

Influence of the Solvent on the Mode of Coordination of 4-Cyanophenylacetonitrile to Silver(I) Ion

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The mode of coordination of 4-cyanophenylacetonitrile to silver ion in propylene carbonate and in nitromethane has been investigated by infrared spectrophotometry. In propylene carbonate, aromatic nitrile coordination is the only mode of nitrile coordination to silver ion; in nitromethane, it constitutes one-half of the nitrile coordination of silver ion. The results are explained in terms of the relative stability of aliphatic nitrile versus aromatic nitrile complexes of silver ion in the two solvents and of the compatibility of the aromatic nitrile and aliphatic nitrile coordinated 4-cyanophenylacetonitrile complexes with the solvent.

Introduction

Earlier, it was shown that in the solvent hydracrylonitrile ($\text{HOCH}_2\text{CH}_2\text{C}\equiv\text{N}$), copper(II) ion is solvated by hydracrylonitrile molecules through the nitrile group.¹ This mode of coordination is contrary to that expected on the basis of the potential data for the copper couples in acetonitrile and in ethanol, which suggest that copper(II) ion is more strongly solvated in ethanol than in acetonitrile, and the observation that in 1:1 ethanol-acetonitrile mixture copper(II) ion is solvated by ethanol molecules. The unexpected mode of coordination of copper(II) ion in hydracrylonitrile and the observed solvation of copper(II) ion by ethanol molecules in 1:1 ethanol-acetonitrile mixture can be explained in terms of the greater compatibility of the more polar-like nitrile coordinated hydracrylonitrile solvate with bulk hydracrylonitrile molecules and of the polar ethanol solvate with the polar ethanol-acetonitrile medium. In the same manner, the mode of coordination of 3-butenitrile and of 3-dimethylaminopropionitrile to silver ion and copper(I) ion in propylene carbonate (dielectric constant 64, dipole moment 4.98 d) and in 1,2-dichloroethane (dielectric constant 10, dipole moment, 1.97 d) is also markedly influenced by the solvent system.² In this study, we have examined the effect of the solvent on the mode of coordination of 4-cyanophenylacetonitrile to silver ion. The ligand of interest has two nitrile groups in different environments. In one case, the nitrile group is bonded to a methylene group, and in the other, to a benzene ring.

Experimental Section

Practical grade (Baker) propylene carbonate was passed through a 2.5 cm (i.d.) \times 35 cm column of neutral, activity grade one, Woelm chromatographic alumina and then distilled at reduced pressure. Distillation was carried out at less than one mm pressure in order to keep the pot temperature below 90°. Above this temperature, there appears to be some decomposition of the propylene carbonate in the pot. The distillates from distillations in which the propylene carbonate was heated above 90° gave a white precipitate within ten minutes following treatment with anhydrous silver perchlorate. A pure propylene carbonate solution of silver perchlorate remains clear indefinitely when protected from sunlight.

The purification of reagent grade nitromethane called for the removal of propionitrile, 2-nitropropane, and nitroethane, detected by gas chromatography. This was accomplished by four recrystallizations of reagent grade material using an acetonitrile-dry ice bath, followed by distillation at reduced pressure (50 mm of mercury, regulated by allowing dry nitrogen to bleed into the system), and then by final distillation at reduced pressure after treatment of the distillate from the previous step with molecular sieves (Linde 4A) for fifteen minutes.³ The middle eighty percent of the distillate was found to have a water content of 3 millimolar and a conductivity of 1.35×10^{-8} ohm⁻¹ cm⁻¹.

4-Cyanophenylacetonitrile was prepared by the procedure of Julia and Chastrette.⁴ The purification of the product was effected by vacuum sublimation at 1 mm pressure and 50° (Purification from organic solvents was unsuccessful.) After sublimation the product was white and melted at 103.0-103.5°. Benzonitrile from Matheson Scientific (superior grade) was purified by distillation from phosphorus pentoxide according to a procedure described earlier.⁵ Phenylacetonitrile (Matheson Scientific superior grade) was purified in a similar manner. 4-Nitrophenylacetonitrile obtained from Fisher Scientific was recrystallized five times from absolute ethanol and sublimed at 80° and 0.25 mm pressure. A pale yellow product which melted at 111-115° was obtained.

(2) F. Farha, Jr. and R.T. Iwamoto, *ibid.*, 13, 390 (1967).

(3) Detailed information is included in W.C. Boring, Ph.D. Thesis, University of Kansas, 1972.

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(5) R.C. Larson and R.T. Iwamoto, *J. Am. Chem. Soc.*, 82, 3259 (1960).

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Table I. Stretching Frequencies of the CN group of the Nitriles Studied When Free and When Coordinated to Silver Ion in Nitromethane and in Propylene Carbonate.

Ligand	Nitromethane ^{a,b,c}		Propylene Carbonate ^{a,b,c}	
	Aromatic	Aliphatic	Aromatic	Aliphatic
Benzonitrile	2228 (u)		2231 (u) 2252 (c)	
Phenylacetonitrile		2252 (u) 2279 (c)		2250 (u) 2280 (c)
<i>p</i> -Nitrophenylacetonitrile		2254 (u) 2290 (c)		
4-Cyanophenylacetonitrile	2235 (u) 2257 (c)	2257 (u) 2282 (c)	2231 (u) 2255 (c)	2255 (u) 2275 (c)

^a (u) and (c) designate uncoordinated and coordinated nitriles, respectively. ^b All values in cm⁻¹. ^c Uncertainty of ±1 cm⁻¹, except for the frequency of the coordinated aromatic nitrile group of 4-cyanophenylacetonitrile which has a somewhat greater uncertainty (see Results section).

Table II. The Stability Constants of the Nitrile Complexes of Silver Ion in Nitromethane and in Propylene Carbonate.

Nitrile	Nitromethane ^a		Propylene Carbonate ^b	
	K ₁₁	K ₁₂	K ₁₂	K ₁₂
Phenylacetonitrile	88 ± 10	13 ± 2	7.5 ± 2.5	12.6 ± 3.2
Benzonitrile	66 ± 10	9 ± 3	32 ± 3	5 ± 1
<i>p</i> -Nitrophenylacetonitrile	110 ± 10	8 ± 2		

^a Determined at 20°C. ^b Determined at 15°C.

Silver perchlorate (G. Frederick Smith Chemical Co.) was dissolved in deionized water and the insoluble particles filtered off. The filtrate was maintained at a temperature just below 80° until the solution decreased to one-half its original volume. (At temperatures above 80°, the solution turned brown.) Silver perchlorate was recovered by cooling the solution with an ice-salt bath and filtration of the mixture through a medium porosity sintered glass filter. After three recrystallizations, small portions (10 g) were dried in a rotary evaporator with the flask maintained at 80° in a silicone oil bath. The salt was stored over anhydrous magnesium perchlorate.

Infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer with the wave number scale expanded 10× and when called for, the transmittance scale expanded 5×. Differential spectra were recorded from 2400 cm⁻¹ to 2100 cm⁻¹ with a variable path length cell (Beckman XL-O) containing the appropriate solvent in the reference beam and a heated liquid cell (0.1 mm, Beckman FH-O) containing the solution to be examined in the sample beam. The cells were outfitted with sodium chloride and barium fluoride windows, respectively. The lead gasket and lead spacer in the heated liquid cell were replaced with teflon gasket and spacer to eliminate reduction of silver ion by the lead. Prior to recording the spectra, the samples in the heated cell were adjusted to temperatures of 15.0 ± 0.2° (for propylene carbonate solutions) and 20.0 ± 0.2° (for nitromethane solutions). The heated liquid cell was maintained in a Beckman WJ-1 jacket. An iron-constantan thermocouple was inserted in a hole provided near the front window of the heated liquid cell.

Solutions for measurement were prepared volumetrically from stock solutions of the ligands and of silver perchlorate. The stock solutions were prepared determinately. All nitromethane solutions were pre-

pared and transferred in a dry bag through which a stream of dry nitrogen was maintained. Prior to use, purified nitrogen was passed through a drying tube filled with Linde 4A molecular sieves. Fresh sieves dried at 350° for eight hours was used each day. The handling of propylene carbonate solutions did not require use of a dry bag. The solutions examined were ca. 0.03 *F* in silver perchlorate and multiples of 0.03 *F* in ligand up to a multiple of six, and were prepared by appropriate dilution of the stock solutions.

The stability constants for the benzonitrile and the phenylacetonitrile complexes of silver ion were determined by (1) obtaining the concentration of free nitrile, [L], from an absorbance vs nitrile conc. plot (Beer's law plot), (2) calculating the average number of nitriles bound to a metal ion, \bar{n} , and (3) using the equation of Rossotti and Rossotti⁶ for the case

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \beta_1 + \beta_2 \frac{(2-\bar{n})}{(1-\bar{n})} [L]$$

\bar{n} equals 2 and obtaining the slope (β_2) and intercept (β_1) of the plot of $\bar{n}/(1-\bar{n})[L]$ vs. $(2-\bar{n})[L]/1-\bar{n}$. In the analyses, the values of \bar{n} were always less than 2.

Results

The nitrile stretching frequencies which were monitored in this study are listed in Table I. The stretching frequencies for the coordinated aromatic nitrile group of 4-cyanophenylacetonitrile in propylene carbonate and nitromethane carry a greater uncertainty than the ±1 cm⁻¹ of the other nitrile stretching frequencies reported because of overlap of the band with

(6) F.J.C. Rossotti and H.S. Rossotti, *Acta. Chem. Scand.*, 9, 1165 (1955).

that of the uncoordinated aliphatic nitrile group. Table II contains the stability constants of the benzonitrile and phenylacetonitrile complexes of silver ion in propylene carbonate and in nitromethane. In addition, the constants for the *p*-nitrophenylacetonitrile silver ion complexes in nitromethane are included.

Discussion

The two basic types of 4-cyanophenylacetonitrile complexes of silver ion are shown in Figure 1. The mode of coordination in Figure 1a will be referred to, for convenience, as aromatic nitrile coordination, and in Figure 1b, aliphatic nitrile coordination. On

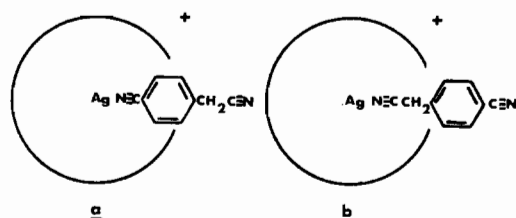


Figure 1. The two basic types of 4-cyanophenylacetonitrile complexes of silver ion.

the basis of our previous studies and from dipole moment data (benzonitrile, $\mu = 4.1$ d; phenylacetonitrile, $\mu = 3.5$ d),⁷ basicity information (phenylacetonitrile more basic than benzonitrile)⁸, and donor number values (phenylacetonitrile, $DN_{SbCl_5} 15.1$; benzonitrile, $DN_{SbCl_5} = 11.9$),⁹ one would expect the favored complex in a polar medium containing silver ion and 4-cyanophenylacetonitrile to be that in which aliphatic nitrile groups are coordinated to silver ion and aromatic nitrile group make up the outer sheath of the complex, a complex in which the more basic nitrile and the better donor is coordinated to silver ion and the more polar nitrile is in the outer sheath of the complex. From the increase in intensity at 2255 cm^{-1} (coordinated aromatic nitrile band) in the infrared spectra of propylene carbonate solutions containing silver ion and 4-cyanophenylacetonitrile and no new band in the spectral region for coordinated aliphatic nitrile (2280 cm^{-1}), it is clear that aromatic nitrile coordination is the only mode of nitrile complexation of silver ions in this polar medium; there is no aliphatic nitrile coordination. This mode of coordination of 4-cyanophenylacetonitrile to silver ion in polar propylene carbonate is completely opposite to that expected on the basis of the properties of phenylacetonitrile and benzonitrile. In nitrome-

thane solutions, about one-half of the nitrile coordination of silver ion by 4-cyanophenylacetonitrile involves the aromatic nitrile group.

To gain additional insight about this phenomenon, the stability constants of the benzonitrile and phenylacetonitrile complexes of silver ion in propylene carbonate and nitromethane were determined, and were used to estimate the extent of aromatic nitrile vs. aliphatic nitrile coordination of silver ion in solutions containing equimolar amounts of benzonitrile and phenylacetonitrile. For propylene carbonate solutions, a value of ca. 70% aromatic nitrile coordination was obtained, and for nitromethane solutions, ca. 40%. There is then a difference of 30% (100% obs. vs. 70% calc.) in the extent of aromatic nitrile coordination between 4-cyanophenylacetonitrile and equimolar mixtures of benzonitrile and phenylacetonitrile in propylene carbonate, and 10% (50% obs. vs. 40% calc.) in the case of nitromethane solutions.

A possible explanation for the difference in the extent of aromatic nitrile coordination of silver ion between 4-cyanophenylacetonitrile and equimolar mixtures of phenylacetonitrile and benzonitrile in propylene carbonate noted above can be found in the stability constants for the benzo- and phenylacetonitrile complexes of silver ion in the two solvents. In nitromethane, the relative order of the stability of the phenylacetonitrile and benzonitrile complexes of silver ion is in accord with the information on the basicity and « donor number » of the two nitriles. The reversal in the order of the stability of these two types of nitrile complexes in propylene carbonate and the small value of the stability constant of the 1:1 complex of phenylacetonitrile and silver ion suggest that phenylacetonitrile or the aliphatic nitrile group is relatively strongly solvated in propylene carbonate. Such a phenomenon would account for the unexpected observation of complete coordination of 4-cyanophenylacetonitrile to silver ion through the aromatic nitrile end in propylene carbonate, with aliphatic nitrile groups in the outer sheath of the solvated silver ion, as opposed to the estimated value of 70% aromatic nitrile coordination with equimolar mixtures of benzonitrile and phenylacetonitrile. The same type of phenomenon may very likely account for the similar situation in the extent of observed vs. estimated aromatic nitrile coordination noted for nitromethane solutions.

The larger value for k_{r1} for the nitrophenylacetonitrile complex of silver ion in nitromethane than that for the phenylacetonitrile complex of silver ion also appears to be a reflection of the same solvation phenomenon.

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