Spectroscopic Studies on Molecular Configurations of Some Aliphatic Dinitriles. III. Infrared Spectra of Adiponitrile and Bis-(adiponitrilo)copper(I) Nitrate

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Recently the author has studied the infrared spectra of some copper(I) complexes of aliphatic dinitriles and showed that they are quite useful in understanding the spectra and molecular configurations of free dinitriles[1,2]. In the course of the spectroscopic studies on the molecular configurations of the series of aliphatic dinitriles, the infrared spectra of adiponitrile and bis(adiponitrilo)copper(I) nitrate, $[Cu\{NC-(CH_2)_4-CN\}_2]NO_3$, have been investigated. Because adiponitrile has three internal axes of rotation, the number of possible staggered rotational isomers becomes large[3], and the complexity of the liquid-state spectrum of this compound may be explained as due to the coexistence of these rotational isomers. X-Ray analysis of bis(adiponitrilo)-copper(I) nitrate[4] has revealed that the ligand adiponitrile takes the planar all-trans(TTT*) configuration in the crystals of this complex. The infrared spectrum of bis(adiponitrilo)-copper(I) nitrate has been explained satisfactorily on the basis of this result, and interpretation of the spectra of adiponitrile both in the liquid and in the crystalline solid states has been made possible by comparing them with that of the complex. The results of the previous spectroscopic studies on other molecules of the type $X-(CH_2)_4-X$ such as *n*-hexane[5-7], tetramethylene halides[8] and adipic acid[9] were also useful in the assignment of the vibrational frequencies of adiponitrile.

Experimental

Bis(adiponitrilo)copper(I) nitrate was prepared in the same way as described in the previous paper[4].

The infrared spectra in the 4000∼400 cm^{-1} region of adiponitrile and the complex were obtained by using a Perkin-Elmer Model 21 and a Perkin-Elmer Model 13 spectrophotometer (with sodium chloride and potassium bromide optics respectively). The spectrum of adiponitrile in the liquid state is shown in Fig. 1a. The spectral simplification

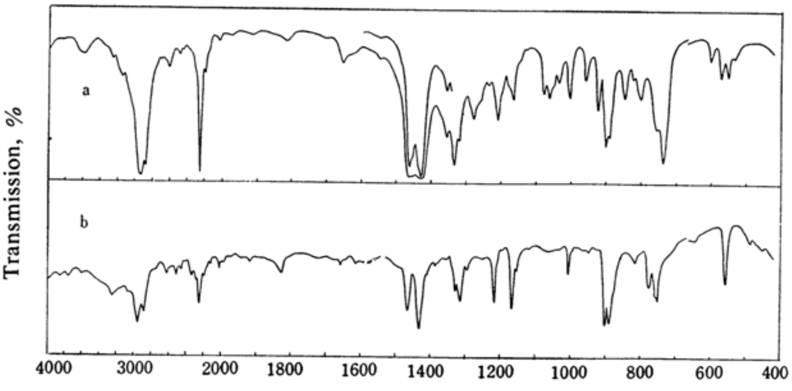

Fig. 1. Infrared spectra of adiponitrile.
(a) at room temperature (liquid); (b) at −20°C (solid).

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[1] I. Matsubara, This Bulletin, **34**, 1710 (1961).

[2] I. Matsubara, ibid., **34**, 1719 (1961).

[3] See for example S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press Inc., New York (1954), Part I, Chap. V.

[4] Y. Kinoshita, I. Matsubara, T. Higuchi and Y. Saito, This Bulletin, **32**, 1221 (1959).

* For the nomenclature of rotational isomers see Ref. 3.

[5] D. W. E. Axford and D. H. Rank, *J. Chem. Phys.*, **18**, 51 (1950).

[6] J. K. Brown, N. Sheppard and D. M. Simpson, *Discussions Faraday Soc.*, No. **9**, 261 (1950).

[7] H. Tschamler, *J. Chem. Phys.*, **22**, 1845 (1954).

[8] J. K. Brown and N. Sheppard, *Proc. Roy. Soc.*, **A231**, 555 (1955).

[9] H. Susi, *Spectrochim. Acta*, **15**, 1063 (1959).

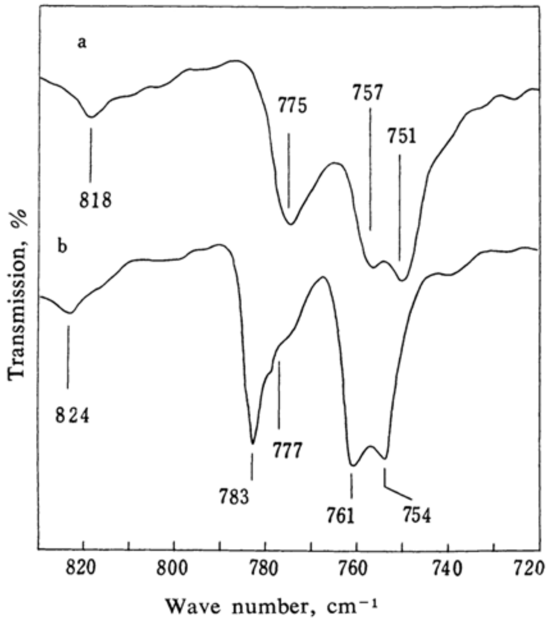
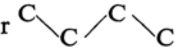


Fig. 2. Infrared spectra in the 830∼720 cm^{-1} region of the solid adiponitrile.
(a) at −20°C; (b) at −150°C.

which occurred when the liquid was cooled down to −20°C is shown in Fig. 1b. The solid-state spectrum of adiponitrile undergoes a reversible change depending on the temperature, although the main features of the spectrum remain the same and no discrete change of the spectrum as observed in the case of glutaronitrile[2] takes place. In Fig. 2 is shown the spectral change in the 830∼720 cm^{-1} region which occurred when the temperature was lowered from −20°C to −150°C. The behavior of adiponitrile is anomalous in that the liquid, if it contains a trace of water, forms a transparent solid phase when rapidly cooled. This has the spectrum shown in Fig. 3. When the solid was warmed up to ca. −20°C, a transition occurred, giving the normal crystalline solid phase which has the spectrum shown in Fig. 1b. The spectrum of bis(adiponitrilo)copper(I) nitrate was obtained using both Nujol mull and potassium bromide disk techniques. Nujol mulls of the complex gave different spectra depending on the type of alkali halide cell windows used as supporting plates. The use of KRS-5 plates and sodium chloride plates resulted in spectra which were at first identical with each other, but the one obtained by using sodium chloride plates soon began to change gradually. When potassium bromide plates were used, the change took place more quickly than in the case of sodium chloride plates. These changes must be attributed to the reaction of the complex with sodium chloride and potassium bromide plates. In Fig. 4a is shown the spectrum obtained by using KRS-5 plates. The spectra in Figs. 4b and 4c are those obtained respectively by the use of sodium chloride and potassium bromide plates. (These two spectra were recorded after the specimens had been placed in the laboratory for one day.) The spectrum obtained from a potassium bromide disk of the complex is shown in Fig. 5. This spectrum agrees quite well with that obtained from Nujol mull by the use of potassium bromide supporting plates (Fig. 4c), showing that the type of reaction which occurs between the complex and potassium bromide is the same in both cases. The absorption frequencies of adiponitrile and bis(adiponitrilo)copper(I) nitrate are listed in Table I, together with the assignment.

Results and Discussion

The symmetry types and the selection rules for the fundamental vibrations of adiponitrile in the 1400∼400 cm^{-1} region are given in Table II[10,11]. Only the rotational isomers with the planar  skeleton are included here, because these are considered the most important among all the isomers of adiponitrile. For the TTT(C_{2h}) and the GTG′(C_i) isomers the existence of a center of symmetry makes the Raman and infrared active fundamentals mutually exclusive, and only nine infrared active modes are expected in this region. For the other isomers, all the fundamentals are expected to be active in both the Raman and infrared spectra. The spectrum of bis(adiponitrilo)-copper(I) nitrate can be explained on the basis of the result of X-ray analysis; the ligand

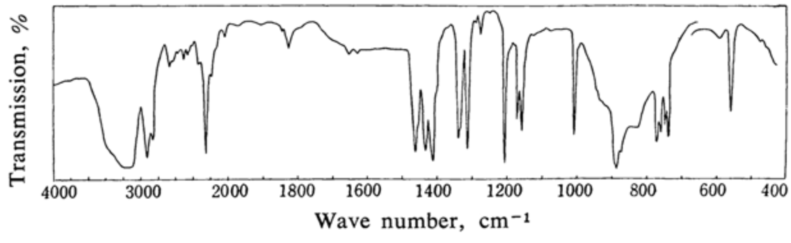


Fig. 3. Infrared spectrum obtained by rapid cooling of adiponitrile containing a trace of water down to −120°C.

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[10] J. K. Brown, N. Sheppard and D. M. Simpson, *Phil. Trans. Roy. Soc. London*, **A 247**, 35 (1954).

[11] E. Funck, *Z. Elektrochem.*, **62**, 901 (1958).

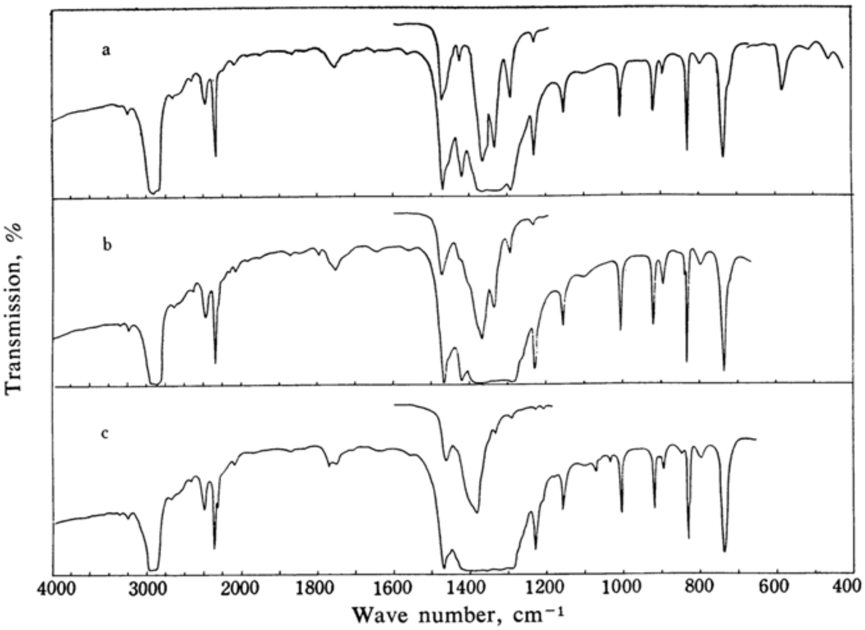

Fig. 4. Infrared spectra obtained from Nujol mulls of bis(adiponitrilo)copper(I) nitrate by using (a) KRS-5, (b) NaCl and (c) KBr supporting plates.

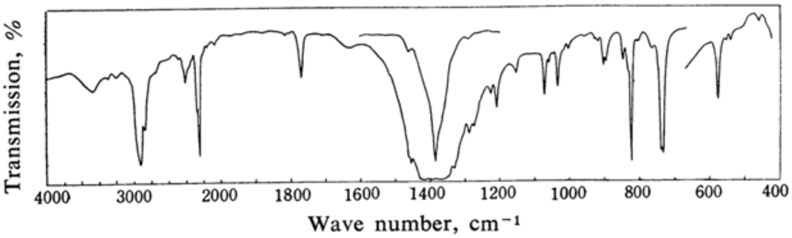

Fig. 5. Infrared spectrum obtained from a KBr disk of bis(adiponitrilo)copper(I) nitrate.

adiponitrile molecule takes the TTT configuration[4]. The Nujol mull spectrum of bis(adiponitrilo)copper(I) nitrate (Fig. 4a) shows quite simple features in good agreement with the selection rules for the centrosymmetric structure. The appearance of an intense band at 737 cm^{-1} is strong evidence for the TTT configuration of adiponitrile, because this band must correspond to the CH_2 rocking vibration of the methylene chain of the planar all-trans configuration[7,10]. Vibrational assignment of the individual bands is made with reference to the spectra of like molecules such as *n*-hexane[5-7]. Thus the strong bands at 1333 and 1290 cm^{-1} are assigned to the CH_2 wagging modes, and those at 1229 and 1155 cm^{-1} to the CH_2 twisting modes. The bands of medium intensity at 1006 and 921 cm^{-1} may correspond to the C–C stretching modes. As mentioned above, the strong band at 737 cm^{-1} is assigned with confidence to one of the CH_2 rocking modes, and the weak band at 895 cm^{-1} may be assigned to another CH_2 rocking mode. The relatively strong band at 581 cm^{-1} should be ascribed to the C–C–C bending mode. A broad weak band at 797 cm^{-1} may be an overtone or combination of some skeletal deformation modes, as has been suggested by Fujiyama and Shimanouchi[12], but no conclusive evidence in support of this view can be found at this stage of investigation.

The strong bands at 1364/57 and 830 cm^{-1} are assigned to the infrared active fundamentals of the nitrate ion, and the weak band at 1751 cm^{-1} must also be correlated with some nitrate vibration. When sodium chloride plates were used to support the mull, new bands appeared at 1795, 1362 and 836 cm^{-1}, as is shown in Fig. 4b. These frequencies correspond well to those of sodium nitrate[13]. In the Nujol mull spectrum obtained by the use

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12) T. Fujiyama and T. Shimanouchi, paper presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

13) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

TABLE I. INFRARED ABSORPTION BANDS OF ADIPONITRILE AND BIS(ADIPONITRILO)COPPER(I) NITRATE

Adiponitrile		Bis(adiponitrilo)-copper(I) nitrate		Assignment	
Liquid (room temp.)	Solid (−20°C)	Nujol mull[a]	KBr disk		
	3861 vw				
	3759 vw				
	3591 vw				
3268 vw	3247 mw	3268 vw	3279 vw		
		3195 w	3205 vw		
3155 vw					
2941 vs	2950 ms		2933 s	TTT, GTG′	C–H stretch.
2874 ms	2882 m		2874 m	TTT, GTG′	C–H stretch.
		2725 vw			
2611 vw	2618 w				
		2513 vw			
2494 vw	2506 w		2488 vw		
2451 vw	2463 w		2433 w sh		
			2404 mw		
		2381 mw			
2315 vw sh	2331 w				
	2278 w				
		2273 ms	2273 m sh	TTT	C≡N stretch. (bound)
2247 vs	2247 ms		2252 ms	TTT, GTG′	C≡N stretch. (free)
2198 w	2193 w	2208 w			
2165 vw sh			2169 vw		
2119 vw	2128 vw				
		2062 vw	2070 vw		
2033 vw	2024 mw				
1972 vw					
1916 vw	1916 vw				
		1866 vw			
1815 vw	1828 mw		1815 vw		
1701 vw					
1653 vw	1658 w	1645 vw			
1548 vw		1560 vw			
1464 vs	1468 ms		1456 s	TTT, GTG′	CH_2 bend.
1456 s sh					
1429 vs	1431 s	1422 ms		TTT, GTG′	CH_2 bend.
	1408 vw				
1377 vw sh	1387 vw				
1357 m					
1335 s	1328 m	1333 vs	1335 s	TTT, GTG′	CH_2 wag.
1319 m	1314 ms			GTG′	CH_2 wag.
1307 vw sh	1295 vw				
1280 mw		1290 s	1289 ms	TTT	CH_2 wag.
			1277 m sh		
1266 vw sh			1267 mw sh		
1258 vw					
1235 vw		1229 ms	1229 mw	TTT	CH_2 twist.
1209 m	1217 ms		1209 m	GTG′	CH_2 twist.
1198 vw sh	1193 vw				
1179 w					
1167 w	1167 s		1163 vw sh	GTG′	CH_2 twist.
1152 vw	1153 w	1155 mw	1156 mw	TTT	CH_2 twist.
1129 vw					
		1101 vw			

TABLE I. (Continued)

Adiponitrile		Bis(adiponitrilo)-copper(I) nitrate		Assignment	
Liquid (room temp.)	Solid (−20°C)	Nujol mull[a]	KBr disk		
1080 mw			1073 m		
1064 mw			1063 w		
1054 w sh			1049 vw		
1038 w		1044 vw	1035 m		
1032 vw sh			1021 vw		
1005 m	1007 m	1006 m	1005 w	TTT, GTG′	C–C stretch.
		971 vw			
960 mw			962 vw		
954 vw sh	948 vw				
			930 w		
923 m		921 m	920 w	TTT	C–C stretch.
900 ms	900 s		905 mw	GTG′	CH$_2$ rock.
891 m	888 s	895 w	897 mw	TTT GTG′	CH$_2$ rock. C–C stretch.
883 vw sh	876 m sh				
848 mw			849 mw		
			833 w sh		
821 vw	818 w		810 vw		
803 mw		797 w	807 vw		
	775 m				
	757 ms			GTG′	CH$_2$ rock.
752 m sh	751 ms		763 w		
734 s		737 s	736 s	TTT	CH$_2$ rock.
			732 s		
602 w					
573 mw		581 mw	576 mw	TTT	C–C–C bend.
553 mw	556 ms		553 vw	GTG′	C–C–C bend.
535 vw			539 vw		
	486 vw				
	457 vw	459 vw	459 vw		

a) KRS-5 supporting plates were used to obtain the spectrum.

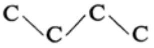
of potassium bromide plates and in the potassium bromide disk spectrum, new bands appear at 1770, 1383 and 824 cm^{-1}, as is shown in Figs. 4c and 5 respectively. These frequencies agree well with those of potassium nitrate[13]. It can be concluded from the above results that the mechanism of reaction of the complex and alkali halides should be ascribed largely to an ion interchange between the two phases. The spectra in Figs. 4c and 5 show absorptions which correspond to those of the liquid adiponitrile (Fig. 1a). This suggests that interaction between the complex and alkali halides results in the isolation of free adiponitrile.

The sharp band observed at 2273 cm^{-1} in the Nujol mull spectrum (Fig. 4a) corresponds to the C≡N stretching mode of the complex. The C≡N vibrational shift of 26 cm^{-1} towards higher frequencies by complex formation may be explained in the same way as in the cases of the lower homologues of this complex series[1,2]. Namely, X-ray analysis of this complex has revealed that the C–N bond distance is 1.13 Å and that the Cu–N–C–CH$_2$ group is close to linear, from which it is to be expected that the C–N bond is essentially of a triple-bond character, the contributions of polar resonance structures such as $-C^{+}=N^{-}$ being decreased and the C≡N stretching frequency being thereby increased. The effect of the interaction with the Cu-N stretching vibration, though small, may also contribute to the increase in the C≡N stretching frequency. As is evident from Figs. 4b, 4c and 5, reaction with alkali halides results in the appearance of the band at 2252 cm^{-1} which is attributed to the C≡N stretching frequency of free adiponitrile. The band observed at 2381 cm^{-1} may correspond to a vibration characteristic of the tetrahedral configuration of the complex[1,2].

Adiponitrile shows a marked spectral simplification on passing from the liquid to the crystalline solid state, as is shown in Fig. 1b.

TABLE II. THE SYMMETRY TYPES AND SELECTION RULES FOR THE FUNDAMENTAL VIBRATIONS OF ADIPONITRILE IN THE $1400\sim400$ cm^{-1} region[a)]

Types of symmetry coordinates	TTT(C_{2h})				GTG′ (C_i)		GTG(C_2)		TTG(C_1)
	A_g	B_g	A_u	B_u	A_g	A_u	A	B	
CH_2 wagging	2	0	0	2	2	2	2	2	4
CH_2 twisting	0	2	2	0	2	2	2	2	4
C–C stretching	3	0	0	2	3	2	3	2	5
CH_2 rocking	0	2	2	0	2	2	2	2	4
C–C–C bending	1	0	0	1	1	1	1	1	2
Selection rules IR	−	−	+	+	−	+	+	+	+
Raman	+	+	−	−	+	−	+	+	+

a) Only the isomers with the planar  skeleton are included.

The isomer of adiponitrile stable in the crystalline solid state is considered to have a center of symmetry, as the number of prominent absorption peaks is close to that expected for such a configuration and much smaller than that required for a less symmetrical form (see Table II). Consideration of the selection rules for the skeletal deformation vibrations is particularly useful for the confirmation of this view. The fact that no strong band other than that at 556cm^{-1} is observed in the $600\sim450$cm^{-1} region gives strong support to this conclusion, because only one vibration corresponding to the C–C–C bending mode is to be expected to appear in this region in a centrosymmetric structure. Determination of the isomeric form of adiponitrile in the crystalline solid state can then be made by comparing its spectrum (Fig. 1b) with that of bis(adiponitrilo)copper(I) nitrate (Fig. 4a). The two spectra are evidently very different from each other. For example, the C–C–C bending frequency of 556 cm^{-1} in the crystalline adiponitrile is much lower than the corresponding value of 581 cm^{-1} in the complex. The band observed at 757/51 cm^{-1} in the spectrum of the crystalline adiponitrile must be assigned to the CH_2 rocking mode, while the absorption corresponding to this mode appears at 737 cm^{-1} in the case of the complex. As the frequencies of these two types of vibration are known to change conspicuously with the azimuthal angle of internal rotation[1,2)], such differences in the observed values will serve to exclude the possibility that adiponitrile takes the TTT form in the crystalline solid state. Therefore, it can be concluded that the isomer of adiponitrile stable in the crystalline solid state is another centrosymmetric one, the GTG′ form. The vibrational assignment of the crystalline adiponitrile may be carried out with reference to the work of Brown and Sheppard[8)] on tetramethylene halides, which are known to take the GTG′ configuration in the crystalline solid state. The fact that the spectral features of the crystalline adiponitrile are quite similar to those of tetramethylene halides may give additional support for the GTG′ configuration of the former. Thus, the bands observed at 1468 and 1431 cm^{-1} in the solid-state spectrum (Fig. 1b) are assigned to the CH_2 bending modes. The bands at 1328 and 1314 cm^{-1} may be ascribed to the CH_2 wagging modes, and those at 1217 and 1167 cm^{-1} to the CH_2 twisting modes. The bands at 1007 and 888 cm^{-1} may correspond to the C–C stretching modes. The band at 757/51 cm^{-1} must be assigned to one of the CH_2 rocking modes, and that at 900 cm^{-1} may correspond to another CH_2 rocking mode. As mentioned above, the band at 556 cm^{-1} should be ascribed to the C–C–C bending mode. By analogy with the cases of the lower homologues of the dinitrile series[1,2)], the energetical contributions of both the C–C–C bending and C–C≡N bending motions are considered to be important in this vibration. The bands observed at 818 and 775 cm^{-1} may be explained as overtones or combinations of some skeletal deformation vibrations. Although the 775 cm^{-1} band seems too intense to be interpreted as such vibrations, this assignment is nevertheless not unreasonable, because the overtone or combination bands of this type are expected to become remarkably intense at low temperatures, as has been observed in the case of succinonitrile[1)].

As shown in Fig. 2, the solid-state spectrum of adiponitrile undergoes a reversible change depending on the temperature, which suggests the occurrence of a change in the crystal structure. However, as the change is not discrete and the overall spectral features are essentially the same at all temperatures, it may not be attributed to a transition to different isomeric forms, as in the case of glutaronitrile[2)].

The anomalous spectrum in Fig. 3 which is obtained when adiponitrile containing a trace of water is rapidly cooled may correspond to some metastable crystalline solid phase. Although this spectrum seems at first sight to be very different from that of the normal crystalline solid phase (Fig. 1b), the one to one correspondence of the individual bands in the two spectra is quite good, showing that adiponitrile also takes the GTG′ form in this metastable solid state.

Many of the bands in the liquid-state spectrum of adiponitrile can be explained as due to the vibrations of the TTT and the GTG′ isomers, as is shown in Table I. Considering the number of the unassigned bands, at least one more isomer can be expected to exist in the liquid state. Determination of the configuration of this isomer will not be attempted here, however, as it would require much more detailed analysis of the spectrum based on a normal coordinate treatment.

Summary

The infrared spectra of adiponitrile and bis(adiponitrilo)copper(I) nitrate, $[Cu\{NC-(CH_2)_4-CN\}_2]NO_3$, have been studied. The spectrum of the complex has been analyzed on the basis of the result of X-ray analysis which disclosed that the ligand adiponitrile takes the TTT(C_{2h}) configuration in the crystals of this compound. This complex reacts with alkali halides such as sodium chloride and potassium bromide, resulting in the isolation of free adiponitrile. Considering the frequency shifts of the nitrate vibrations, the reaction of the complex with alkali halides should be ascribed largely to an ion interchange between the two phases. The increase of 26 cm^{-1} in the $C\equiv N$ stretching frequency by complex formation may be understood by considering the linear structure of the $Cu-N-C-CH_2$ group, which suggests that the carbon-nitrogen bond is essentially of a triple-bond character, the contributions of polar resonance structures such as $-C^+=N^-$ being decreased. Adiponitrile shows a marked spectral simplification on passing from the liquid to the crystalline solid state. From a comparison of the solid-state spectrum with that of the complex, and from a consideration of the vibrational selection rules, it has been concluded that adiponitrile takes the GTG′(C_i) configuration in the crystalline solid state. The fact that the solid-state spectrum of adiponitrile is subject to a reversible change depending on the temperature may be explained as due to a slight change in the crystal structure. Many of the bands in the liquid-state spectrum of adiponitrile have been assigned to the vibrations of the TTT and the GTG′ isomers, and the number of the remaining bands suggests the existence of at least one more isomer in the liquid state.

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