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The Infrared Spectra of Silver–Ammine Complexes

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Received October 8, 1968

The infrared absorption spectra of crystalline bis(diamminesilver) sulfate, diamminesilver nitrate, and their deuterium analogs have been measured in the region from 3500 to 30 cm^{-1}. The spectra have been interpreted in terms of group theoretical predictions of the absorption characteristics of the complex cations and the anions, based on crystallographic considerations. The symmetric and asymmetric silver–nitrogen stretching bands were observed near 380 and 460 cm^{-1}, respectively, and the stretching force constant, calculated on the basis of a simple valence force field, is about 1.65 mdyn/Å.

Introduction

Although a considerable amount of information is available on the infrared spectra of various metal–ammine complexes,[1] the existing spectra of the silver–ammine complexes are rather fragmentary. Some of the ammine frequencies have been reported for diamminesilver complexes in KBr dispersions[2] and in mulls.[3,4] The frequencies obtained by the KBr pellet technique are subject to question owing to reaction of the complex with the matrix. Furthermore, the spectra obtained by the mull method were not sufficiently well defined to resolve the silver–nitrogen stretching vibration, to yield accurate frequency values or to reveal all of the splitting multiplicities of the observed fundaental bands.

Raman spectra of aqueous solutions of diamminesilver complexes show that the symmetric silver–nitrogen stretching frequency comes near 370 cm^{-1}.[3] It should be noted that the value of 410 cm^{-1} quoted by Powell and Sheppard[4] for the Raman-active symmetric silver–nitrogen stretching mode in $Ag(NH_3)_2Cl$ was apparently a misquote of the 410-cm^{-1} line of $Cu(NH_3)_4SO_4$ referred to by Hibben[5] and measured by Damaschun.[6]

In the present investigation the infrared spectra of crystalline $[Ag(NH_3)_2]_2SO_4$, $[Ag(ND_3)_2]_2SO_4$, $Ag(NH_3)_2NO_3$, and $Ag(ND_3)_2NO_3$ have been studied in some detail in the region from 3500 to 30 cm^{-1}. Particular attention was given to the location of the Ag–N vibrational frequencies. The spectra are interpreted in terms of group theoretical predictions based on crystallographic considerations.

Experimental Section

Bis(diamminesilver) sulfate and bis((diammine-d_6)silver) sulfate were formed by dissolving silver sulfate in warmed, concentrated ammonium hydroxide (or ND_4OD). The white crystalline products were precipitated by cooling in an ice bath, drained, and dried in a desiccator. *Anal.* Calcd for $[Ag(NH_3)_2]_2SO_4$: Ag, 56.9; NH_3, 17.9; S, 8.4. Found: Ag, 56.6; NH_3, 17.7; S, 8.2. Calcd for $[Ag(ND_3)_2]_2SO_4$: Ag, 55.1; ND_3, 20.4; S, 8.2. Found: Ag, 53.3; ND_3, 20.4; S, 8.4.

Diamminesilver nitrate and (diammine-d_6)silver nitrate were formed by dissolving silver nitrate in concentrated ammonium hydroxide (or ND_4OD) at room temperature. The white crystalline products were separated by direct drying in a desiccator containing molecular sieves. *Anal.* Calcd for $Ag(NH_3)_2NO_3$: Ag, 52.9; NH_3, 16.7. Found: Ag, 53.0; NH_3, 17.0. Calcd for $Ag(ND_3)_2NO_3$: Ag, 51.4; ND_3, 19.0. Found: Ag, 51.0; ND_3, 18.7. These compounds are quite stable if stored in subdued light in a dry atmosphere. They lose ammonia rapidly if heated to about 70°. X-Ray powder patterns showed that deuteration does not change the crystal structure of either the nitrate or the sulfate complexes at room temperature. However, differential thermal analyses showed that the deuterated sulfate undergoes a reversible phase change at 2.5°, not observed for the undeuterated complex.

The infrared spectra were measured in the 3500–400-cm^{-1} region to an accuracy of about ±2 cm^{-1} with a Perkin-Elmer Model 521 spectrophotometer. For the 500–30-cm^{-1} region, a Perkin-Elmer Model 301 spectrophotometer was used in the double-beam mode, with an accuracy of about ±1 cm^{-1}. Both instruments were calibrated against the spectrum of water vapor.[7–9] In the far-infrared region, low-temperature spectra were obtained by using a cryostat of conventional design, fitted with a copper block. Thermocouple readings showed that the samples attained a temperature of about 143°K when liquid nitrogen was used as a coolant.

The samples were prepared as mulls in mineral oil for the mid-infrared region and as mulls in vaseline for the far-infrared region. Silver chloride or low-density polyethylene was used for cell windows. The KBr pellet technique was tried and abandoned because of evidence of reaction between the complexes and the matrix. In the case of $Ag(NH_3)_2NO_3$ we were successful in preparing a pressed polycrystalline film sufficiently thin (about 0.1 mm) to provide useful data. Solutions of $Ag(NH_3)_2NO_3$ in N,N-dimethylformamide and in dimethyl sulfoxide were measured in high-density polyethylene cells. No suitable solvent was found for the sulfate complex.

Results

The spectra are shown in Figures 1 and 2. The ordinate scale is linear but is not in absolute values of

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(1) See, for example, K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

(2) G. M. Barrow, R. H. Krueger, and F. Basolo, *J. Inorg. Nucl. Chem.*, **2**, 340 (1956); G. F. Svatos, D. M. Sweeny, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 3313 (1957); G. F. Svatos, C. Curran, and J. V. Quagliano, *ibid.*, **77**, 6159 (1955).

(3) M. G. Milles, J. H. Patterson, C. W. Hobbs, M. J. Hopper, J. Overend, and R. S. Tobias, *Inorg. Chem.*, **7**, 1721 (1968).

(4) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 3108 (1956).

(5) J. H. Hibben, "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corp., New York, N. Y., 1939, p 462.

(6) I. Damaschun, *Z. Physik. Chem.*, **16B**, 81 (1932).

(7) K. N. Rao, C. J. Humphreys, and D. H. Rank, "Wavelength Standards in the Infrared," Academic Press, New York, N. Y., 1966.

(8) "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworths Inc., Washington, D. C., 1961.

(9) R. T. Hall, D. Vrabec, and J. M. Dowling, *Appl. Opt.*, **5**, 1147 (1966).

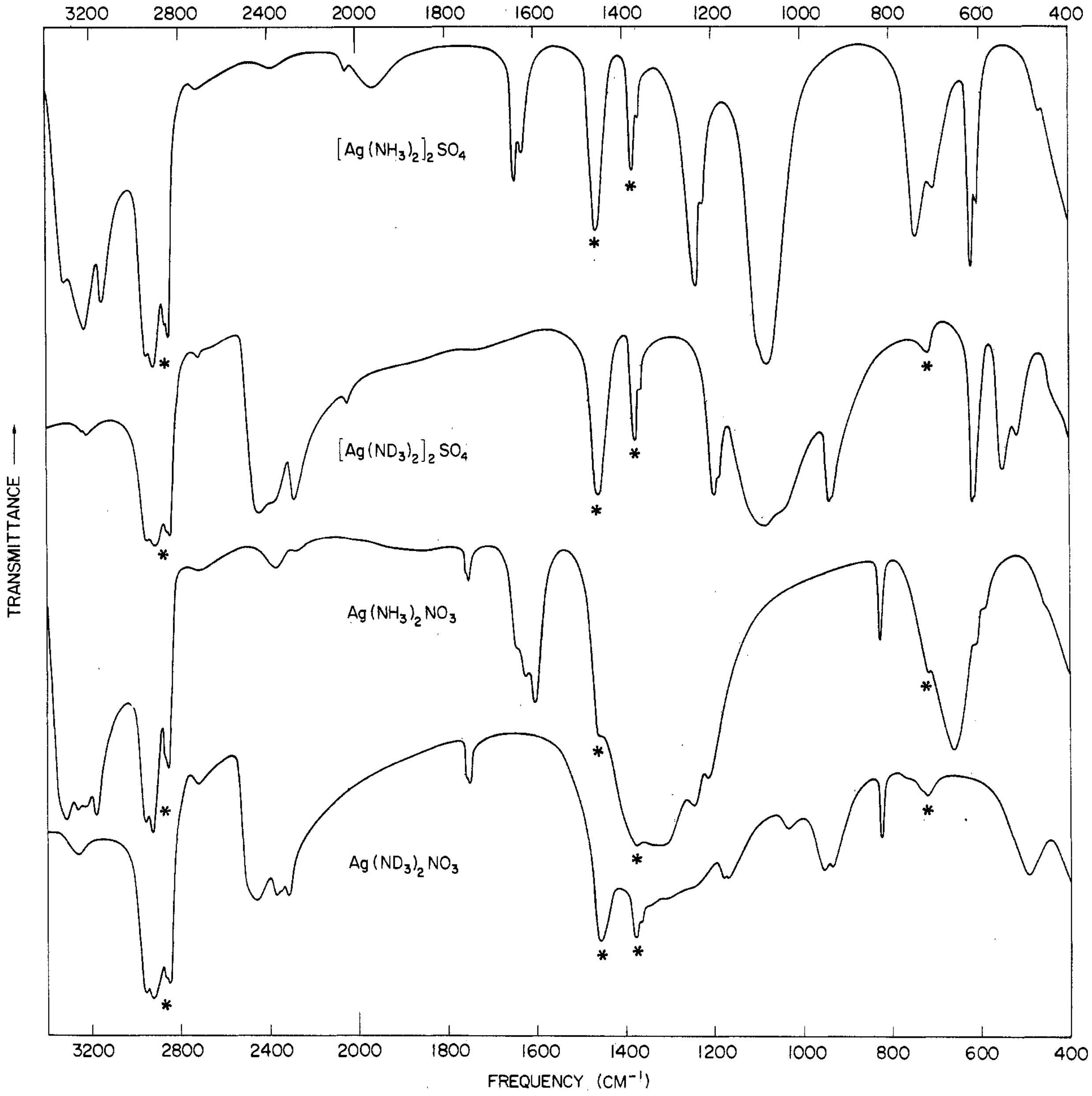

Figure 1.—Infrared spectra of crystalline silver–ammine complexes suspended in mineral oil at 298°K.

per cent transmittance because of uncertainties in the base lines. The far-infrared spectra have been replotted on a contracted abscissa scale. The weak bands near 3250 and 1030 cm^{-1} in the spectra of the deuterated compounds reveal the incorporation of a very small amount of hydrogen, presumably resulting mainly in the formation of some ND_2H groups. In Figure 1 the absorption bands attributable to the mineral oil are marked by asterisks.

The observed fundamental frequencies of the complex cations, the sulfate and nitrate ions, and some lattice modes of the crystals are listed in Tables I and II. The low-temperature values are given for the far-infrared region because of the increase in band sharpness obtained by cooling the samples. These values are a little higher than the corresponding frequencies observed at room temperature. In addition to the tabulated fundamentals and lattice modes, a few weak bands appear in the spectra which are attributable to combinations or possibly to impurities.

Discussion

In crystalline $[Ag(NH_3)_2]_2SO_4$ linear coordination of silver(I) ions to two ammonia molecules has been demonstrated by X-ray diffraction.[10] The same type of coordination is expected in crystalline $Ag(NH_3)_2NO_3$ and has been found in similar compounds such as diamminemercury halides[11] and dimethylcadmium.[12] Although the ammine groups may conceivably have either free or restricted rotation, the free rotational model (D_{3h}') is favored for the hypothetical isolated $Ag(NH_3)_2^+$

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(10) R. B. Corey and R. W. G. Wyckoff, *Z. Krist.*, **87**, 264 (1934).

(11) E. P. Bertin, I. Nakagawa, S. Mizushima, T. J. Lane, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 525 (1958).

(12) H. S. Gutowsky, *ibid.*, **71**, 3194 (1949); *J. Chem. Phys.*, **17**, 128 (1949).

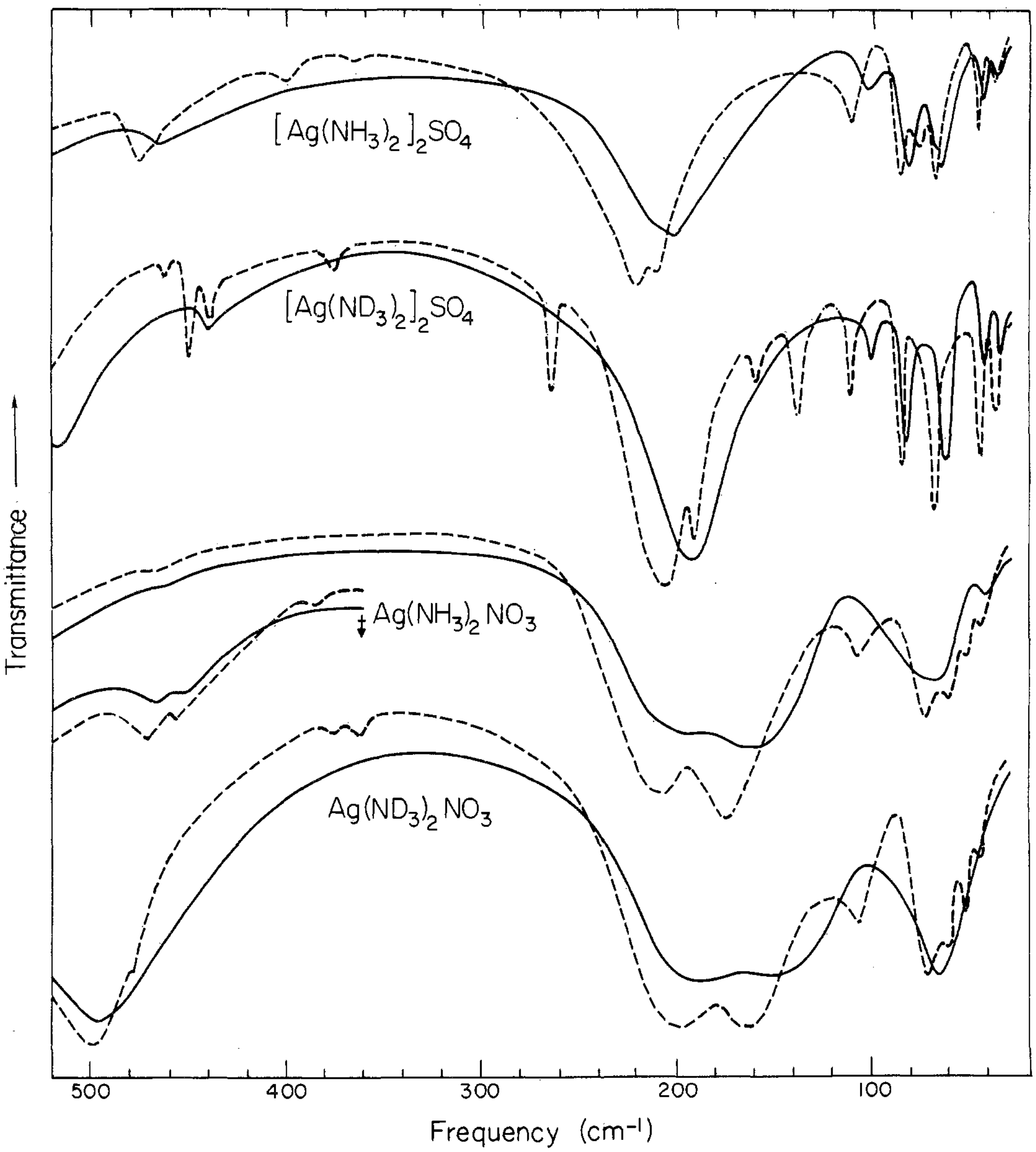

Figure 2.—Infrared spectra of crystalline silver—ammine complexes suspended in vaseline: solid lines, 298°K; dashed lines, 143°K; ‡, pressed film of $Ag(NH_3)_2NO_3$, 0.1 mm thick.

ion.[12] Using the conventional nomenclature[13] for D_{3h}' symmetry, the selection rules predict that three type $\bar{A}_2$ and four type E vibrations of the complex ion will be infrared active. These fundamental modes are assigned in Table I according to the notation of Gutowsky.[12] If rotation is in fact restricted in the solid state,[14] the selection rules for the resulting D_{3d} model predict no change in the number of infrared-active fundamental vibrations expected on the basis of the D_{3h}' point group. The observed fundamentals of the sulfate and nitrate ions are assigned in Table II with standard nomenclature.[13]

$[Ag(NH_3)_2]_2SO_4$ crystallizes in the tetragonal system with a space group symmetry $P\bar{4}2c$ (D_{2d}^4) and with two molecules per unit cell.[10] The $Ag(NH_3)_2^+$ ions are located at sites of C_2 symmetry, and the SO_4^{2-} ions, at sites of S_4 symmetry. $Ag(NH_3)_2NO_3$ crystallizes in the orthorhombic system with a space group symmetry Pnn2 (C_{2v}^{10}) and with four molecules per unit cell.[15] Both the $Ag(NH_3)_2^+$ ions and the NO_3^- ions are located at sites of trivial symmetry, C_1.

The correlation mappings shown in Figures 3 and 4 predict that, for linear $Ag(NH_3)_2^+$ ions at sites of either C_1 or C_2 symmetry, the degeneracy of the E vibrations is removed and the A_1, $\bar{A}_1$, and $\bar{\bar{E}}$ vibrations, which are infrared inactive for the hypothetically isolated ion, become active in the crystalline compounds. Thus,

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[13] N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 152.

[14] Raman spectra of the crystalline compounds can determine whether or not the ammine groups are freely rotating. The E vibrations are Raman active for D_{3h}' symmetry (free rotation), while they are not for D_{3d} symmetry (restricted to the staggered orientation).

[15] R. B. Corey and K. Pestrecov, *Z. Krist.*, **89**, 528 (1934).

TABLE I

FUNDAMENTAL CATION FREQUENCIES AND SOME LATTICE MODES OF THE SILVER–AMMINE COMPLEXES[a]

Species	Assignment[b]	Mode	$[Ag(NH_3)_2]_2SO_4$	$[Ag(ND_3)_2]_2SO_4$	R(H/D)	$Ag(NH_3)_2NO_3$	$Ag(ND_3)_2NO_3$	R(H/D)
A_1	NH_3 str	ν_1	....	....		....	....	
A_1	NH_3 bend	ν_2	1222	930	1.32	1214	932	1.31
A_1	Ag–N str	ν_3	400[c]	376[c]	1.06	386[c]	363[c]	1.06
$\bar{A}_1$	NH_3 tors	ν_4	....	265?[c]		....	....	
$\bar{A}_2$	NH_3 str	ν_5	3150	2290	1.37	3180	2320	1.37
$\bar{A}_2$	NH_3 bend	ν_6	1236	937	1.32	1246	953	1.31
$\bar{A}_2$	Ag–N str	ν_7	476[c]	449[c]	1.06	470[c]	....	
E	NH_3 str	ν_8	3230	2380	1.36	3270	2375	1.38
			3320	2450	1.36	3320	2465	1.35
E	NH_3 def	ν_9	1626	1185	1.37	1602	1167	1.37
			1642	1196	1.37	1624	1177	1.38
E	NH_3 rock	ν_{10}	703	517	1.36	610	479[c]	....
			740	548	1.35	660	495	1.33
E	N–Ag–N bend	ν_{11}	211[c]	192[c]	1.10	176[c]	166[c]	1.06
			221[c]	206[c]	1.07	208[c]	200[c]	1.04
$\bar{E}$	NH_3 str	ν_{12}	....	....		....	....	
$\bar{E}$	NH_3 def	ν_{13}	....	....		1642	1240	1.32
$\bar{E}$	NH_3 rock	ν_{14}	....	....		590?	....	
..	Lattice mode	L_1	111[c]	112[c]		108[c]	108[c]	
..	Lattice mode	L_2	86[c]	86[c]		74[c]	73[c]	
..	Lattice mode	L_3	76[c]	....		62[c]	61[c]	
..	Lattice mode	L_4	68[c]	69[c]		53[c]	53[c]	
..	Lattice mode	L_5	46[c]	46[c]		45[c]	45[c]	
..	Lattice mode	L_6	37[c]	37[c]		....	....	

[a] Frequencies are in cm^{-1}. [b] The corresponding assignments for ND_3 modes apply to the deuterium analogs. [c] These values were obtained at 143°K; all others were obtained at 298°K.

TABLE II

OBSERVED ANION FREQUENCIES OF THE SILVER–AMMINE COMPLEXES[a]

Species	Assignment	Mode	$[Ag(NH_3)_2]_2SO_4$	$[Ag(ND_3)_2]_2SO_4$
E	SO_4 def	ν_2	...	439[b]
F_2	SO_4 str	ν_3	1078	1040
			1098	1082
F_2	SO_4 def	ν_4	605	610
			619	618
			$Ag(NH_3)_2NO_3$	$Ag(ND_3)_2NO_3$
A_2''	NO_3 bend	ν_2	825	822
E'	NO_3 str	ν_3	1320	1310

[a] Frequencies are in cm^{-1}; temperature 298°K, unless noted otherwise. [b] Temperature 143°K.

although the sulfate and nitrate complexes have different crystal structures, the cation spectra of both compounds are expected to be quite similar, on the basis of site group considerations. The observed spectra reveal that this is indeed the case, and they agree quite well with the site group predictions. All of the type E bands appear as doublets and several of the type A_1 and $\bar{E}$ bands are strong enough to be resolved. These are assigned in Table I.

The site group analysis shown in Figure 3 predicts that, for the SO_4^{2-} ions at sites of S_4 symmetry, the E and F_2 vibrations are split but only one E component is infrared active. Similarly, the mapping shown in Figure 4 for the NO_3^- ions at sites of C_1 symmetry predicts that the E' vibrations are split and that the A_1' vibration becomes infrared active. The splitting of both F_2 bands of the SO_4^{2-} ions is observed (see Table II), but the splitting of the ν_3 (E') mode of the NO_3^- ions is uncertain because of overlapping of the mineral oil absorption. Apparently the ν_1 (A_1') and ν_4 (E') bands of the nitrate ion are either obscured or too weak to be observed.

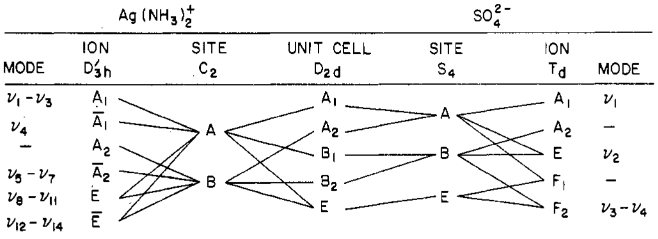

Figure 3.—Correlation mapping of symmetry species for crystalline bis(diamminesilver) sulfate.

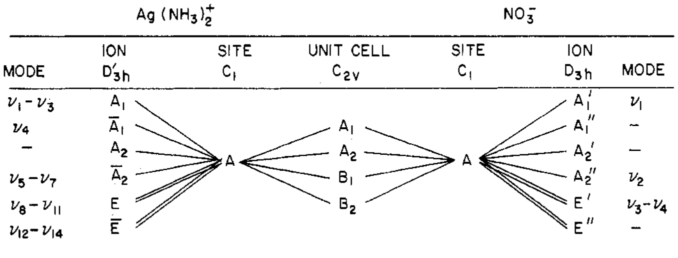

Figure 4.—Correlation mapping of symmetry species for crystalline diamminesilver nitrate.

A consideration of the intermolecular coupling between the vibrations of like ions in the unit cell leads to the prediction of further splitting in most of the bands. These factor group selection rules are shown in Figures 3 and 4. The observed band splittings are adequately explained on the basis of site group considerations alone, and the additional band multiplicity predicted by the factor group analysis is evidently not resolved in this study. This suggests, but does not prove, that the observed splittings are due to the static field at the site rather than to the effects of intermolecular coupling.

The assignments of the ammine (NH_3 or ND_3) bands seem to be unequivocal[1] except for the multiple N–H stretching absorptions. Of the six N–H stretching vibrations predicted, only three are resolved. The first overtone of the ammine deformation vibrations, in some cases enhanced by Fermi resonance, also contributes to the absorption in this region. This accounts for the differences in relative intensities of the N–H stretching bands observed in the deuterated and undeuterated sulfate complexes. In the case of the deuterated and undeuterated nitrate complexes, the overtone is observed as a weak shoulder at 2350 and 3230 cm^{-1}, respectively. In general, the assignments for the ammine bands are supported by the satisfactory agreement between the NH_3/ND_3 frequency ratios, listed in Table I as $R(H/D)$, and the value of 1.37 calculated from the simple reduced mass relation $(M_{N-H}/M_{N-D})^{1/2}$. The band at 265 cm^{-1} in the low-temperature modification of the deuterated sulfate complex is tentatively assigned to the ammine torsional mode, ν_4, although it could be assigned alternatively to the combination ν_{11} (192 cm^{-1}) + L_4 (69 cm^{-1}). The appearance of this band in the deuterated sulfate, but not in the normal sulfate, is related to the previously mentioned phase change in the deuterated compound. The frequencies of the N–H stretching vibrations suggest that any possible hydrogen bonding of NH_3 groups to oxygen atoms of the anions is quite weak.[16]

The doublets appearing in the 200-cm^{-1} region are assigned to the N–Ag–N bending modes. These assignments are supported by the observation that the frequency shifts of the doublets on deuteration are nearly alike for both components, and the frequency ratios (see Table I) are in good agreement with the value of 1.06 calculated from the simple reduced mass relation for a linear XY_2 type of molecule. Further support is provided by the observation that the spectra of $Ag(NH_3)_2NO_3$ in solution in dimethylformamide and in dimethyl sulfoxide show a single band near 184 cm^{-1}—close to the average frequency values of the doublet found for the solid at room temperature. The greater band width and band splitting in the case of the nitrates are probably related to peculiarities of the crystal structure, but the existing crystallographic information is not sufficient to yield a detailed explanation. A contribution to the absorption of the nitrates in this region might arise from Ag–O interaction, such as is indicated to exist in solid $AgNO_3$,[17] but again the crystallographic data are insufficient to confirm the presence or absence of such interaction. A contribution from an NH···O bridging vibration is unlikely in view of the absence of strong hydrogen bonding in the system, as indicated by the NH stretching frequencies.

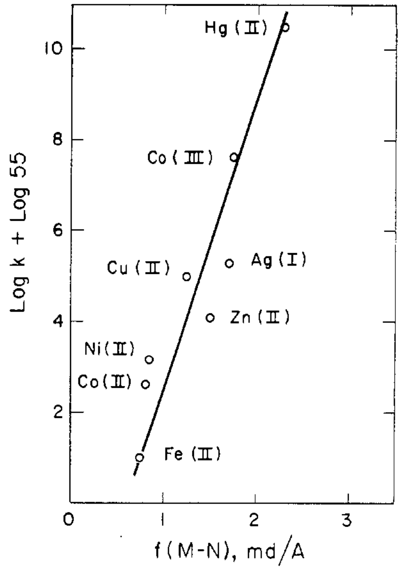

Figure 5.—Relation between the stability constant, log k + log 55, and the metal–nitrogen stretching force constant, f(M–N), for various metal–ammine complexes.

The asymmetric Ag–N stretching bands are observed near 460 cm^{-1}, except in the spectra of $Ag(ND_3)_2NO_3$ in which they are obscured by the relatively strong ND_3 rocking band. In general, asymmetric M–N stretching bands tend to be quite weak in symmetrical metal-ammine complexes, so some uncertainties may exist in reported assignments. However, in spite of this difficulty, many of the assignments can be accepted with considerable confidence. These bands usually appear in the 400–500-cm^{-1} region for complexes in which the coordination number is twice the oxidation number of the central metal atom.[18–21] Newman and Powell[22] observed two weak bands at 475 and 460 cm^{-1} in the spectrum of $(Ag_2(en)_2)Cl_2$ (en = ethylenediamine) which probably arise from linear N–Ag–N stretching frequencies. The symmetric Ag–N stretching bands found near 380 cm^{-1} in this study agree with the symmetric Ag–N Raman frequencies reported for aqueous diamminesilver complexes.[3] Our assignments are further supported by the band shifts of about 6% in the spectra of the deuterium analogs, which agrees well with the calculated ratio of 1.06.

The Ag–N stretching force constants of the various complexes were calculated by assuming a simple valence force field and by representing the ammonia group as a point mass of 17 for NH_3 and 20 for ND_3. On this basis, the average value for the sulfates and nitrates

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[19] W. P. Griffith, *J. Chem. Soc.*, *A*, 899 (1966).

[20] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 759, 1707 (1966); J. Hiraishi, I. Nakagawa, and T. Shimanouchi, *ibid.*, **24A**, 819 (1968).

[21] C. H. Perry, D. P. Athans, E. F. Young, J. R. Durig, and B. R. Mitchell, *ibid.*, **23A**, 1137 (1967).

[22] G. Newman and D. B. Powell, *J. Chem. Soc.*, 3447 (1962).

calculated from the ν_7 frequencies is 1.72 mdyn/Å and from the ν_3 frequencies is 1.58 mdyn/Å. The disagreement between these values is a measure of the approximations inherent in this approach. The values are intermediate in the range of the metal–nitrogen stretching force constants, f(M–N), reported for numerous other metal–ammine complexes.[20,23,24] The magnitude of these force constants decreases in the order Hg(II) > Pt(II) > Pd(II) > Co(III) > Ag(I) > Zn(II) > Cr(III) > Cu(II) > Ni(II) > Co(II) > Fe(II),[25] and the covalent character of the metal–nitrogen bonds is expected to show the same general trend. Although the uncertainties in the assignments and in the various force constant calculations somewhat limit the reliability of this approach in obtaining relative covalent character, it is interesting to note that Bjerrum's stability constant data[26] offer considerable support for the indicated ordering of covalency (see Figure 5).

The bands in the region below 120 cm^{-1} are attributable to lattice vibrations. The low-temperature spectra show typical band sharpening and displacement to higher frequencies. The lattice bands observed appear to be of translational origin, since no significant frequency displacements result from deuteration of the ammine groups. From reduced mass considerations, deuteration would be expected to induce measurable frequency changes in the librational modes of the cations but not in the translational modes of the crystal lattice. The two bands at 161 and 139 cm^{-1} in the low-temperature spectrum of $[\mathrm{Ag(ND_3)_2}]_2\mathrm{SO_4}$ are tentatively assigned to the combination of L_1 (112 cm^{-1}) + L_5 (46 cm^{-1}) and to the overtone of L_4 (69 cm^{-1}), respectively. The weak bands consistently found near the ν_7 fundamentals are ascribed to a combination band of the type $\nu_{11} + \nu_4$.

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[23] R. J. H. Clark and C. S. Williams, *J. Chem. Soc., A*, 1425 (1966).

[24] P. J. Hendra and N. Sadasivan, *Spectrochim. Acta*, **21**, 1271 (1965).

[25] The Fe(II)–N force constant is estimated to be about 0.65 mdyn/Å from the reported stretching frequency: L. Sacconi, A. Sabatini, and P. Gans, *Inorg. Chem.*, **3**, 1772 (1964).

[26] J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

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Transition Metal Complexes of 1,5-Diazanaphthalene[1]

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Received August 5, 1968

Coordination compounds have been formed between 1,5-diazanaphthalene and $\mathrm{CoCl_2}$, $\mathrm{Co(NCS)_2}$, $\mathrm{NiCl_2}$, $\mathrm{CuCl_2}$, $\mathrm{ZnCl_2}$, and $\mathrm{AgNO_3}$. The complexes have been characterized by means of infrared spectra, visible spectra, and magnetic susceptibilities. 1,5-Diazanaphthalene behaves either as a bridging bidentatate ligand or as a nonbridging monodentate ligand depending upon the metal and the reaction conditions.

Introduction

Complexes of aromatic, heterocyclic amines, especially pyridine, 1,10-*o*-phenanthroline, and dipyridyl, have been widely synthesized and characterized. Considerably less attention has been given to systems containing two or more nitrogen atoms and having a configuration which requires bridging if both nitrogens are involved in coordination. Lever and coworkers[2] have reported complexes of Co(II), Ni(II), and Cu(I) with pyrazine and methyl-substituted pyrazines. They found that some of the compounds were polymeric in nature owing to bridging pyrazine groups. Quinoxaline (1,4-diazanaphthalene) forms stable complexes with Cu(II) salts[3] in contrast to Cu(II) complexes of pyrazine which have a strong tendency to be reduced to Cu(I) compounds. The copper(II) quinoxaline adducts have been found to be analogous to the cobalt(II) and nickel(II) pyrazine complexes. Chelates of 4-hydroxy-1,5-diazanaphthalene have been reported[4,5] but not characterized.

The similar nature of 1,5-diazanaphthalene (1,5-naphthyridine) compared to that of pyrazine led us to believe that complexes of the former should easily be prepared. Since the two nitrogens are in different rings, it was expected that 1,5-diazanaphthalene would be a somewhat stronger base than pyrazine (pyridine is a stronger base than pyrazine[6]) and would form bridged coordination compounds more readily. We wish to report the preparation of complexes of Co(II), Ni(II),

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[1] Presented in part at the 18th Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., 1966.

[2] (a) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *Nature*, **189**, 58 (1961); (b) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1235 (1962); (c) A. B. P. Lever J. Lewis, and R. S. Nyholm, *ibid.*, 3156 (1963); (d) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *ibid.*, 5042 (1963).

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[6] D. A. Keyworth, *J. Org. Chem.*, **24**, 1355 (1959).