BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2353—2356 (1968)

Infrared Spectra and Conformations of Succinonitrile in Silver and Copper Complexes

Masako SUZUKI and Takehiko SHIMANOUCHI

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

(Received April 22, 1968)

Succinonitrile silver nitrate $[Ag(NCCH_2CH_2CN)]NO_3$ and succinonitrile disilver nitrate $[Ag(NCCH_2CH_2CN)Ag](NO_3)_2$ were prepared and the infrared spectra down to 60 cm^{-1} were measured. It was shown that the ligand molecule takes only the trans form in these complexes. The far infrared spectra were also measured for the free succinonitrile ligand at room and liquid nitrogen temperatures and for the copper complex. The assignments of bands for the nitrate ion and the trans and the gauche forms of succinonitrile were given.

Vibrational spectra of succinonitrile show that this molecule takes both the trans and gauche forms in the solid state at room temperature and only the latter form remains at low temperature.[1,2] As for the crystal of bis(succinonitrile)copper(I) nitrate, $[Cu(NCCH_2CH_2CN)_2]NO_3$, infrared spectra,[3] and X-ray analysis[4] show that the ligand succinonitrle takes the gauche form.

We have succeeded in preparing two kinds of silver complexes, succinonitrile silver nitrate $[Ag(NCCH_2CH_2CN)]NO_3$ and succinonitrile disilver nitrate $[Ag(NCCH_2CH_2CN)Ag](NO_3)_2$. We have measured the infrared spectra of these complexes down to 60 cm^{-1} and found that the ligand succinonitrile molecule takes only the trans form in these complexes. This fact has been confirmed for the disilver nitrate by the X-ray analysis as reported by Nomura and Saito.[5] In the present paper the results of the infrared spectra of silver nitrate and disilver nitrate complexes are reported. The fact that we have only the trans form in the silver complexes and only the gauche form in the copper complex enables us to obtain the spectra of the two conformations separately. Accordingly, the spectra of the copper complex and the free succinonitrile ligand have also been measured down to 60 cm^{-1} and the assignments of bands have been reinvestigated.

Experimental

Silver complexes were prepared from succinonitrile and silver nitrate. Succinonitrile (bp 158—160°C/20 mmHg) was melted at about 60°C and silver nitrate powder was added. The excess nitrile was extracted by an alcohol-ether mixture. The complexes were recrystallized from ethanol and colorless needle-like crystals were obtained. Microscopic investigation showed that two kinds of crystals exist. One was transparent and of regular shapes and the other was opaque and of irregular shape. These two kinds of crystals were separated manually. The following elementary analysis showed that the former kind is succinonitrile disilver nitrate and the latter is succinonitrile silver nitrate.

Found: C, 11.80; H, 0.84; N, 13.32%. Calcd for $[Ag(NCCH_2CH_2CN)Ag](NO_3)_2$: C, 11.44; H, 0.96; N, 13.34%.

Found: C, 19.57; H, 1.77; N, 16.91%. Calcd for $[Ag(NCCH_2CH_2CN)]NO_3$: C, 19.22; H, 1.61; N, 16.80%.

The copper complex was prepared according to the method given by Morgan.[6]

The infrared spectra were recorded by the following grating spectrometers: Hitachi EPI-2 and Perkin-Elmer 112G (4000—650 cm^{-1}), Japan Spectroscopic Co. 401G (700—300 cm^{-1}) and Hitachi FIS-1 (500—60 cm^{-1}). Nujol mull and HCB mull were used except in the far infrared region, where the samples mixed with paraffin were used. The copper complex in a KBr disk or in contact with alkali halide windows was reported to decompose gradually.[8] For the present complexes the same phenomena were observed. In order to avoid the decomposition, thin polyethylene films were inserted between the alkali halide windows and the sample. Sometimes the sample was purposely put in contact with the KBr window, since the changes in spectra were useful for discriminating the nitrate ion bands from those belonging to the ligand molecule. Succinonitrile was melted and solidified between the KBr plates in the 4000—500 cm^{-1} region or between the silicon plates in the 500—60 cm^{-1} region and was used for the measurement at room temperature and at liquid nitrogen temperature. The spectra are shown in Fig. 1.

Result and Discussion

The complexes dealt with in the present study contain nitrate ions and the absorption bands

1) W. E. Fitzgerald and G. J. Janz, *J. Mol. Spectry.*, **1**, 49 (1957).
2) T. Fujiyama, K. Tokumaru and T. Shimanouchi, *Spectrochim. Acta*, **20**, 415 (1964).
3) I. Matsubara, This Bulletin, **34**, 1710 (1961).
4) Y. Kinoshita, I. Matsubara and Y. Saito, *ibid.*, **32**, 741 (1959).
5) T. Nomura and Y. Saito, *ibid.*, **39**, 1468 (1966).
6) H. H. Morgan, *J. Chem. Soc.*, **123**, 2901 (1923).

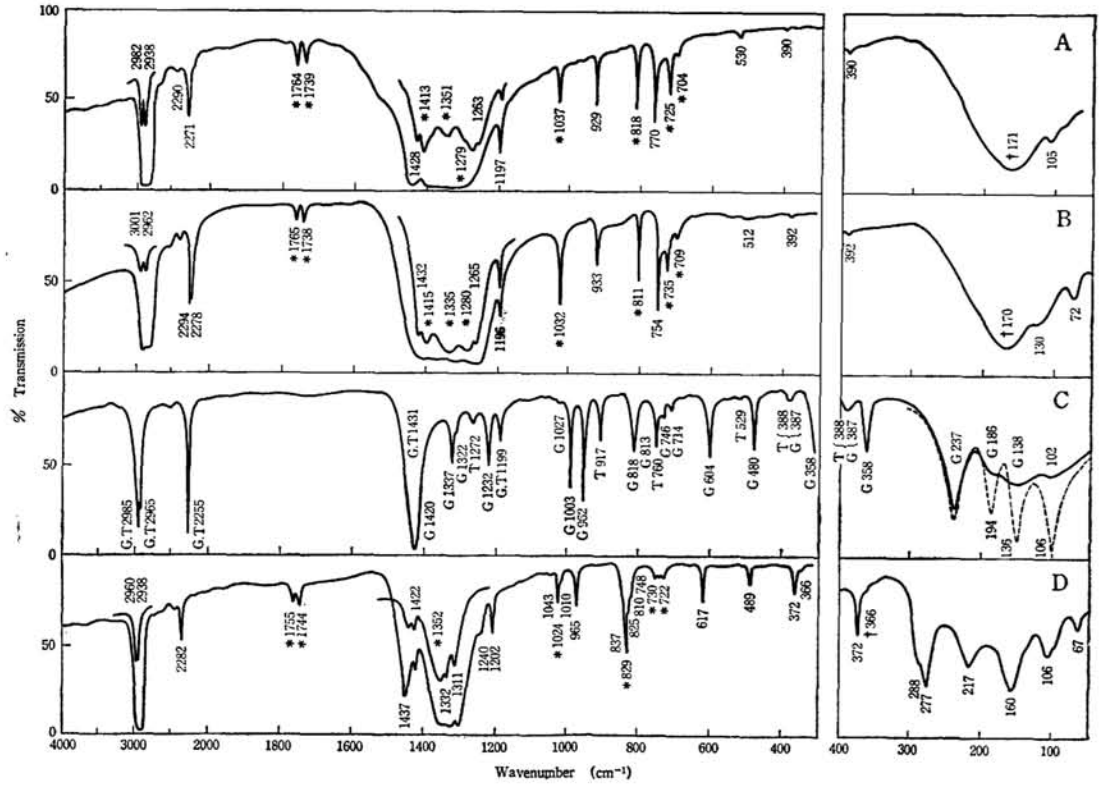
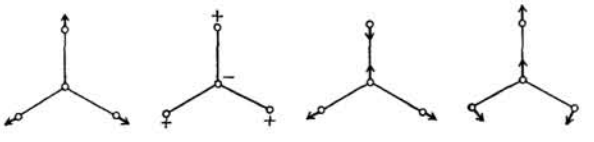


Fig. 1. Infrared spectra of succinonitrile and complexes.
(A) $[Ag(sn)]NO_3$, (B) $[Ag(sn)Ag](NO_3)_2$, (C) free succinonitrile, solid at room temperature, (D) $[Cu(sn)_2]NO_3$.
The dotted line of (C) gives the spectrum at liquid nitrogen temperature.
Bands with an asterisk are assigned to the modes of the nitrate ion. Bands with a dagger are assigned to the metal-ligand stretching and deformation vibrations.



	ν_1	ν_2	ν_3	ν_4
	A_1'	A_2''	E'	E'
Infrared	ia	a	a	a
Raman	a	ia	a	a
	~1050	~800	1350~1400	700~750

Fig. 2. Vibrational modes of nitrate ion, symmetry species, infrared and Raman selection rule and approximate region (in cm^{-1}) in which these vibration bands appear.

due to this ion are discussed first. Figure 2 shows the modes of normal vibrations, their selection rule in infrared and Raman spectra and the frequencies which these vibrational modes are expected to have. The spectra given in Fig. 1 were compared with those of some inorganic nitrate salts and the bands asterisked in Fig. 1 are assigned to the nitrate ion vibrations. The totally symmetric vibration, ν_1, is infrared inactive. However, a weak band appears near 1035 cm^{-1} for the three complexes and is assigned to this mode which becomes infrared active owing to the crystalline field effect. The out-of-plane vibration, ν_2, is infrared active and appears near 820 cm^{-1} as a sharp band. The degenerate N–O stretching vibration, ν_3, appears very strongly in the region 1250—1450 cm^{-1}.

TABLE 1. FREQUENCIES OF INFRARED BANDS DUE TO NITRATE ION IN cm^{-1}

$[Ag(sn)]NO_3$	$[Ag(sn)Ag](NO_3)_2$	$[Cu(sn)_2]NO_3$	Assignment
1764 1739	1765 1738	1755 1744	$\nu_1+\nu_4$ (E′)
1413 1351 1279	1415 1335 1280	1352	ν_3 (E′)
1037	1032	1024	ν_1 (A_1')
818	811	829	ν_2 (A_2'')
725 704	735 709	730 722	ν_4 (E′)

TABLE 2. OBSERVED FREQUENCIES IN cm^{-1} AND ASSIGNMENTS OF SUCCINONITRILE AND COMPLEXES

Succinonitrile	Complexes*			Assignment
	Ag(i)	Ag(ii)	Cu	
2985 (T, G)	2982	3001	2960	CH str. (a_u, b)
2965 (T, G)	2938	2962	2938	CH str. (b_u, a)
2255 (T, G)	2290 2271	2294 2278	2282	CN str. (b_u, a, b)
1431 (T, G)	1428	1432	1437	CH_2 scis. (b_u, b)
1420 (G)			1422	CH_2 scis. (a)
1337 (G)			1332	CH_2 wag. (b)
1322 (G)			1311	CH_2 wag. (a)
1272 (T)	1263	1265		CH_2 wag. (b_u)
1232 (G)			1240	CH_2 twist. (b)
1199 (T, G)	1197	1196	1202	CH_2 twist. (a_u, a)
1027 (G)			1043	CC str. (a)
1003 (G)			1010	CH_2 rock. (a)
962 (G)			965	CCN str. (b)
917 (T)	929	933		CCN str. (b_u)
818 (G)			825	CCN str. (a)
813 (G)			810	CH_2 rock. (b)
760 (T)	770	754		CH_2 rock. (a_u)
604 (G)			617	CCC deform. (b)
529 (T)	530	512		CCC deform. (b_u)
480 (G)			489	CCC deform. (a)
388 (T)	390	392		CCN deform. (a_u)
387 (G)				CCN deform. (a)
358 (G)			372	CCN deform. (b)
			366	Cu···N str.
237 (G)			288 277	CCN deform. (b)
186 (G)			217	CCN deform. (a)
	171	170		Ag···ligand vibration CCN deform. (b_u)
138 (G)			160	CC torsion (a)
	105	130		CC torsion (a_u)
102		72	106 67	intermolecular vibrations

* Ag(i), and Ag(ii) and Cu denote succinonitrile silver nitrate, disilver nitrate, and copper nitrate, respectively.

For the copper complex only one peak appears at 1352 cm^{-1}. For the silver complexes three bands appear in this region as shown in Fig. 1. When the sample was fresh, the central peak at 1351 cm^{-1} for silver nitrate and at 1335 cm^{-1} for disilver nitrate appeared strongly. The intensities of the two bands near 1410 cm^{-1} and 1280 cm^{-1} relative to that of the central peak increased when the sample was in contact with alkali halide plates. We did not investigate the spectral changes in

detail, since they were not related with the problem dealt with in the present study. The degenerate ONO deformation vibration, ν_4, appears as a doublet near 725 and 704 cm^{-1}, the splitting being caused by the crystalline field effect. In addition to the fundamental bands discussed above two peaks appear at 1764 and 1739 cm^{-1} for silver nitrate. These peaks are assigned to the combination bands, 1037+725 and 1037+704 in cm^{-1}. For the disilver nitrate and copper complexes the doublets near 1750 cm^{-1} are interpreted similarly. The results are summarized in Table 1.

As for the free ligand, the spectra of succinonitrile are interpreted as the overlap of the trans and gauche bands.[1,2] In the present measurement the spectrum was extended down to 60 cm^{-1} and three very broad bands were found at 186, 138 and 102 cm^{-1} and a sharp band at 237 cm^{-1} at room temperature. In this region the CCN deformation vibration (b_u) and the CC torsion (a_u) of the trans form and the CCN deformation vibration (a) and the CC torsion (a) of the gauche form are expected to appear. In order to make the situation clear, the spectrum at liquid nitrogen temperature was measured and is shown as a dotted line in Fig. 1. The spectrum above 300 cm^{-1} shows that only the gauche form exists at liquid nitrogen temperature and, accordingly, the four bands at 237, 186, 138 and 102 cm^{-1} should be assigned to the gauche form. The frequencies of the 237 and 186 cm^{-1} bands are compared with the calculated[2] and are assigned to the two CCN deformation bands. The remaining two bands at 138 and 102 cm^{-1} are tentatively assigned to CC torsion and an intermolecular vibration, since for the nitrile group a considerably strong intermolecular interaction is expected. The results are summarized in Table 2 and Fig. 1, where the trans and gauche forms are denoted by T and G, respectively.

The spectrum of the copper complex shown in Fig. 1 supports the conclusion obtained by Matsubara[3] and Kinoshita, Matsubara and Saito[4] that only the gauche form exists. As shown in Table 2 almost all the bands are assigned to those of the gauche form. There are some very weak bands, such as those at 837 and 748 cm^{-1}, which are not given in the table. They are assigned to the combination bands. In the region lower than 400 cm^{-1} metal-ligand vibrations are also expected. They may be coupled with the low frequency vibrations of the ligand gauche molecule. In fact, six bands appear below 300 cm^{-1} instead of the four bands of the free ligand gauche form. They are tentatively assigned as shown in Table 2, although they may be strongly coupled with each other.

The spectra of silver nitrate and disilver nitrate are of interest, when they are compared with those of the free ligand and copper complex. It is surprising that all the bands assigned to the gauche form disappear and only those assigned to the trans form remain. From these spectra we can conclude undoubtfully that the ligand molecule takes the trans form in the silver nitrate and disilver nitrate complexes. This conclusion was confirmed by the X-ray analysis by Nomura and Saito.[5] The detail of the assignments are given in Table II. The gauche bands at 962, 604, 480, 358, 237, 186 and 138 cm^{-1} disappear. Silver nitrate has two bands at 929 and 530 cm^{-1} and disilver nitrate has two bands at 933 and 512 cm^{-1}. They definitely correspond to the 917 and 529 cm^{-1} bands of the trans form of free ligand. As for the region below 300 cm^{-1}, silver nitrate has two bands at 171 and 105 cm^{-1} and disilver nitrate has three bands at 170, 130 and 72 cm^{-1}. In this region, CCN deformation (b_u), CC torsion (a_u), and metal ligand vibrations are expected to appear. The band at 170 cm^{-1} is very broad and is interpreted to be the overlapped band. Tentative assignments are given in Table 2, although three vibrations are strongly coupled with each other.