frequencies of the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^4T_{1g}(P)$ to calculate[6] $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ for an octahedral complex, a value of 15,993 cm.$^{-1}$ is obtained compared to an experimental value of 16,502 cm.$^{-1}$. The ratio of the frequencies for the transitions to $^3T_{1g}(F)$ and $^3T_{2g}$ is 1.68, which is in agreement with that expected for an octahedral complex.

When the nitrate complex is dissolved in nitromethane, a blue-green solution is obtained whose electronic spectrum and conductance value indicate that the same species is formed as in dichloromethane solution. When excess pyridine is added, a solution is obtained whose color is blue and whose electronic spectrum has shifted to lower wave lengths. A conductance measurement indicates that one nitrate ion has been removed from the coordination sphere of the nickel ion. This phenomenon, which does not occur in dichloromethane, can be attributed to the higher dielectric constant of nitromethane.

The cyanate complex is soluble in nitromethane with excess pyridine added. The electronic spectrum is identical with that of the dichloromethane solution previously mentioned. The conductance value indicates that no ionic species are present despite the excess pyridine and suggests that the species present is $Ni(C_5H_5N)_4(NCO)_2$.

Acetonitrile and Benzonitrile.—The absence of free pyridine in the solution of the perchlorate complex in benzonitrile and the marked difference in the electronic spectrum of this solution and the mull spectrum of the perchlorate complex indicate that the species in solution is $Ni(C_5H_5N)_4(C_6H_5CN)_2^{2+}$. The addition of excess pyridine has no effect upon the electronic spectrum of this solution. The behavior of the n.m.r. signal is further evidence for benzonitrile coordination as manifested by a contact shift. The contact shift, an increase in line width and a shift to higher or lower fields, is typical for ligand protons in complexes of paramagnetic metal ions.[13] Unpaired electron spin is delocalized onto the ligand through σ or π electron systems, affecting shielding and relaxation times. The stability of this species in the presence of excess pyridine is probably due to less steric strain when the ligands on the z axis are benzonitrile than when they are pyridine.

In acetonitrile, a better base than benzonitrile for electronic and steric reasons, the species produced when the perchlorate complex is dissolved contains less than four coordinated pyridine molecules. Addition of excess pyridine does not change the electronic spectrum. The complex is formulated on the basis of the far-infrared measurements as $Ni(C_5H_5N)_2(CH_3CN)_4^{2+}$. As in the case of the benzonitrile solvent, acetonitrile coordination is indicated by the n.m.r. contact shift of the acetonitrile protons.

Acknowledgment.—The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758.

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CONTRIBUTION FROM THE CHEMICAL LABORATORY
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The Preparation and Infrared Examination of the 2-, 3-, and 4-Cyanopyridine Complexes of Copper(I), Silver(I), and Gold(I) Perchlorates

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Received January 13, 1965

The preparation of the bis 2-, 3-, and 4-cyanopyridine complexes of copper(I), silver(I), and gold(I) perchlorates and the tris 3-cyanopyridine complex of silver(I) perchlorate is described. Because both the nitrile group and the pyridine group in the cyanopyridine are capable of coordinating strongly with these ions, the infrared spectra of the complexes were examined to determine the coordination site of the metal ions. In 3- and 4-cyanopyridine, the metal ions are bound to the pyridine nitrogen, and in 2-cyanopyridine they are bound to the nitrile nitrogen.

An attempted extension of a previously reported study from this laboratory[1] on solvent-effected reorientation in the coordination sphere of metal ions of organic ligands with two active functional groups has led us into this study of the cyanopyridine complexes of copper(I), silver(I), and gold(I) ions. Both the nitrile group and the pyridine group in the cyanopyridine are capable of coordinating strongly with these ions. The preferential coordination of metal ions by one group rather than by the other and the relative ability of the three cyanopyridines to form complexes with these metal ions depend upon polar, resonance, and steric effects. Preparation and analysis of ten metal complexes of 2-, 3-, and 4-cyanopyridine are reported. The position of the metal ion in these complexes is deduced from infrared spectral data.

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Experimental

The organic solvents were purified by treatment with appropriate reagents and fractional distillation. Reagent grade 2-butanol was treated with calcium hydride and sodium borohydride, refluxed for 1 hr., then fractionally distilled. Reagent grade acetonitrile was dried over and distilled from phosphorus pentoxide. Nitroethane was passed twice through a 2.5 cm. (i.d.) × 35 cm. column of neutral Woelm chromatographic alumina, activity grade 1, and fractionally distilled. Spectroscopic grade carbon tetrachloride was used without further purification.

Anhydrous silver perchlorate and hexaaquocopper(II) perchlorate (G. F. Smith Chemical Co.) were dried in a vacuum oven at 70° and stored over anhydrous magnesium perchlorate. Purified precipitated gold metal powder from Fisher Scientific Co. and 2-, 3-, and 4-cyanopyridine from Aldrich Chemical Co. were used without purification. Analytical grade copper wire was cleaned in dilute nitric acid prior to use. Nitrosyl perchlorate was prepared by passing into 70% reagent grade perchloric acid the oxides of nitrogen liberated by the dropwise addition of concentrated nitric acid to solid sodium nitrite. The nitrosyl perchlorate precipitate was collected in a nitrogen atmosphere on a sintered glass filter and washed thoroughly with dry analytical grade ethyl acetate. The dry nitrosyl perchlorate was stored in a desiccator over phosphorus pentoxide. Bis(acetonitrile)gold(I) perchlorate was prepared according to the method reported by Bergerhoff.[2]

The infrared spectral data were obtained with a Perkin-Elmer model 421 spectrophotometer. Nujol and Halocarbon mulls pressed between sodium chloride windows were used in the 4000 to 600 cm.$^{-1}$ region, and Nujol mulls pressed between thin polyethylene sheets, "Baggies," were used in the 800 to 300 cm.$^{-1}$ region.

Preparation of Cyanopyridine Complexes.—The 2-, 3-, and 4-cyanopyridine complexes of copper(I) and silver(I) perchlorate were prepared by the addition of a 2-butanol solution of cyanopyridine to a 2-butanol solution of the metal perchlorate. The mole ratio of added cyanopyridine to metal ion was 10:1. The resulting precipitate was washed with 2-butanol and with dry ether and either air dried or dried in an oven at 100°. This procedure gave 2:1 complexes, except with 3-cyanopyridine and silver(I) perchlorate, in which case a 3:1 product was obtained. The 3:1 complex was converted readily to the 2:1 complex by washing with hot 2-butanol. The 2:1 complex of 3-cyanopyridine and silver(I) can be made directly by lowering the amount of excess ligand. Solutions of copper(I) perchlorate in 2-butanol were prepared by the treatment of deoxygenated 2-butanol solutions of copper(II) perchlorate dihydrate with copper wire at a temperature of approximately 80° until the solutions became colorless. During the course of the heating, a stream of nitrogen was passed through the solution to prevent copper(I) ion from being air oxidized. Deoxygenated cyanopyridine solutions were added to the copper(I) solutions.

Bis(4-cyanopyridine)copper(I) perchlorate is yellow. Bis(2-cyanopyridine)copper(I) perchlorate and bis(3-cyanopyridine)-copper(I) perchlorate are white. All of the silver(I) complexes are white.

The 2-, 3-, and 4-cyanopyridine complexes of gold(I) perchlorate were obtained by the following procedure: Bis(acetonitrile)gold(I) perchlorate was dissolved in a mixture of nitroethane and carbon tetrachloride. Cyanopyridine, dissolved in the same solvent mixture, in the mole ratio of 10:1 cyanopyridine to gold(I), was then added. The cyanopyridine complex of gold(I) perchlorate was precipitated by adjusting the relative proportion of carbon tetrachloride and nitroethane and by lowering the temperature. The gold(I) cyanopyridines were washed with dry ether, air dried, and stored in a desiccator over anhydrous magnesium perchlorate.

All of the gold(I) complexes also are white. After long storage, however, they take on a slightly purple tint, indicating the presence of a small amount of gold metal.

Analysis of Complexes.—Copper(I) ion in the complexes was determined by treating the complex with dilute nitric acid and titrating with standard disodium ethylenediaminetetraacetic acid in an ammonia–ammonium chloride buffer solution with murexide as the indicator.

Silver ion was determined gravimetrically as silver chloride by precipitation from a dilute nitric acid solution.

Gold(I) ion was determined by polarography in acetonitrile 0.1 M in lithium perchlorate. The diffusion current at 0 v. *vs.* s.c.e. was found to be proportional to the gold(I) concentration. The gold(I)–cyanopyridine complexes in polarographic concentration appear to be dissociated completely in acetonitrile.

The perchlorate content of the copper(I) and silver(I) complexes was determined gravimetrically by precipitation of the perchlorate as the tetraphenylarsonium salt.

3- and 4-cyanopyridine were analyzed by (1) acid–base titration in glacial acetic acid and (2) spectrophotometry. For 2-cyanopyridine, only the latter method worked successfully.

Standard 0.1 N perchloric acid in glacial acetic acid (excess acetic anhydride is present) was used to titrate the cyanopyridines in acetic acid 0.1 M in lithium chloride. The titration was followed potentiometrically with a glass and silver–silver chloride electrode system. For 3- and 4-cyanopyridine, approximately 100-mv. breaks were obtained, whereas for 2-cyanopyridine, no break was observed. The titration curves indicate that in glacial acetic acid the pyridine group of 4-cyanopyridine is slightly more basic than the pyridine group of 3-cyanopyridine and that of 3-cyanopyridine is more basic than that of 2-cyanopyridine.

For spectrophotometric analysis of 2-, 3-, and 4-cyanopyridine, the complex is dissolved in acetonitrile. The absorptions of 2-, 3-, and 4-cyanopyridine follow Beer's law at $\lambda_{\max}$ 265, 240, and 255 mμ, respectively. The three cyanopyridines have the following molar absorptivities: 3.29×10^3, 2.17×10^3, and 2.85×10^3. The presence of metal ion (copper(I), silver(I), or gold(I)) does not alter the spectra of the cyanopyridines in acetonitrile. A Cary Model 14 recording spectrophotometer was used.

Results

The empirical formulas of the different complexes are presented in Table I. In Table II, we have tabulated the infrared data on the nitrile stretching vibration, the symmetric and antisymmetric C–C and C–N stretching vibrations, and the first and second ring breathing vibrations.

Discussion

Structure of the Cyanopyridine Complexes.—The coordination site of copper(I), silver(I), and gold(I) ions in their complexes with 2-, 3-, and 4-cyanopyridine has been determined from the nitrile stretching, C–C and C–N(ring) stretching, and ring breathing frequencies of the free bases and the complexes.

When the free pair of electrons on the nitrogen of a nitrile is involved in coordination, the stretching frequency of the nitrile group is shifted to a higher value than that for the free nitrile.[3-11] The nitrile stretching frequencies of the cyanopyridines and their copper(I), silver(I), and gold(I) complexes, therefore, should pro-

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[2] G. Bergerhoff, *Z. anorg. allgem. chem.*, **327**, 139 (1964).

[3] H. J. Coerver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958).

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TABLE I

EMPIRICAL FORMULAS OF THE COPPER(I), SILVER(I), AND GOLD(I) CYANOPYRIDINE COMPLEXES[a]

Ligand	Cu(I) complexes	Ag(I) complexes	Au(I) complexes[b]
4-Cyanopyridine	$Cu_{1.00}R_{2.29}(ClO_4)_{1.00}$	$Ag_{1.00}R_{2.00}(ClO_4)_{1.00}$	$Au_{1.00}R_{2.03}(ClO_4)_{0.97}$
3-Cyanopyridine	$Cu_{1.00}R_{1.94}(ClO_4)_{0.97}$	$Ag_{1.00}R_{2.01}(ClO_4)_{1.00}$ $Ag_{1.00}R_{2.97}(ClO_4)_{1.07}$	$Au_{1.00}R_{2.00}(ClO_4)_{0.97}$
2-Cyanopyridine	$Cu_{1.00}R_{2.01}(ClO_4)_{1.00}$	$Ag_{1.00}R_{2.07}(ClO_4)_{1.02}$	$Au_{1.00}R_{1.98}(ClO_4)_{1.00}$

[a] Average of at least three determinations on each analysis. [b] Perchlorate evaluated by difference.

TABLE II

INFRARED DATA[a]

Compound[b]	Nitrile[d] stretching	C–C and C–N stretching[c]				Ring breathing[d]	
		(1)	(2)	(3)	(4)	1st	2nd
4-Cyanopyridine	2240	1591	1535	1490	1408	985	1078
$Cu(4\text{-}C.P.)_2ClO_4$	2240	1602 1597	1540	1490	1417 1408	1057	1092
$Ag(4\text{-}C.P.)_2ClO_4$	2240	1600	1541	1497	1416	1060	1085
$Au(4\text{-}C.P.)_2ClO_4$	2240	1615	1540	1495	1425	1045	1082
3-Cyanopyridine	2225	1582	1552	1460	1410 1389	967	1008
$Cu(3\text{-}C.P.)_2ClO_4$	2250	1592	1567	1470	1412	1025	1082
$Ag(3\text{-}C.P.)_2ClO_4$	2235	1595	1567	1475	1418	1025	1075
$Ag(3\text{-}C.P.)_3ClO_4$	2240 2247	1595	1567	1475	1417	1028	1082
$Au(3\text{-}C.P.)_2ClO_4$	2252	1605	1570	1475	1427 1418	1023	1075
3-Cyanopyridinium chloride	2245						
2-Cyanopyridine	2235	1595[e] 1580	1570[f]	1461	1430	985	1038
$Cu(2\text{-}C.P.)_2ClO_4$	2260	1585	1565	1472	1431	985	1050
$Ag(2\text{-}C.P.)_2ClO_4$	2250	1587	1558	1467	1430	980	1040
$Au(2\text{-}C.P.)_2ClO_4$	2240	1593	1558	1470	1430	988	1035
Benzonitrile	2230						

[a] All frequencies in wave numbers (cm.$^{-1}$) with uncertainty of ±2 cm.$^{-1}$. [b] Cyanopyridine abbreviated by C.P. [c] Obtained in Halocarbon mulls. [d] Obtained in Nujol mulls. [e] Blue shoulder. [f] Red shoulder.

vide valuable information concerning which nitrogen, that of the pyridine or that of the nitrile, is coordinated to the metal ion. The nitrile stretching frequencies of the various complexes isolated and those of the free bases are listed in Table II. No change in the nitrile stretching frequencies of the copper(I), silver(I), and gold(I) complexes of 4-cyanopyridine from that of the free base indicates that in the 4-cyanopyridine complexes it is the pyridine nitrogen which is coordinated to the metal ions. With 2- and 3-cyanopyridine, the nitrile stretching frequencies of the copper(I), silver (I), and gold(I) complexes are shifted blue. These data suggest that in these complexes, it is the nitrile nitrogen which is coordinated to the metal ions.

Gill, *et al.*,[12] and Greenwood and Wade[13] have pointed out that when the infrared spectrum of a coordinated pyridine is compared with that of the free base, fairly major changes in the positions of some of the bands can be observed. Two of the changes noted by these investigators are: (1) a blue shift of the four principal bands of pyridine between 1430 and 1600 cm.$^{-1}$, which are due to ring C–C and C–N stretching vibrations, with the highest frequency band giving the largest shift, and (2) a blue shift of the ring breathing frequencies and C–H in-plane deformations, which occur in the 985 to 1250 cm.$^{-1}$ region. The frequencies of the four principal bands found for the cyanopyridines and their metal complexes in the region 1410 to 1615 cm.$^{-1}$ are listed in Table II. Two of these bands are attributable to symmetric and the other two to antisymmetric in-plane ring deformations arising from the C–C and C–N stretching vibrations. Also listed in Table II are the two lower frequency bands for these compounds in the 985 to 1250 cm.$^{-1}$ region. These two bands are assigned to the first and second ring breathing frequencies, in line with the assignments made by Greenwood and Wade in their study of coordinated pyridine.

Comparison of these six bands for 4-cyanopyridine and its complexes shows that the bands are shifted blue, indicating that the pyridine group is coordinated to the metal ions. A similar conclusion was reached previously from consideration of the nitrile stretching frequency.

In the case of 2-cyanopyridine and its metal complexes, we notice that these six bands remain fairly constant or are shifted slightly red. The pyridine group, therefore, is not coordinated to the metal ions in the 2-cyanopyridine complexes. This interpretation is also consistent with the information provided by the nitrile stretching frequencies. Because the basicity of the pyridine group of 2-cyanopyridine is expected to be only slightly less than that of 4-cyanopyridine, com-

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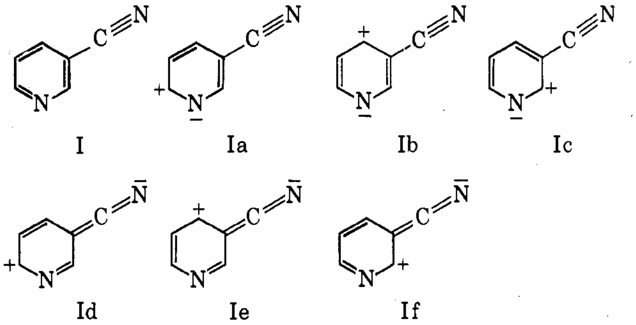
(12) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

(13) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1130 (1960).

plex formation of these metal ions with 2-cyanopyridine through the nitrile group results from inaccessibility of the electron pair on the ring nitrogen owing to steric factors.

Comparison of the four bands arising from ring C–C and C–N stretching vibrations and the first and second ring breathing frequencies of the 3-cyanopyridine complexes with those for the free base indicates definite blue shifts in the frequencies of the bound 3-cyanopyridines similar to those observed for the 4-cyanopyridine complexes. These infrared results suggest that in 3-cyanopyridine complexes the pyridine group must be coordinated to the metal ions. This finding is contrary to that indicated by the blue shift of the nitrile stretching frequency—that the nitrile group is bound to the metal ions. If the resonance forms Ia, Ib, and Ic and IIa and IIb, which contribute to the complex-forming ability of 3- and 4-cyanopyridine, are considered, the conflict between the conclusions from the two sets of infrared data is resolved easily. In 3-cyanopyridine, the electron density localized at the ring nitrogen by the contribution of resonance forms Ia, Ib, and Ic is delocalized by resonance forms Id, Ie, and If. Coordination of the ring nitrogen to the metal ions relocalizes the electron density at the ring nitrogen and, therefore, decreases the contribution of Id, Ie, and If to the electronic structure of 3-cyanopyridine. With less contribution from resonance forms Id, Ie, and If, the nitrile stretching frequency of bound cyanopyridine shifts to values higher than that for the free base. This shift to higher frequencies makes it appear as though the nitrile group is bound to the metal ions. In 4-cyanopyridine, the electron density localized at the ring nitrogen is not delocalized as in 3-cyanopyridine; consequently, coordination at the ring nitrogen does not affect the nitrile stretching frequency.

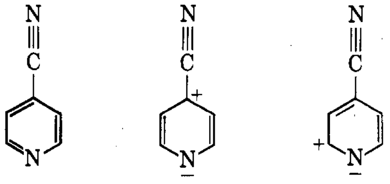
3-Cyanopyridine



I Ia Ib Ic

Id Ie If

4-Cyanopyridine



II IIa IIb

Coordination of the pyridine nitrogen to copper(I), silver(I), and gold(I) ions in the 3- and 4-cyanopyridine complexes and the nitrile nitrogen to the metal ions in the 2-cyanopyridine complexes appears to be definitely established.

The isolation of tris(3-cyanopyridine)silver(I) perchlorate was unexpected. Absence of any features of the infrared spectrum of unbound 3-cyanopyridine in the spectrum of the 3:1 complex indicates that all three cyanopyridines are bound. The most striking difference between the spectra of the 2:1 and 3:1 complexes is in the nitrile stretching band. The 3:1 complex has two bands near 2240 cm.$^{-1}$. One appears at 2247 cm.$^{-1}$ and the other at 2240 cm.$^{-1}$, with the former about half the intensity of the latter. The spectrum of the 2:1 complex, on the other hand, has essentially one band, at 2235 cm.$^{-1}$, in this region. At 2247 cm.$^{-1}$, there is only a hint of an absorption band. The intensity of this higher frequency band is *ca.* 1% of that of the major nitrile band. The two bands in the 2240 cm.$^{-1}$ region for the 3:1 complex suggest that 3-cyanopyridine is bound to silver(I) ion in two ways. In addition, the fact that the intensity of the 2247 cm.$^{-1}$ band is approximately one-half that of the 2240 cm.$^{-1}$ band points to two of the cyanopyridines being bound to silver(I) ion in a manner similar to that in the 2:1 complex and the third in a different manner. The higher value for the frequency of the nitrile stretching vibration of the third 3-cyanopyridine indicates that its interaction with silver(I) is much greater than that of the other two. One possible arrangement of the third cyanopyridine which would account for the larger blue shift exhibited by its nitrile group is for the cyanopyridine to be a bridging group between two 2:1 complexes. In this case, although the interaction of the pyridine nitrogen and of the nitrile nitrogen with silver(I) individually could be weaker than that of the pyridine nitrogen of the two other cyanopyridines with silver(I), the combination of the two interactions could produce a larger blue shift in the nitrile stretching frequency than the interaction of the two other cyanopyridines with silver(I).

At this time, we can offer no explanation for the repeated isolation of $Cu(4\text{-C.P.})_{2.29}ClO_4$.

Far-Infrared Data.—Although there is no direct proof of double bonding in complexes of this type,[14] Murmann and Basolo[15] conclude from stability studies of silver(I) complexes of 3- and 4-cyanopyridine that their results are consistent with the concept of π-bonding between silver(I) ion and the ligand. If π-bonding exists to an appreciable extent between the metal and cyanopyridine, it may be possible to observe the metal–nitrogen stretching frequency in the far-infrared.[13] The following far-infrared data (cm.$^{-1}$) have been obtained. 4-Cyanopyridine: 555 (br), 545 (red shoulder), 367 (m). $Cu(4\text{-C.P.})_2ClO_4$: 622 (s), 558 (s), 473 (w). $Ag(4\text{-C.P.})_2ClO_4$: 620 (s), 557 (s), 470 (w). $Au(4\text{-C.P.})_2ClO_4$: 622, 558 (s), 550 (red shoulder). 3-Cyanopyridine: 700, 548, 467, 453, 410, 392.

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(14) W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

(15) R. K. Murmann and F. Basolo, *J. Am. Chem. Soc.*, **77**, 3484 1955).

Cu(3-C.P.)$_2$ClO$_4$: 690, 645, 622, 548, 510 (vw), 473, 455, 408, 397. Ag(3-C.P.)$_3$ClO$_4$: 692, 640, 622, 552, 543 (red shoulder), 513 (vw), 482, 470, 400, 395. Ag(3-C.P.)$_2$ClO$_4$: 695, 652, 622, 557, 547, 480, 470, 405, 394. Au(3-C.P.)$_2$ClO$_4$: 687, 670, 666, 622, 559, 546, 480, 472, 422, 413. 2-Cyanopyridine: 630, 545 (br), 358 (w), 347 (w). Cu(2-C.P.)$_2$ClO$_4$: 637, 622, 553, 542, 525, 408, 395 (red shoulder), 367 (w), 347 (w). Ag(2-C.P.)$_2$-ClO$_4$: 641, 620, 551, 548, 482, 408, 396 (red shoulder), 367 (w), 355 (w). Au(2-C.P.)$_2$ClO$_4$: 622, 559, 543, 496, 440, 413 (w), 397 (w), 370 (w), 350 (w).

All the metal perchlorate complexes have a band at approximately 620 cm.$^{-1}$, which is attributable to ν_4 of the perchlorate anion.[16] The one-to-one correspondence of the spectra of the 4-cyanopyridine complexes with that of 4-cyanopyridine indicates that the metal–nitrogen frequency is below 300 cm.$^{-1}$. In the case of the 3-cyanopyridine complexes, a new peak appears between 640 and 670 cm.$^{-1}$. However, in light of the absence of a new band in this region for the 4-cyanopyridine complexes and because the stability of the 4-cyanopyridine–silver(I) complex is approximately the same as that of the 3-cyanopyridine–silver(I) complex,[15] it is difficult to justify the assignment of this band to the metal–nitrogen stretching vibration. If π-bonding is involved in the metal–nitrogen bond, it certainly does not strengthen the bond sufficiently so that the metal–nitrogen stretching band occurs above 300 cm.$^{-1}$. These observations are consistent with the results obtained by Gill, *et al.*,[12] for pyridine complexes.

In the 2-cyanopyridine complexes the metal ions are coordinated to the nitrile nitrogen. Lott[11] has examined the far-infrared spectra of benzonitrile complexes of transition metal ions and has shown that the new band in the 480–520 cm.$^{-1}$ region is due to the metal ion–nitrile nitrogen stretching vibration. The far-infrared spectra of the 2-cyanopyridine complexes of copper(I), silver(I), and gold(I) also show a new absorption band in this region.

Basicity of the Cyanopyridines.—The order of basicity of the three cyanopyridines with respect to perchloric acid in glacial acetic acid has been shown by potentiometric titration data to be 4-cyanopyridine > 3-cyanopyridine ≫ 2-cyanopyridine. The basicity of 2-cyanopyridine is so low that it cannot be titrated with perchloric acid. The latter situation can be attributed to the steric problem of placing the acetic acid solvated proton adjacent to the nitrile group. Brown[17] has shown that steric effects are marked in *ortho*-substituted pyridines and the extent of the effects depends on the size of the acid group. The difference in basicity between 4- and 3-cyanopyridine is due to the lower electron density at the ring nitrogen in 3-cyanopyridine than in 4-cyanopyridine because of the greater electron withdrawal effect of the nitrile group in the 3- position than in the 4- position.

Acknowledgment.—We wish to acknowledge the generous support of the Directorate of Chemical Sciences, Air Force Office of Scientific Research (AFOSR Grant 220-63), the University of Kansas (General Research Fund), and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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Polarography and Oxidation–Reduction Reactions of the Chromium(II) and Chromium(III) Complexes of 2,2′-Bipyridine

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Received June 15, 1964

Tris(2,2′-bipyridine)chromium(III) is reduced reversibly in a one-electron reduction to $Cr(bipy)_3^{2+}$ at the dropping mercury electrode at −0.49 v. A second wave at −0.72 v. is attributed to the reversible one-electron reduction of $Cr(bipy)_2(H_2O)_2^{3+}$ formed at the electrode surface from $Cr(bipy)_3^{3+}$, the dissociation of which is catalyzed by $Cr(bipy)_3^{2+}$ formed at −0.49 v. The rate law for the homogeneous catalytic dissociation of $Cr(bipy)_3^{3+}$ in the presence of $Cr(bipy)_3^{2+}$ is $d[Cr(bipy)_3^{3+}]/dt = -k_1[Cr(bipy)_3^{2+}]$, where k_1 is the rate of dissociation of $Cr(bipy)_3^{2+}$ with a value of 0.38 sec.$^{-1}$ at 25° and an activation energy of 22.6 kcal. Chemical oxidation of $Cr(bipy)_3^{2+}$ by $Co(bipy)_3^{3+}$, I_2, and O_2 produces $Cr(bipy)_2(H_2O)_2^{3+}$ in a reaction that may proceed first to $Cr(bipy)_3^{3+}$ which is catalytically dissociated to the diaquo species in the presence of unreacted $Cr(bipy)_3^{2+}$.

Introduction

There have been conflicting reports in the literature regarding the mechanism of the oxidation of the tris(2,2′-bipyridine)chromium(II) ion and the nature of the chromium(III) products. Zwickel and Taube[2] determined the successive formation constants for the

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[2] A. M. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**, 42 (1960).