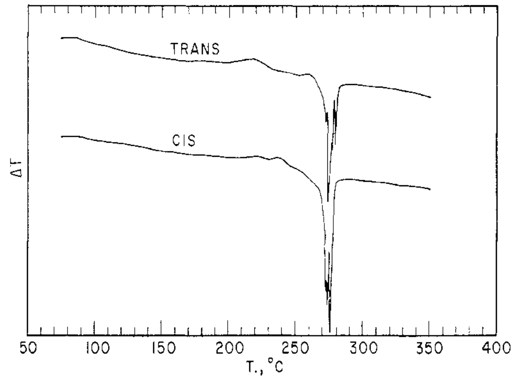

Figure 1.—Differential thermal analysis curves for *cis*- and *trans*-dichlorotetraamminecobalt(III) chloride in N_2 at 1 atm, 2 ft^3/hr; heating rate, 8°/min.

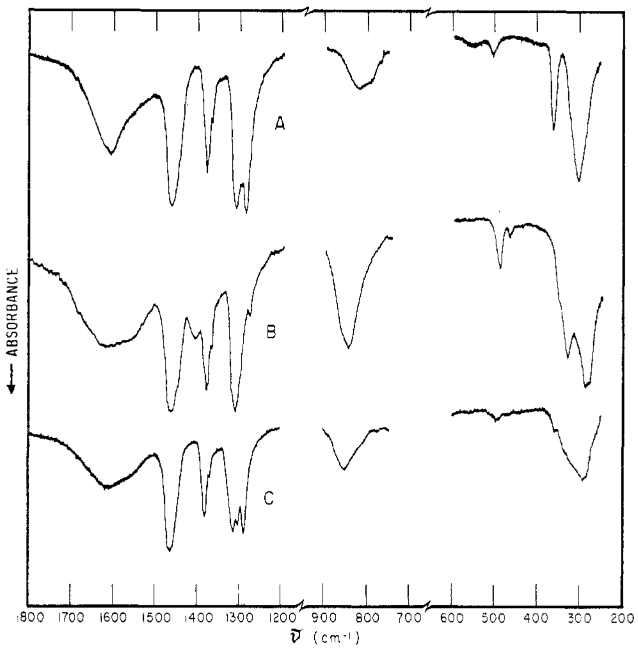

Figure 2.—Infrared spectra of: A, *trans*-[$Co(NH_3)_4Cl_2$]Cl; B, product from heating *trans* isomer to 210°; C, *cis*-[$Co(NH_3)_4Cl_2$]-Cl.

tion, the decomposition occurs in a manner essentially the same as that of [$Co(NH_3)_5Cl$]Cl_2.[1] The main endothermal peak between 270 and 280° encompasses the temperature range over which the rates of N_2 and NH_4Cl liberation and of generation of paramagnetic species[6] are maximum. The small differences in the exact position of these endotherms are believed to be within experimental error. The virtual identity of the mode of decomposition of *cis*-[$Co(NH_3)_4Cl_2$]Cl and [$Co(NH_3)_5$-Cl]Cl_2 is further shown by the X-ray diffraction and infrared spectral data for the tetraammines at and above 270° (Tables IV and VI and Figure 3) and for the chloropentaammine[1] at and above 289°. For example, every *d* spacing for the product obtained by heating the chloropentaammine[1] to 287° is duplicated

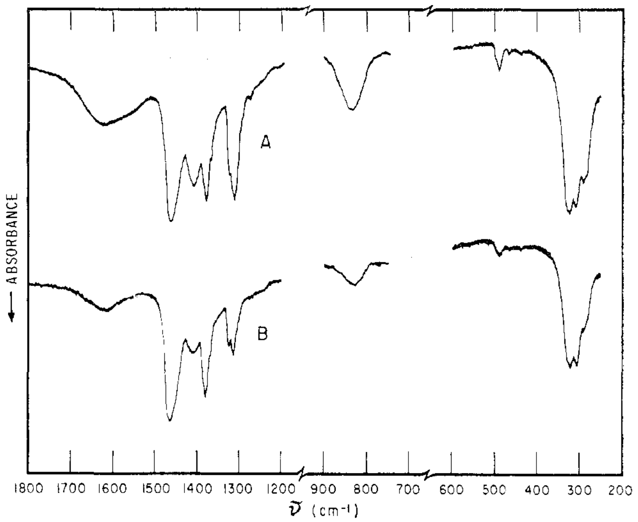

Figure 3.—Infrared spectra of: A, product from heating *cis*-[$Co(NH_3)_4Cl_2$]Cl to 279°; B, product from heating *trans*-[$Co(NH_3)_4Cl_2$]Cl to 274°.

in the 260° product from the *cis*-dichloro compound and the 255° product from the *trans* isomer.

With regard to species possibly generated over the range of *ca.* 200–300°, involvement of [$Co(NH_3)_3Cl_3$] is suggested by the work of Wendlandt[7] and Mori, *et al.*[8] Despite the undoubtedly fortuitous fact that the cobalt content (27.5%) of the 279° decomposition product compares favorably with that calculated for the trichlorotriammine (27.2%), other evidence indicates that this complex cannot be present in significant quantities. Conversion of *cis*-[$Co(NH_3)_4Cl_2$]Cl to low-spin [$Co(NH_3)_3Cl_3$] involves only the loss of NH_3 and thus could not account for the strong NH_4^+ band at 1400 cm^{-1} nor the high paramagnetic moment of the 279° product.

In earlier work,[1] the possible intermediation of $(NH_4)_2CoCl_4$ was largely discounted because of failure to observe an infrared band attributable to the Co–Cl stretching frequency. In the present work however, this strong band was observed (Table VI and Figure 3) at 312 cm^{-1}, which is well within the range of 295–316 cm^{-1} for known $(CoCl_4)^{2-}$ salts.[9] We therefore believe that this, together with the earlier X-ray evidence, is sufficient to establish the presence of $(NH_4)_2$-$CoCl_4$. The presence also of six-coordinated cobalt(II) ammines is shown by the infrared data,[10,11] *e.g.*, the strong band at 634 cm^{-1} that has been assigned as an NH_3 rocking mode.

Finally, it is of interest to note that the *cis* isomer prepared by Werner[2] was probably not a hemihydrate.

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[6] Data on the paramagnetic susceptibility of samples corresponding to the temperatures in Tables I and II are not reported here since they essentially duplicate and lead to the same conclusions as those given previously in Figure 3 of ref 1.

[7] W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **25**, 545 (1963).

[8] M. Mori, M. Shibata, K. Hirota, K. Masuno, and Y. Suzuki, *Nippon Kagaku Zasshi*, **79**, 1251 (1958).

[9] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

[10] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 149, Table III-2.

[11] N. Tanaka, M. Sato, and M. Nanjo, *Sci. Rept. Tohoku Univ., First Ser.*, **48**, 1 (1964).

Neither the data of Table I nor Figure 1 show evidence of change over the temperature range in which dehydration would be expected. Further, the infrared spectrum does not show the ν_1 and ν_3 water bands at 3400 and 3220 cm^{-1}.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MISSOURI AT ST. LOUIS, ST. LOUIS, MISSOURI

Ion Association between Quaternary Ammonium Ions and Hexacyanochromate(III) Ion. Study of Proton Transverse Relaxation Times

BY DAVID W. LARSEN

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A study was made of the changes that occur in the proton transverse relaxation times of aqueous quaternary ammonium ions upon ion-pair formation with hexacyanochromate(III) ions. The observed decrease in transverse relaxation times is attributed to a dipolar interaction, and a previously proposed model is used to explain the observed T_2 values. Tumbling times for the ion pairs and the possibility of tumbling of the separate ions within the ion pair are discussed.

Introduction

Recently, nmr methods have been used to study ion-pair formation in both aqueous[1–3] and nonaqueous solvents.[4,5] When one of the ions in the ion pair is paramagnetic, isotropic hyperfine interactions are present owing to close association between cation and anion.[3] If T_{1e}, the spin-lattice relaxation time of the unpaired electron(s), is relatively short, the large chemical shifts, due to "contact" or "pseudo-contact" interactions,[6] which accompany ion-pair formation may be observed. Aqueous solutions containing quaternary ammonium ions and ferricyanide ion have been shown[3] to exhibit large chemical shifts due to "pseudo-contact" interactions, from which information about the geometry was obtained.

If T_{1e} is relatively long, a decrease[7] in the transverse relaxation time, T_2, of the nucleus in question will accompany ion-pair formation. Aqueous solutions containing quaternary ammonium ions and chromicyanide ion exhibit short T_2 values owing to the relatively long T_{1e} value for the chromicyanide ion. This paper presents detailed experimental T_2 data from nmr measurements. The data are evidence for ion-pair formation, and inferences may be drawn about the geometry within the ion pair.

Experimental Section

Reagents.—The following reagents were used without further purification: quaternary ammonium salts (Eastman Organic Chemicals) and deuterium oxide (Liquid Carbonic). Potassium chromicyanide (K & K Laboratories) was recrystallized twice from water and dried for 1 hr at 100° before use.

Nmr Measurements.—The proton magnetic resonance spectra of D_2O solutions containing R_4N^+ were recorded using a Varian Associates DA-60 nmr spectrometer operating at 60 Mcps. Values of T_2 were determined from the line widths of the recorded spectra. Sets of solutions contained 0.05 M quaternary ammonium salts and 0 to $\sim$0.015 M potassium chromicyanide.

Results

Determination of T_2 Values.—Addition of $Cr(CN)_6^{3-}$ to solutions containing R_4N^+ causes line broadening of the proton spectra which increases with increasing concentration of the paramagnetic anion. The line widths for each set of magnetically equivalent protons in all R_4N^+ systems studied may not be measured directly from the recorded spectra because of the presence of spin–spin coupling.

The proton spectrum of $(CH_3)_4N^+$ is a 1:1:1 triplet[3,8] due to spin coupling with N^{14}, with $J_{N\alpha} = 2.0$ cps.

The spectrum of $(C_2H_5)_4N^+$ is essentially an ethyl pattern (A_2X_3 case[9]) with additional splitting of the methyl resonance due to coupling with N^{14}. Values of coupling constants have been reported:[3,10] $J_{N\alpha} = 0$; $J_{N\beta} = 2.0$; $J_{\alpha\beta} = 7.4$ cps.

The spectrum of the methyl (γ) protons in $(n\text{-}C_3H_7)_4N^+$ is essentially the B part of an A_2B_3 case[9] with $J = 7.0$ cps and $\nu_0\delta = 45$ cps. The spectrum of the α-methylene protons is essentially one-half of an A_2B_2 case[9] with $J \neq J'$. Spin-decoupling experiments indicate that the only observable coupling for both the α-CH_2 and γ-CH_3 sets of protons is to the β-CH_2 protons. It was possible to reduce either the α or the γ multiplet to a sharp Lorentzian singlet by H_2 irradiation

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[1] R. P. H. Gasser and R. E. Richards, *Mol. Phys.*, **2**, 357 (1959).

[2] M. Alei, *Inorg. Chem.*, **3**, 44 (1964).

[3] D. W. Larsen and A. C. Wahl, *ibid.*, **4**, 1281 (1965).

[4] R. L. Buckson and S. G. Smith, *J. Phys. Chem.*, **68**, 1875 (1964).

[5] G. N. LaMar, *J. Chem. Phys.*, **41**, 2992 (1964).

[6] H. M. McConnell and R. E. Robertson, *ibid.*, **29**, 1361 (1958).

[7] I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

[8] E. Grunwald, A. Lowenstein, and S. Meiboom, *J. Chem. Phys.*, **25**, 382 (1956).

[9] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 6.

[10] J. M. Anderson, J. D. Baldeschwieler, D. C. Dittmer, and W. D. Phillips, *J. Chem. Phys.*, **38**, 1260 (1963).