sidered as tentative. In chloroform and dichloromethane the tris(pyridine) complexes yield octahedral species in which the nitrate groups remain coordinated. The visible spectrum of $[Co(py)_3(NO_3)_2]$ is essentially the same in both solvents, as is true for the nickel(II) complex. Rosenthal and Drago[4] have shown that $[Ni(py)_3(NO_3)_2]$ loses 1 mole of pyridine in dichloromethane to form octahedral $[Ni(py)_2(NO_3)_2]$, which has bidentate nitrate groups. It is probable that the nickel(II) complex undergoes a similar reaction in chloroform, and it is possible that $[Co(py)_3(NO_3)_2]$ takes part in an analogous reaction, in both solvents.

The absorption maximum of $[Co(py)_3(NO_3)_2]$ in these two solvents is shifted to a lower wavelength upon addition of pyridine, with a corresponding large decrease in the extinction coefficient. The spectra of these solutions closely resemble the spectra of the hexakis(pyridine) solutions, both as to position of the maxima and magnitude of the extinction coefficients. The shift to lower wavelength would be expected for the substitution of pyridine for nitrate in the coordination sphere. The infrared spectrum of the hexakis(pyridine) complex in chloroform shows, however, that the nitrate group remains coordinated. It is suggested, therefore, that in these two solvents the hexakis(pyridine)cobalt(II) complex forms $[Co(py)_4(NO_3)_2]$, in which a bidentate nitrate has become monodentate by substitution with pyridine. The decrease in molar extinction coefficients upon addition of pyridine to the solutions of the tris(pyridine) complex also agrees with the formulation of an octahedral species having four coordinated pyridine molecules since $[Co(py)_4(NO_3)_2]$ would be expected to approach cubic symmetry more closely than the tris(pyridine) complex.

It has been reported that the electronic spectrum of $[Ni(py)_3(NO_3)_2]$ in dichloromethane is unaffected by the addition of pyridine to the solution,[4] but our results are not in agreement with this observation. The same spectral changes were noted with the nickel(II) complex as with the cobalt(II) complex, and we have concluded that $[Ni(py)_4(NO_3)_2]$ is formed in the presence of excess pyridine in these solvents.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVEY MUDD COLLEGE, CLAREMONT, CALIFORNIA,
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Complexes of Succinonitrile with Silver(I). A Nitrato–Silver Compound

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The compounds $2AgNO_3 \cdot (CN)_2C_2H_4$ and $AgNO_3 \cdot (CN)_2C_2H_4$ have been isolated from solutions of silver nitrate in succinonitrile. In these silver nitrate complexes and in the compounds bis(succinonitrile)silver(I) perchlorate and bis(succinonitrile)silver(I) tetrafluoroborate, the ligand succinonitrile bridges two silver atoms and assumes the *trans* rotomeric conformation. Nitrato–silver bonding is indicated in the compound $2AgNO_3 \cdot (CN)_2C_2H_4$.

Introduction

The interaction of copper(I) and silver(I) with nitriles is similar in many respects.[2] While the structure of the compound $CuNO_3 \cdot 2(CN)_2C_2H_4$ is now well established,[3,4] the analogous silver(I) compound $AgNO_3 \cdot 2(CN)_2C_2H_4$ has not yet been reported. It was of interest to synthesize this compound and the compounds $Ag((CN)_2C_2H_4)_2BF_4$ and $Ag((CN)_2C_2H_4)_2ClO_4$ in order to study the effects of the metal ions and anions on the rotational conformation[4,5] assumed by succinonitrile in these complexes. Attempts to isolate the compound $AgNO_3 \cdot 2(CN)_2C_2H_4$, however, led to the syntheses of the compounds $2AgNO_3 \cdot (CN)_2C_2H_4$ and $AgNO_3 \cdot (CN)_2C_2H_4$. Infrared evidence shows that the nitrate ligand is coordinated to silver in the compound $2AgNO_3 \cdot (CN)_2C_2H_4$.

While nitrato–metal bonding is well known for other transition metals,[6] only few examples exist for nitrato–silver bonding. Silver–oxygen bond lengths of 2.36 and 2.43 A suggest nitrato–silver bonding in the silver nitrate–cyclooctatetraene complex.[7] Recent crystallographic studies indicate that each nitrate is bonded to two silver atoms in the silver tris(acetylacetonato)-nickelate(II)–silver nitrate adduct, $AgNi(C_5H_7O_2)_3 \cdot$

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[1] (a) Harvey Mudd College, Claremont, Calif.; (b) Petroleum Research Fund Undergraduate Research Scholar, 1965; (c) Mellon Institute, Pittsburgh, Pa.

[2] F. Farha, Jr., and R. T. Iwamoto, *Inorg. Chem.*, **4**, 844 (1965).

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[7] (a) F. S. Mathews and W. N. Lipscomb, *J. Am. Chem. Soc.*, **80**, 4745 (1958); (b) F. S. Mathews and W. N. Lipscomb, *J. Phys. Chem.*, **63**, 845 (1959).

$2AgNO_3$.[8] The indication of nitrato–silver bonding in $2AgNO_3\cdot(CN)_2C_2H_4$ prompted us to study the compounds $AgNO_3\cdot R_2S$,[9] where R is methyl, ethyl, and *n*-propyl, and the compound $AgNO_3\cdot CH_2I_2$.[10]

Experimental Section

Materials.—Anhydrous silver perchlorate (G. F. Smith Chemical Co.) was dried *in vacuo* at 100° and dispensed in a drybox. Hydrated cupric perchlorate (G. F. Smith Chemical Co.) was dried *in vacuo* at 100°. Reagent grade silver nitrate was dried at 110°. Anhydrous silver tetrafluoroborate (Alfa Inorganics, Inc.) was used without further purification. Dichloromethane and acetonitrile were fractionated from phosphorus pentoxide. Succinonitrile was sublimed *in vacuo*. Reagent grade benzene was stored over sodium wire. Matheson Coleman and Bell methyl sulfide, *n*-propyl sulfide, diiodomethane, and 2-butanol were used without further purification. Ethyl sulfide was distilled just prior to use.

Physical Measurements.—Ultraviolet spectra were obtained with a Cary Model 13 spectrophotometer. Infrared spectra were obtained with Perkin-Elmer spectrophotometers, Models 21, 137, and 621. Low-frequency data from 550 to 33 cm^{-1} were obtained with a Beckman IR-11. Nujol and hexachlorobutadiene mulls between silver chloride plates were used for sampling in the 4000–500-cm^{-1} region, and Nujol mulls between high-density polyethylene were used in the 600–33-cm^{-1} region. The spectrum of $2AgNO_3\cdot(CN)_2C_2H_4$ was also obtained in a silver chloride pellet.[11] Infrared spectra of acetonitrile solutions were determined in silver chloride liquid cells. Conductivities were measured with an Industrial Instruments Type RC bridge.

Analyses.—Silver was determined by the Volhard method or by a gravimetric method as the chloride. Copper was determined by titration with EDTA, and perchlorate was determined gravimetrically as the tetraphenylarsonium salt. Carbon, hydrogen, and nitrogen analyses were performed by Drs. G. Weiler and F. B. Strauss, Oxford, England, and the Galbraith Laboratories, Inc., Knoxville, Tenn. The molecular weight of $2AgNO_3\cdot(CN)_2C_2H_4$ in ethanol was determined by the Galbraith Laboratories.

Silver Nitrate–Succinonitrile.—Dry silver nitrate (0.85 g, 5 mmoles) was pulverized in a mortar and added to 1.5 g (19 mmoles) of succinonitrile. The mixture was heated to 70° and stirred vigorously until all of the silver nitrate was dissolved. The addition of 30 ml of dichloromethane yielded a copious white precipitate which was washed with three 20-ml portions of dichloromethane and dried *in vacuo;* mp 92–93°. *Anal.* Calcd for $2AgNO_3\cdot(CN)_2C_2H_4$: Ag, 51.4; C, 11.44; H, 0.96; N, 13.35. Found: Ag, 51.4; C, 11.71; H, 1.28; N, 13.43.

A solution of 5 mmoles of silver nitrate in 19 mmoles of succinonitrile was vigorously stirred at 70° for 10 min. Benzene (30 ml) was added, and the solution upon stirring yielded white crystals, which were washed with benzene and dried *in vacuo* at 58°; mp 76–77°. *Anal.* Calcd for $AgNO_3\cdot(CN)_2C_2H_4$: Ag, 43.2; C, 19.22; H, 1.61; N, 16.71. Found: Ag, 43.3; C, 19.62; H, 1.74; N, 16.65.

Silver Perchlorate–Succinonitrile.—Dropwise addition of a solution of 0.50 g (6.2 mmoles) of succinonitrile in 20 ml of benzene to a solution of 0.50 g (2.5 mmoles) of anhydrous silver perchlorate[12] in 15 ml of benzene yielded a white precipitate, which was washed with benzene and dried *in vacuo* at 58°. The compound began to decompose at 148°. *Anal.* Calcd for $Ag((CN)_2C_2H_4)_2ClO_4$: Ag, 29.4; C, 26.14; H, 2.19; N, 15.24. Found: Ag, 29.4; C, 26.10; H, 2.52; N, 15.01.

Silver Tetrafluoroborate–Succinonitrile.—Addition of ether to a solution of silver tetrafluoroborate in succinonitrile yields the compound $Ag((CN)_2C_2H_4)_2BF_4$.[13] However, an alternate method which does not require the use of succinonitrile as a solvent was employed in the present study. Dropwise addition of a solution of 0.60 g (7.5 mmoles) of succinonitrile in 20 ml of benzene to a solution of 0.50 g (2.6 mmoles) of silver tetrafluoroborate in 40 ml of benzene gave a white precipitate which was washed with benzene and dried *in vacuo* at 58°. The compound begins to decompose at 120°. *Anal.* Calcd for $Ag((CN)_2C_2H_4)_2BF_4$: Ag, 30.4; C, 27.08; H, 2.27; N, 15.78. Found: Ag, 30.2; C, 26.92; H, 2.66; N, 15.09.

Silver Nitrate–Diiodomethane.—The complex was prepared from concentrated aqueous silver nitrate solution.[10] The sample, which was dried *in vacuo* at 58°, melts at 80–81° with decomposition. *Anal.* Calcd for $AgNO_3\cdot CH_2I_2$: Ag, 24.64; C, 2.74; H, 0.46; N, 3.20. Found: Ag, 24.44; C, 2.80; H, 0.73; N, 3.02.

Silver Nitrate–Dialkyl Sulfide.—Complexes of silver nitrate with alkyl sulfides were prepared by the addition of the sulfide to concentrated aqueous solutions of silver nitrate.[9] The white products were recrystallized from alcohol. *Anal.* Calcd for $AgNO_3\cdot(CH_3)_2S$: Ag, 46.6. Found: Ag, 46.3. Calcd for $AgNO_3\cdot(C_2H_5)_2S$: Ag, 41.5. Found: Ag, 41.2. Calcd for $AgNO_3\cdot(CH_3CH_2CH_2)_2S$: Ag, 37.4. Found: Ag, 36.7.

Silver Nitrate–Acetonitrile and –Benzonitrile.—The addition of excess dichloromethane to solutions of silver nitrate in acetonitrile and silver nitrate in benzonitrile yielded white precipitates which were found to be silver nitrate. *Anal.* Calcd for $AgNO_3$: Ag, 63.5. Found: Ag, 63.2, 63.4.

Bis(succinonitrile)copper(I) Perchlorate.—A solution of 3.06 g (38 mmoles) of succinonitrile in 20 ml of dichloromethane was purged with nitrogen and added to a solution of 3.8 mmoles of copper(I) perchlorate in 2-butanol.[2] The white precipitate which immediately formed was washed with dichloromethane and dried *in vacuo*. *Anal.* Calcd for $Cu((CN)_2C_2H_4)_2ClO_4$: Cu, 19.7; ClO_4, 30.8; C, 29.8; N, 17.3; H, 2.50. Found: Cu, 18.9; ClO_4, 30.7; C, 30.2; N, 18.0; H, 2.42.

Results and Discussion

In complexes of nitriles with silver(I) and copper(I), four-coordination of the metal ion is illustrated by the compounds $Cu(CH_3CN)_4NO_3$, $Cu(CH_3CN)_4BF_4$,[13] and $Ag(CH_3CN)_4BF_4$.[13] The compounds $Ag((CN)_2C_2H_4)_2BF_4$, $Ag((CN)_2C_2H_4)_2ClO_4$, and $Cu((CN)_2C_2H_4)_2ClO_4$ synthesized in this study are analogous to the well-known compound $Cu((CN)_2C_2H_4)_2NO_3$, in which copper(I) is four-coordinate and succinonitrile is a bridging ligand.[3,4] Efforts to obtain the analogous $Ag((CN)_2C_2H_4)_2NO_3$ compound instead resulted in the compound $AgNO_3\cdot(CN)_2C_2H_4$ when precipitation was effected with benzene and the compound $2AgNO_3\cdot(CN)_2C_2H_4$ when precipitation was effected with dichloromethane. The greater affinity of benzene compared to dichloromethane for the silver ion may account for the two different products obtained. The existence of these two compounds had been suggested by an early phase study of the silver nitrate–succinonitrile system.[14]

The high ratio of silver to succinonitrile in the compounds $2AgNO_3\cdot(CN)_2C_2H_4$ and $AgNO_3\cdot(CN)_2C_2H_4$ compared to $Ag((CN)_2C_2H_4)_2ClO_4$ and $Ag((CN)_2C_2H_4)_2BF_4$ warrants consideration. High silver nitrate to ligand ratios have been reported in a number of

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[11] L. L. Pytlewski and V. Marchesani, *Anal. Chem.*, **37**, 618 (1965).

[12] Extreme caution must be exercised in the handling of the silver perchlorate–benzene system. Explosions have been reported by S. R. Brinkley, Jr., *J. Am. Chem. Soc.*, **62**, 3524 (1940), and F. Hein, *Chem. Tech.* (Berlin), **9**, 96 (1957).

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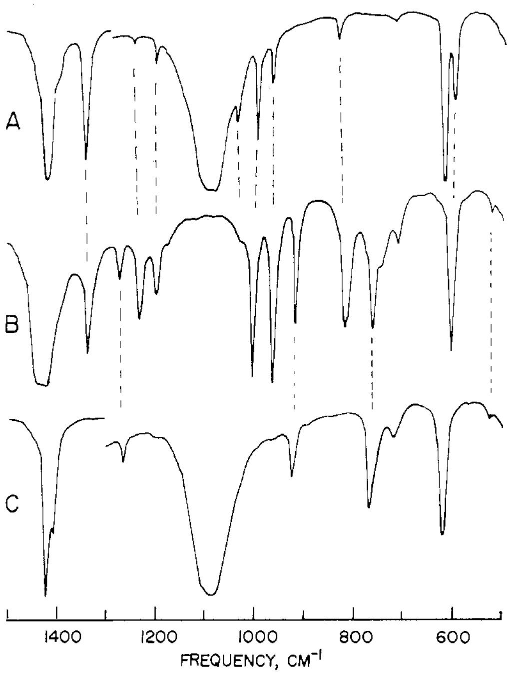

Figure 1.—Infrared spectra of complexes of succinonitrile: A, bis(succinonitrile)copper(I) perchlorate; B, succinonitrile (25°); C, bis(succinonitrile)silver(I) perchlorate.

systems in which compounds have been isolated or indicated. These include $8AgNO_3 \cdot O(CH_2)_4O$,[15] $4AgNO_3 \cdot (CN)_2C_2H_4$,[14] $AgNO_3 \cdot (C_2H_5)_3N$,[16] $AgNO_3 \cdot CH_2I_2$,[10] and $AgNO_3 \cdot R_2S$.[9]

Bonding of the Nitrile Moiety with Silver.—The shift in the frequencies of infrared absorption in the nitrile stretching region from 2257 cm^{-1} in unbound succinonitrile to 2290 and 2270 cm^{-1} in the complexes with silver and to 2276 cm^{-1} in bis(succinonitrile)copper(I) perchlorate is indicative of a linear C–C–N–metal bond.[4,5,17] The absence of absorption at 2257 cm^{-1} indicates that both nitrile moieties of succinonitrile are bound to the metal atoms. The dinitrile thus serves as a bridge between two metal atoms.

Infrared Absorption due to the Ligand Succinonitrile.—To facilitate interpretation and discussion, the infrared spectra of succinonitrile and its complexes with copper(I) and silver(I) with the perchlorate anion are shown in Figure 1. Frequencies at 1094 and 623 cm^{-1} are ν_3 and ν_4 of the perchlorate anion. Compared to the spectrum of succinonitrile, it is readily apparent that there is distinct simplification in the spectra of the complexes. Assignments for the *trans* and *gauche* rotational conformers of succinonitrile have been established by infrared and Raman studies at low temperatures and normal coordinate analyses.[4,18,19] In the 500–1500-cm^{-1} region, eight absorption bands marked on the spectrum of bis(succinonitrile)copper(I) perchlorate correspond closely to bands at similar frequencies in the spectrum of succinonitrile. A comparison of the frequencies in the spectrum of bis(succinonitrile)copper(I) perchlorate with those of succinonitrile at −50° indeed suggests that the *gauche* conformation is assumed by the ligand in this complex. The frequencies given in Table I augment earlier assignments made to the *gauche* conformer.[4,18,19] The spectrum of bis(succinonitrile)-copper(I) perchlorate displays distinct absorption bands at 395, 602, and 1342 cm^{-1}, which are frequencies which were not clearly characterized in the spectrum of bis(succinonitrile)copper(I) nitrate.[4]

TABLE I

INFRARED SPECTRUM OF BIS(SUCCINONITRILE)COPPER(I) PERCHLORATE

Succinonitrile (solid, −50°)[a]	$Cu((CN)_2C_2H_4)_2ClO_4$	Assignment (C_2 *gauche*)
356 m	367 m	B C–C–N bend
385 w	395 m	A C–C–N bend
483 ms	484 ms	A C–C–C bend
601 vs	602 s	B C–C–C bend
	622 vs	ν_4 ClO_4
810 s		A C–CN stretch
820 s	835 m	B CH_2 rock
963 vs	966 m	A CH_2 rock
999 vs	996 vs	B C–CN stretch
1032 m	1035 m	A C–C stretch
	1092 vs, b	ν_3 ClO_4
1189 m	1201 m	A CH_2 twist
1225 s	1248 w	A CH_2 wag
1332 s	1342 s	B CH_2 wag
1414 vs	1412 vs	A CH_2 bend
1431 vs, sh		B CH_2 bend
	2028 m	
2257 vs		C–N stretch
	2276 s	C–N–Cu

[a] From ref 4.

Four absorption bands at 530, 762, 917, and 1270 cm^{-1} in the spectrum of succinonitrile are not observed in the spectrum of bis(succinonitrile)copper(I) perchlorate but are observed in the spectrum of bis(succinonitrile)silver(I) perchlorate. Absorption bands at these four frequencies and at 1197 and 1417 cm^{-1} have been assigned to the *trans* conformer.[4,5] Thus, it is proposed that succinonitrile assumes the *trans* conformation in bis(succinonitrile)silver(I) perchlorate. As shown in Figure 2, the absorption pattern characteristic of the *trans* conformation is also observed in the spectrum of bis(succinonitrile)silver(I) tetrafluoroborate. Absorption bands at 1058–1095 and 520 cm^{-1} are ν_3 and ν_4 of the tetrafluoroborate anion. For purposes of comparison, the spectrum of $SnCl_4 \cdot (CN)_2C_2H_4$ in which the *trans* conformation of the ligand has been assigned[5] is shown in Figure 2. In the spectra of the complexes of succinonitrile with silver nitrate, the absence of intense absorption at or near 484, 602, 966, and 996 cm^{-1}, which among others are characteristic of the *gauche* conformation, strongly suggests that succinonitrile is not in the *gauche* conformation. Confirming this suggestion and supporting

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[16] J. T. Yoke, III, and H. M. Hilliard, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April, 1965, p 17-M.

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TABLE II

INFRARED SPECTRA OF COMPLEXES OF SUCCINONITRILE

$Ag((CN)_2C_2H_4)_2ClO_4$	$Ag((CN)_2C_2H_4)_2BF_4$	$AgNO_3\cdot(CN)_2C_2H_4$	$2AgNO_3\cdot(CN)_2H_4$	$SnCl_4\cdot(CN)_2C_2H_4$	$(CN)_2C_2H_4$[a]	Assignment (C_{2h}, *trans*)
	37 m	77 w	43 w, 76 sh	45 m, 63 m		
			131 s	113 wsh, 141 s	135 sb	
				157 s	155 sb	B_u C–C–N bend
174 vs	173 vs	166 vs, 189 vs	178 vs, 196 s	198 w	200 sh	
256 w				217 sh, 263 s	242 s[b]	
				320 s, 350 s	356 vs[b]	
396 w	397 m	390 m	394 w	373 s	390 s	A_u C–C–N bend
404 w, 490 wb	470 wb	455 wb		400 sh		
529 m	520 vs[c]	530 w	530 w	536 m	530 w	B_u C–C–C bend
623 vs[c]		732 w, 753 w[c]	706 w, 731 m[c]			
757 sh, 768 s	770 s	768 vs	752 s	756 ms	762 s	A_u CH_2 rock
		810 w, 818 m[c]	810 s, 815 w[c]			
925 s	925 m	930 s	930 m	932 m	917 s	B_u C–CN stretch
1096 vsb[c]	1058–1095 vsb[c]	1030 w, 1035 m[c]	1030 s[c]			
1206 wsh	1205 w	1195 sh	1196 w	1197 s	1197 m	A_u CH_2 twist
1268 m	1289 m	1272 wsh	1260 sh	1267 s	1270 m	B_u CH_2 wag
1293 w		1332 vsb[c]	1275 vsb, 1405 vsb[c]			
1409 sh, 1420 s	1421 s	1425 sh	1429 sh	1417 s	1417 s	B_u CH_2 bend
2008 w	1639 w	1738 w, 1760 w[c]	1735 w, 1760 m[c]			
2270 s, 2289 s	2270 s, 2290 m	2270 s, 2290 s	2271 s, 2290 s	2306 s		C–N–metal
2947 m, 2990 m	2950 s, 2996 s	2967 s, 3012 msh	2935 sh, 2960 m		2952 s	C–H stretch
			2980 m, 3000 m		2988 s	

[a] Complete spectrum only for the 400–33-cm^{-1} region and other frequencies assigned to the *trans* conformation. [b] Frequencies assigned to the *gauche* conformation (ref 4, 19). [c] Frequencies assigned to anions.

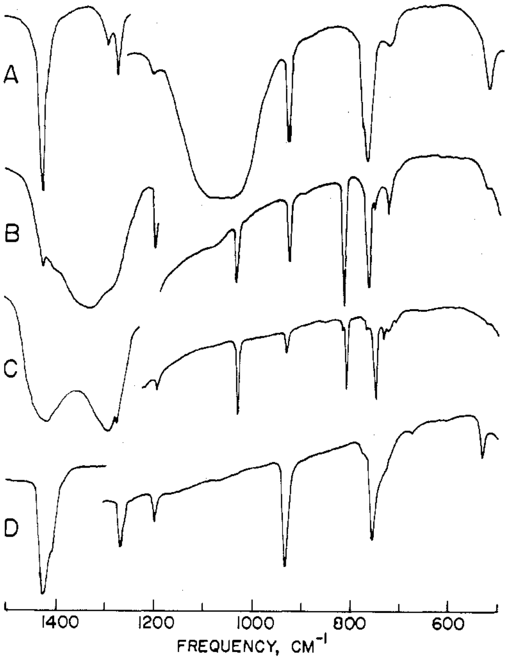

Figure 2.—Infrared spectra of complexes of succinonitrile: A, bis(succinonitrile)silver(I) tetrafluoroborate; B, $AgNO_3\cdot(CN)_2C_2H_4$; C, $2AgNO_3\cdot(CN)_2C_2H_4$; D, $SnCl_4\cdot(CN)_2C_2H_4$.

the assignment of the *trans* conformation of succinonitrile in the complexes with silver nitrate are the absorption bands at 530, 760, 930, and 1270 cm^{-1}. As shown in Table II, the frequencies assigned to the *trans* conformation of succinonitrile in its complexes are shifted only slightly as compared to the unbound ligand. While earlier workers[4,18] assigned the band at 1197 cm^{-1} to the CH_2 twisting mode of the *trans* conformer, the most recent report[19] assigned this band to the *gauche* conformer and a band at 1232 cm^{-1} to the *trans* conformer. Absorption at 1200 cm^{-1} by the *trans* conformer of succinonitrile in the complexes with silver(I) and tin(IV) and the absence of peaks at 1232 cm^{-1} support the assignments made by the earlier workers.[4,18]

Infrared Spectra of Complexes of Silver Nitrate.—The very intense band at 1332 cm^{-1} in the spectrum of $AgNO_3\cdot(CN)_2C_2H_4$ is indicative of the nitrate anion with point group symmetry D_{3h}. In support of this assignment are absorption bands at 818 and 732 cm^{-1} which are ν_2 and ν_4 of the nitrate anion. However, distortion of the nitrate ion is indicated by absorption at 1035, 810, and 189 cm^{-1}. In the region 700–1500 cm^{-1} the infrared spectrum of $2AgNO_3\cdot(CN)_2C_2H_4$ resembles the spectrum of ammonium hexanitratocerate(IV).[20] The strikingly intense doublet at 1405 cm^{-1} (ν_4)[21] and 1275 cm^{-1} (ν_1) reveals the presence of a coordinated nitrato–silver bond in $2AgNO_3\cdot(CN)_2C_2H_4$.[22] Intense absorption at 1030 cm^{-1} (ν_2) further verifies this conclusion. A comparison of the relative intensities of the band at 1030 cm^{-1} with the band at 930 cm^{-1} supports the assignment of the 1030-cm^{-1} band to the nitrato ligand rather than to the succinonitrile ligand. In other complexes of succinonitrile the band at 930 cm^{-1} is relatively intense. Succinonitrile does not absorb strongly in the 1030-cm^{-1} region. Other assignments to the nitrato ligand with C_{2v} symmetry are 810 cm^{-1} (ν_6), 731 cm^{-1} (ν_3), and 706 cm^{-1} (ν_5). An actual lowering of ligand symmetry from D_{3h} to C_{2v} owing to nitrato coordination rather

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

(21) The nomenclature identifying frequencies of the nitrato ligand with C_{2v} point group symmetry is given by C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 598 (1965).

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than mere reduction in symmetry of the nitrate ion in its lattice site[23] is suggested by the high intensities of the ν_3 and ν_2 bands. The 130-cm^{-1} separation of ν_1 and ν_4 exceeds the minimum of 100 cm^{-1} suggested by Katzin[24] for classifying nitrate as a coordinating ligand. The ν_4 frequency at 1405 cm^{-1} compares favorably with ν_4 at 1425 cm^{-1} reported for $Co(NO_3)_2 \cdot 2H_2O$,[25] 1416 cm^{-1} for monodentate nitrato–amine nickel(II) complexes,[26] and 1435 cm^{-1} reported for the α form of anhydrous copper(II) nitrate.[27,28] In the latter compound each nitrate forms a bridge between two copper atoms, and the third oxygen atom of the nitrate forms a weaker bond to a third copper atom.[29] The small magnitude of separation of the pair of bands (ν_4–ν_1) suggests the absence of a bidentate chelate nitrato bond[26] in $2AgNO_3 \cdot (CN)_2C_2H_4$. The stoichiometry of the compound and the infrared spectrum leads us to propose the existence of structural units such as O_2NO–Ag–$NCCH_2CH_2CN$–Ag–ONO_2, possibly with intermolecular bonding between units utilizing the demonstrated capacity of the nitrato ligand to form bridges between silver atoms.[8,29] The coordination number of silver will then be greater than two.

Compounds of Silver Nitrate with Alkyl Sulfides and Diiodomethane.—If the coordination number of silver(I) is greater than one in the compounds $AgNO_3 \cdot R_2S$[9] and $AgNO_3 \cdot CH_2I_2$,[10] nitrato bonding may be expected. The infrared spectra of the compounds $(CH_3)_2S \cdot AgNO_3$, $(C_2H_5)_2S \cdot AgNO_3$, and $(CH_3CH_2CH_2)_2S \cdot AgNO_3$ indicate that the nitrate anion retains its D_{3h} symmetry in these compounds. The broad intense ν_3 band at 1370 cm^{-1} is not split, ν_2 is at 819 cm^{-1}, and there is no indication of absorption by the nitrate in the 1030-cm^{-1} region. The sulfur atoms may serve as bridges between silver atoms.

The broad intense doublet, 1395 cm^{-1} (ν_4) and 1297 cm^{-1} (ν_1), immediately suggests nitrato–silver bonding in the compound $AgNO_3 \cdot CH_2I_2$. An intense ν_2 band at 1038 cm^{-1} confirms this proposal. Other C_{2v} nitrato frequencies are 808 cm^{-1} (ν_6) and 731 cm^{-1} (ν_3), and ν_5 was too weak to be observed.

Nitrato Combination Bands.—Strong absorption by ethylenediamine in the 1030-cm^{-1} region precluded the observation of the ν_2 nitrato band in several nitrato complexes of nickel(II).[26] By assigning absorption in the 2400-cm^{-1} region to combination bands $\nu_2 + \nu_1$ and $\nu_2 + \nu_4$ and absorption in the 1700-cm^{-1} region to combination bands $\nu_2 + \nu_3$ and $\nu_2 + \nu_5$, the frequency of ν_2 could be calculated. Since succinonitrile and diiodomethane do not obscure any of the nitrate absorption frequencies, it was possible to test these assignments. The data given in Table III support the assignment of combination bands. The overtone of ν_2 expected at 2060 cm^{-1} was too weak to be observed in these compounds.

Table III

Nitrato Combination Bands (cm^{-1})

	$2AgNO_3 \cdot (CN)_2C_2H_4$	$AgNO_3 \cdot CH_2I_2$
$\nu_2 + \nu_4$ (obsd)	2435	2424
(calcd)	2435	2430
$\nu_2 + \nu_1$ (obsd)	*a*	2312
(calcd)	2305	2332
$\nu_2 + \nu_3$ (obsd)	1760	1759
(calcd)	1761	1766
$\nu_2 + \nu_5$ (obsd)	1735	1735
(calcd)	1736	*b*

[a] Nitrile absorbs in this region. [b] ν_5 was not observed.

Far-Infrared Spectra.—Assignments of frequencies in the 480–520-cm^{-1} region to metal–nitrile nitrogen stretching modes have been recently proposed.[2] More recently, the assignment of absorption bands in the 400–500-cm^{-1} region to aluminum–nitrile nitrogen stretching frequencies was questioned.[30] Earlier reports[31] gave no indication of intense absorption in the 400–500-cm^{-1} region which could be assigned to metal–nitrile nitrogen stretching frequencies. Beattie suggested that metal–nitrile nitrogen stretching frequencies may be expected between 200 and 244 cm^{-1}.[31c]

In the spectra of the silver–succinonitrile complexes, only weak absorption is observed in the 480–500-cm^{-1} region. The most predominant feature of the spectra is the intense bands at 174, 173, and 178 cm^{-1}. While a CCN bending frequency is observed at 155 cm^{-1} in unbound succinonitrile, its intensity is considerably lower than the bands at 175 cm^{-1} in the silver complexes. We propose that the absorption at 175 cm^{-1} is due to the metal–nitrogen stretching mode. The lack of dependence of the 175 cm^{-1} on the nitrate, tetrafluoroborate, and perchlorate anions indicates that the absorption is not due to lattice vibrations.[32] In addition to the band at 178 cm^{-1}, the compound $2AgNO_3 \cdot (CN)_2C_2H_4$ absorbs strongly at 196 and 131 cm^{-1}. The absorption at 196 cm^{-1} is tentatively assigned to the silver–oxygen bond. This assignment is reasonable when compared to the assignment of a band at 199 cm^{-1} to the cadmium–oxygen stretching frequency in anhydrous cadmium nitrate.[32]

Absorption at 320 and 350 cm^{-1} in the spectrum of $SnCl_4 \cdot (CN)_2C_2H_4$ is assigned to tin–chlorine stretching modes.[31] Succinonitrile in this compound is a bridging ligand and the coordination number of tin is six.[5] The two tin–chlorine stretching frequencies may be taken as evidence for the *cis* arrangement of the two nitrile nitrogen atoms about the octahedral tin atom.[31b,c] The band at 263 cm^{-1} is tentatively assigned to the Sn–N stretching mode.

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Complexes of Silver Nitrate in Solution.—Since silver nitrate is associated to a certain extent in acetonitrile,[33,34] it was of interest to determine whether the nitrato–silver bonds of the compound $2AgNO_3 \cdot (CN)_2C_2H_4$ would prevail in acetonitrile. The infrared spectra of $2AgNO_2 \cdot (CN)_2C_2H_4$, $AgNO_3 \cdot (CN)_2C_2H_4$, and silver nitrate in acetonitrile all show the same features in the regions where absorptions due to the nitrato ligand are expected. Unfortunately, the solvent absorbs strongly in these regions, *viz.*, 1410, 1270, and 1030 cm^{-1}. Intensification of absorption is perceptible at 1270 cm^{-1}, and this suggests the possibility of nitrate ion deformation,[34] presumably by interaction with the silver ion. In any event, the infrared spectra are consistent with the interpretation that a common type of nitrate–silver species exists in these solutions.

That the species conducting electricity in solutions of $2AgNO_3 \cdot (CN)_2C_2H_4$ and in solutions of $AgNO_3 \cdot (CN)_2C_2H_4$ in acetonitrile are alike is indicated by the same molar conductance of these substances (Table IV). The molar conductances at the concentrations cited indicate the presence of 1:1 electrolytes.[35] The average molecular weight calculated for complete dissociation of $2AgNO_3 \cdot (CN)_2C_2H_4$ into $2Ag^+$, $2NO_3^-$, and $(CN)_2C_2H_4$ is 84, while dissociation to Ag^+, $Ag(CN)_2C_2H_4$, and $2NO_3^-$ leads to an average molecular weight of 105. The molecular weight in ethanol determined with an osmomometer was 108.

The ultraviolet n–π^* absorption of nitrates has been observed at lower wavelengths for those nitrates in which the separation of the nitrate infrared ν_1 and ν_4 frequencies is larger.[36] The absorption maxima in acetonitrile for $2AgNO_3 \cdot (CN)_2C_2H_4$, $AgNO_3 \cdot (CN)_2C_2H_4$, and silver nitrate are at 313 mμ. Since the n–π^* maximum is sensitive to the nature of the cation and to solvent effects, there is good indication that the environment about the nitrate ion is approximately the same for the three compounds, namely, that the extent of nitrate–solvent and nitrate–silver interactions are the same.

TABLE IV

ABSORPTION MAXIMA AND CONDUCTIVITY OF SILVER COMPLEXES IN ACETONITRILE

Compd	Ultraviolet maxima, mμ	Molar conductivity, cm^2/ohm-mole	Concn, *M*
$2AgNO_3 \cdot (CN)_2C_2H_4$	313, 314[a]	120	0.0122
$AgNO_3 \cdot (CN)_2C_2H_4$	313	123	0.0123
$AgNO_3$	313, 314[a]		
$LiNO_3$	299, 303[a,b]		
$AgClO_4 \cdot 2(CN)_2C_2H_4$		155	0.0126
$AgBF_4 \cdot 2(CN)_2C_2H_4$		156	0.0127

[a] Maxima in tri-*n*-butyl phosphate solvent. [b] Data from J. L. Woodhead, *J. Inorg. Nucl. Chem.*, **27**, 1111 (1965).

The lower wavelength of the maxima for solutions of lithium nitrate in acetonitrile and in tri-*n*-butyl phosphate is in accord with the charge to size ratio[32] (e^2/r) of lithium (1.64) compared to silver (0.78). This latter consideration, however, should not detract attention from the affinity of silver(I) for nitrate ions. Association of ions in molten silver nitrate is indicated by Raman spectra.[37]

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The Infrared Spectra of Rare Earth Metal Chloride Complexes of 2,2'-Bipyridyl and 1,10-Phenanthroline from 650 to 70 Cm^{-1} [1]

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The infrared spectra of rare earth metal chloride complexes of 2,2'-bipyridyl and 1,10-phenanthroline are reported from 650 to 70 cm^{-1}. From the infrared spectra in this region, frequency assignments are suggested for the ν_{M-N} vibrations. The position of the ν_{M-N} vibration is observed to vary with the properties of the metal and ligand.

Introduction

It has been generally believed that the only stable complexes of the rare earth elements involved oxygen-containing ligands. However, recently stable complexes involving nitrogen-containing ligands have been prepared. For example, Hart and Laming[2] isolated stable solid 1,10-phenanthroline complexes of

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission; presented at the Fourth Pacific SAS Conference, Pasadena, Calif., Sept 22–24, 1965.

[2] F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem.*, **26**, 579 (1964).