CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, SANTA BARBARA, CALIFORNIA 93106

Benzonitrile and Acetonitrile Complexes of Ruthenium Ammines[1,2]

BY RICHARD E. CLARKE AND PETER C. FORD

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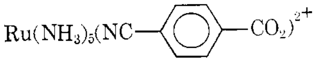
The syntheses and spectral properties of the pentaammineruthenium(II) and pentaammineruthenium(III) complexes of several substituted benzonitriles, acetonitrile, and trideuterioacetonitrile are described. The ruthenium(II) species, which are analogs of the molecular nitrogen complex $Ru(NH_3)_5N_2^{2+}$, are the only cationic metal complexes known in which the nitrile stretching frequency of a coordinated monodentate organonitrile shows a decrease from the free ligand value. This result is interpreted in terms of the unusually strong π-back-bonding ability of the pentaammineruthenium(II) species. The corresponding ruthenium(III) complexes show the increase in the CN stretching frequency "typical" for coordinated organonitriles. The linkage isomers of the 4-cyanobenzoatopentaammineruthenium(III) ion



are reported as the respective products of different specific synthetic routes. The isomers *cis*- and *trans*-tetraamminebis(benzonitrile)ruthenium(II), $Ru(NH_3)_4(C_6H_5CN)_2^{2+}$, are also described.

Introduction

The discoveries of pentaammine- and tetraammineruthenium(II) complexes of molecular nitrogen[3] stimulated our interest in corresponding organonitrile compounds. An analogy can be drawn between :N≡N: and :N≡CR in that the coordination site is a nitrogen atom attached to the balance of the uncharged ligand by a triple bond. Consequently, RCN complexes are potential models for N_2 species coordinated *via* a linear metal–N–N linkage. Comparison of the chemical and spectral properties of these models with those properties of RCN complexes where N_2 compounds are unknown and presumably unstable, *e.g.*, pentaammineruthenium(III), should enhance our understanding of special conditions leading to the stability of an N_2–metal bond.

Complexes between organic nitriles and metal moieties in both zero[4] and positive[5] oxidation states are well known. With very few exceptions, the coordinate bond consists of the linear array of the metal, nitrogen, and carbon atoms MN≡CR.[5a] Infrared spectra of complexes of this type consistently show an increase in the C≡N stretching frequency [ν(CN)]. In a preliminary communication,[2] we reported that coordination to pentaammineruthenium(II) led to an atypical but substantial decrease in the ν(CN) of coordinated benzonitriles and interpreted this effect in terms of the unusually strong π-back-bonding ability of the $Ru(NH_3)_5^{2+}$ moiety. In this article, we describe more completely spectral and chemical properties of these and other pentaammineruthenium(II)- and ruthenium(III)–benzonitrile complexes and of the corresponding acetonitrile complexes. Also reported are the syntheses and properties of *cis*- and *trans*-$[Ru(NH_3)_4(C_6H_5CN)_2]X_2$ which are analogs of the recently reported dinitrogen species $[Ru(NH_3)_4(N_2)_2]Br_2$[3c] and [*cis*-$Ru(en)_2(N_2)_2][B(C_6H_5)_4]_2$.[3b]

Experimental Section

Reagents.—Pentafluorobenzonitrile was purchased from the Imperial Smelting Corp., trideuterioacetonitrile (99.5% D) was purchased from Stohler Isotope Chemicals, and all other nitriles were purchased from either the Aldrich Chemical Co. or Matheson Coleman and Bell. The organonitriles were used without further purification unless discolored in which cases the solid nitriles were recrystallized from ethanol and liquid nitriles were distilled. Chloropentaammineruthenium(III) chloride, $[Ru(NH_3)_5Cl]Cl_2$, was prepared by the method of Allen, *et al.*,[6] from ruthenium trichloride (Engelhard Industries). The isomers *cis*- and *trans*-dichlorotetraammineruthenium(III) chloride, $[Ru(NH_3)_4Cl_2]Cl$, were prepared from $[Ru(NH_3)_5Cl]Cl_2$ by the methods of Gleu and Breuel.[7] Hydroxopentaammineruthenium(III) dithionate $[Ru(NH_3)_5OH][S_2O_6]$ was prepared from $[Ru(NH_3)_5Cl]Cl_2$ using the procedure of Gleu and Cuntze.[8]

Syntheses.—Pentaammine(organonitrile)ruthenium(II) and -(III) species were prepared from chloropentaammineruthenium(III) chloride and *cis*- and *trans*-tetraamminebis(organonitrile)ruthenium(II) species were prepared from the corresponding dichlorotetraammineruthenium(III) chlorides by procedures very similar to those used to prepare the analogous pyridine complexes.[9,10] The general methods given for the pentaamminebenzonitrile complexes (below) were applicable to all of the complexes.

$[Ru(NH_3)_5C_6H_5CN][ClO_4]_2$.—$[Ru(NH_3)_5Cl]Cl_2$ (0.10 g, 0.35 mmol) was digested in 2 ml of silver trifluoroacetate solution (made by dissolving Ag_2O (0.06 g, 0.26 mmol) in sufficient aqueous trifluoroacetic acid). The resulting solution was filtered to remove silver chloride, and benzonitrile (0.3 g, 2.9 mmol), methanol (0.5 ml, to improve ligand solubility), and granular zinc amalgam (0.5 g) were added. After stirring the mixture for 30 min at room temperature, the solution was filtered and then extracted with chloroform to remove the excess ligand.

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[1] Taken in part from the M.A. dissertation of R. E. C. Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969. A portion of this work has been reported in a preliminary communication.[2]

[2] P. C. Ford and R. E. Clarke, *Chem. Commun.*, 1109 (1968).

[3] (a) A. D. Allen and C. V. Senoff, *ibid.*, 621 (1965); (b) L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **90**, 5295 (1968); (c) J. E. Fergusson and J. L. Love, *Chem. Commun.*, 399 (1969).

[4] B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, **2**, 1023 (1963).

[5] (a) R. A. Walton, *Quart. Rev.* (London), **19**, 126 (1965); (b) R. Ugo, F. Bonati, and M. Fiore, *Inorg. Chim. Acta*, **2**, 463 (1968).

[6] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Am. Chem. Soc.*, **89**, 5595 (1967).

[7] K. Gleu and W. Breuel, *Z. Anorg. Allgem. Chem.*, **237**, 197 (1938).

[8] K. Gleu and W. Cuntze, *ibid.*, **237**, 187 (1938).

[9] P. Ford, D. F. P. Rudd, R. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).

[10] P. C. Ford and C. Sutton, *Inorg. Chem.*, **8**, 1544 (1969).

TABLE I

ELEMENTAL COMPOSITION MICROANALYSIS RESULTS

Compd	% calcd				% found			
	C	H	N	X	C	H	N	X
$[Ru(NH_3)_5(CH_3CN)][BF_4]_2$	5.99	4.53	20.96		5.69	4.65	20.64	
$[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_2$	17.22	4.13	17.21		17.41	4.37	16.77	
$[Ru(NH_3)_5(4\text{-}ClC_6H_4CN)]Br_2$	17.38	3.97	17.38		17.78	4.04	17.60	
$[Ru(NH_3)_5(4\text{-}CH_3OC_6H_4CN)][BF_4]_2$	19.49	4.51	17.05		20.31	4.74	16.57	
cis-$[Ru(NH_3)_4(C_6H_5CN)_2][ZnBr_4]$	22.11	2.91	11.05	42.03 Br	22.79	3.18	11.05	41.31 Br
$[Ru(NH_3)_5(CH_3CN)][ClO_4]_3$	4.57	3.46	15.99		4.61	3.69	15.37	
$[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_3$	14.31	3.43	14.30		14.82	3.79	14.41	
$[Ru(NH_3)_5(4\text{-}CH_3C_6H_4CN)]Br_3$	17.68	4.09	15.48	44.14 Br	16.87	4.20	14.40	43.54 Br
$[Ru(NH_3)_5(4\text{-}CH_3OC_6H_4CN)][ClO_4]_3$	15.55	3.60	13.61		15.62	3.90	13.07	

TABLE II

INFRARED ABSORPTION BANDS[a] FOR $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_2$ AND $Ru(NH_3)_5(C_6H_5CN)][ClO_4]_3$ (CM^{-1})

$[Ru(NH_3)_5\text{-}(C_6H_5CN)][ClO_4]_2$	$[Ru(NH_3)_5\text{-}(C_6H_5CN)][ClO_4]_3$	Assignment
3450 m, br, sh	3430 s, vbr	N–H str[b]
3285 s		
3225 s	3300–3050 s, vbr	
3160 s		
3045 w		C–H str
2188 vs	2267 m	C–N str
1623 s, br	1625 s, br	NH_3 degen def
1592 w, sh	1593 s, sh	C–C str (phenyl ring)
1485 m	1485 w	
1445 m	1445 m	
1382 m	1400 w, br	
1256 s	1315 s	NH_3 sym def
1235 m, sh		
1140, 1115, 1085 vs	1140, 1115, 1085 vs	ClO_4^-
940 m	939 m	C–H out-of-plane def
776 s	820 s, vbr	NH_3 rocking mode
752 s	758 s	C–H out-of-plane def
688 m	682 s	Phenyl ring out-of-plane def
636, 629, 625 vs	636, 629, 626 vs	ClO_4^-
522 s	548 s	Phenyl ring out-of-plane def
	464 m, br	Ru–NH_3 str
415 w, br		
345 w, br		
284 w	283 w[c]	
271 m	274 m[c]	
252 w	242 m[c]	
241 m		

[a] KBr pellet except where noted. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad. [b] Also possible O–H stretch from water(s) of hydration. [c] Hydrocarbon mull, polyethylene plates.

The yellow ruthenium(II) perchlorate salt precipitated on addition of saturated sodium perchlorate solution. This product was recrystallized from hot water giving an over-all yield of 0.092 g, 0.19 mmol (55%).

$[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_3$.—The procedure was identical with that used to prepare the Ru(II) complex with the exception that, after chloroform extraction to remove excess ligand, silver trifluoroacetate solution (made by dissolving Ag_2O (0.10 g, 0.43 mmol) in sufficient aqueous trifluoroacetic acid) was stirred into the reaction solution. The mixture was filtered to remove metallic silver, chloride was added to precipitate excess Ag(I), and the new mixture was filtered again. The light yellow ruthenium(III) perchlorate salt precipitated on addition of saturated sodium perchlorate solution, and recrystallization from hot water gave an over-all yield of 0.085 g, 0.15 mmol (41%).

$[Ru(NH_3)_5(4\text{-}O_2CC_6H_4CN)][S_2O_6]$.—A mixture of $[Ru(NH_3)_5OH][S_2O_6]$ (0.135 g, 0.37 mmol), 4-cyanobenzoic acid (0.10 g, 0.68 mmol), and water (5 ml) was heated at 80° with stirring for about 2 hr. The resulting orange slurry was cooled, and the solid was collected by filtration. This material was washed successively with cold ethanol and ether and then recrystallized from slightly acidic hot water (pH 4) to which had been added a small amount of sodium dithionate. The result was a brownish orange crystalline solid; yield, 0.14 g, 0.29 mmol (77%).

Analyses.—The compositions of a number of the complexes synthesized were checked by elemental analysis (Elek Microanalytical Laboratories, Torrance, Calif.). Several of these were somewhat poor, although consistent with the molecular formula. The instability of some of the complexes to recrystallization conditions (see Results) is undoubtedly a factor. These results are reported in Table I.

Spectra.—All spectra in the visible and ultraviolet regions were obtained with a Cary Model 14 or a Cary Model 15 recording spectrophotometer. All spectra were taken at room temperature as dilute solutions in redistilled water. Solutions for extinction coefficient measurements were prepared gravimetrically followed by quantitative serial dilutions to give appropriate concentrations. In all cases reported, extinction coefficient values were determined from duplicate solutions and found to be reproducible within 3%.

Infrared spectra were obtained with a Perkin-Elmer Model 225 recording spectrophotometer. The frequencies of absorption maxima were determined either by direct reading of the spectrometer frequency scale during a very slow scan or by measuring from calibrated paper used with the spectrometer in an expanded-scale mode. With sharp peaks, these values were reproducible to within ±1 cm^{-1}. Spectra of solids were taken either as KBr pellets or as Nujol or perfluorokerosene mulls. Spectra of nonaqueous liquids were taken in sodium chloride solution cells while spectra of aqueous solutions were taken in Irtran solution cells.

Results

Reaction of a substituted benzonitrile or acetonitrile with aquopentaammineruthenium(II) (eq 1) in aqueous solution gives the corresponding pentaammine (organonitrile) ruthenium(II) ion which can be isolated as an air-stable salt. The benzonitrile species, $Ru(NH_3)_5(C_6H_5CN)^{2+}$, is quite unreactive toward aquation. In deaerated 10^{-3} *M* aqueous HCl, the concentration of $Ru(NH_3)_5(C_6H_5CN)^{2+}$, initially 10^{-4} *M*, decreased less than 4% over 96 hr in the dark. White light irradiation, however, led to rapid decomposition to unidentified products. Air slowly oxidizes aqueous $Ru(NH_3)_5(C_6H_5CN)^{2+}$ to a species identified from its visible–uv spectrum as $Ru(NH_3)_5(C_6H_5CN)^{3+}$.

$$Ru(NH_3)_5H_2O^{2+} + RCN \longrightarrow Ru(NH_3)_5(RCN)^{2+} + H_2O \quad (1)$$

Oxidation of aqueous $Ru(NH_3)_5(C_6H_5CN)^{2+}$ with

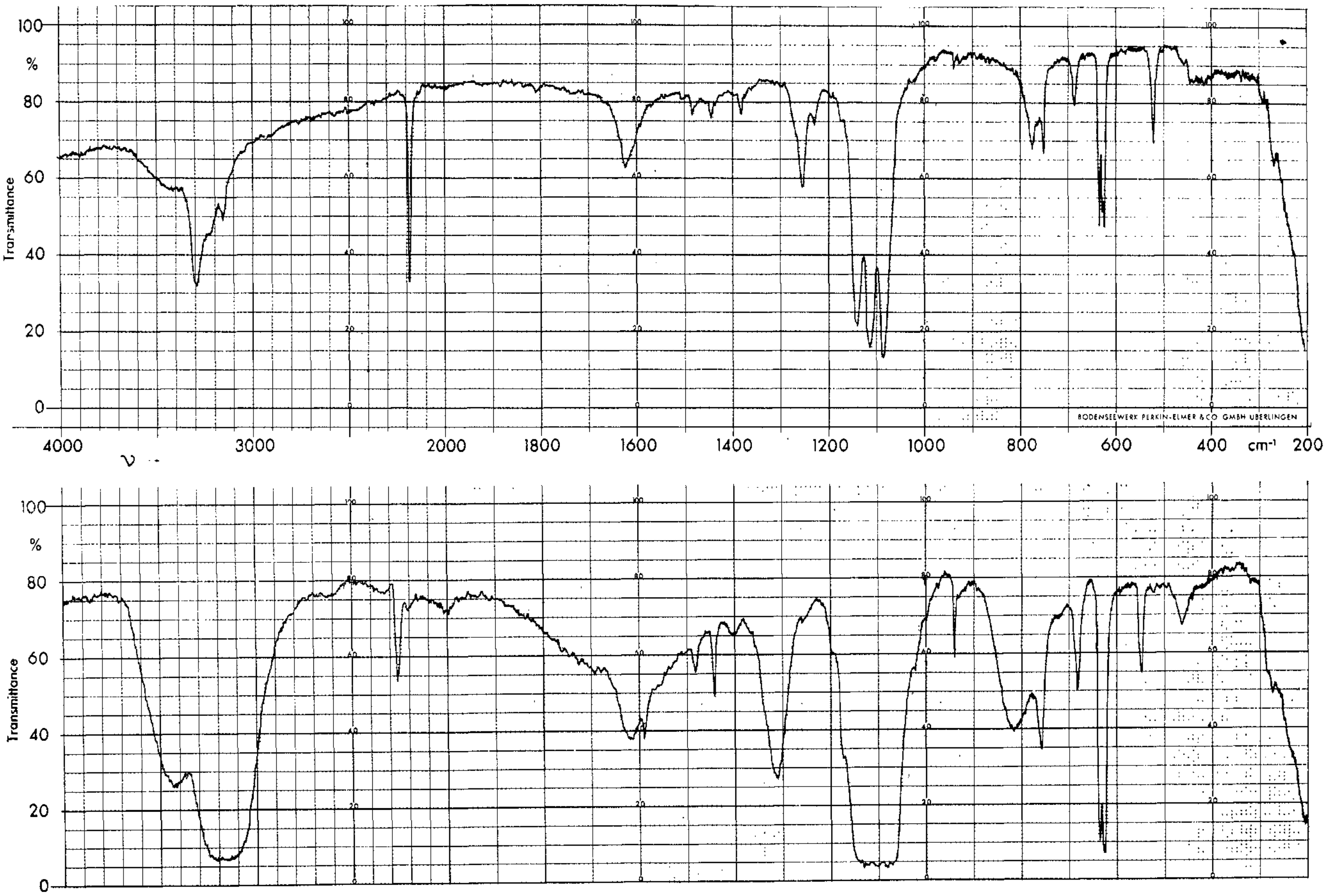

Figure 1.—Infrared spectra of $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_2$ (upper) and $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_3$ (lower); KBr pellets.

either Ag(I) or Ce(IV) gives $Ru(NH_3)_5(C_6H_5CN)^{3+}$ also isolable as a variety of salts. The Ru(III) complexes of acetonitrile and a variety of benzonitriles were synthesized in this manner. The pentaammineruthenium(III) complexes of benzonitrile and of acetonitrile could be recrystallized from hot aqueous solution, but complexes of benzonitriles substituted with electron-withdrawing groups underwent partial decomposition to aquopentaammineruthenium(III) on attempted recrystallization. Oxidation of the Ru(II) complex of either perfluorobenzonitrile or 1,4-dicyanobenzene gave decomposition products.

The ions *cis*- or *trans*-$Ru(NH_3)_4(C_6H_5CN)_2^{2+}$ were synthesized by reaction of excess benzonitrile with the appropriate diaquo ion, $Ru(NH_3)_4(H_2O)_2^{2+}$. The similar reaction with pyridine has previously been shown to be stereospecific.[10] Both bis(benzonitrile) complexes are less stable toward aquation than $Ru(NH_3)_5(C_6H_5CN)^{2+}$, the *cis* isomer being more stable than the *trans*, which cannot be recrystallized without partial decomposition to a mononitrile species (see below). Oxidation with Ag(I) or Ce(IV) gave unidentified products.

Infrared Spectra.—The ir spectra of $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_2$ and $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_3$ (Figures 1 and 2) are typical for the pentaammineruthenium complexes synthesized with other substituted benzonitriles. Recognizable absorption bands are summarized in Table II.

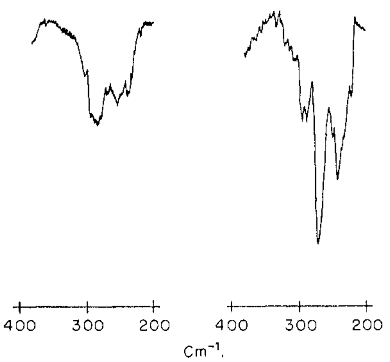

Figure 2.—Far-infrared spectra of $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_3$ (left) and $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_2$ (right); Nujol mulls, polyethylene plates.

The assignments are based on comparison with the spectra of other ruthenium(II) and -(III) ammines,[11a] of free benzonitrile,[11b] and of sodium perchlorate. The NH_3 symmetrical deformation and rocking modes both occur at higher frequency for $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_3$ than for the Ru(II) salt, an observation consistent with the position of these bands in the ruthenium(II) and -(III) hexaammine spectra.[11a] The ir spectrum of each salt has several fairly strong bands in the 500–200-cm^{-1} region. The $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_3$ band at 464 cm^{-1} is assigned to the ruthenium-

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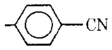
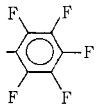
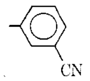
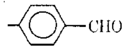
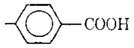
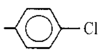
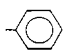
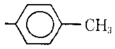
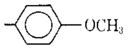
[11] (a) A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337 (1967); (b) J. H. S. Green, *Spectrochim. Acta*, **17**, 607 (1961).

Table III

C≡N Stretching Frequencies, ν(CN), in Cm^{-1}, for Pentaammineruthenium(II) Complexes of Organonitriles, $[Ru(NH_3)_5(RCN)]X_2$^{a}

-R	X	Free	Coordinated	σ^b	$\Delta\nu$(CN)^c
	Br	2232	2186 s	0.660	−46
	BF_4		2182 s		−50
	ClO_4		2183 s		−49
	Br	2246	2189 s	. . .	−57
	ClO_4	2234	2231 m	0.56	−3
			2189 s		−45
	ClO_4	2229	2177 s	>0.5	−52
	Br	2231	2172 s	0.406	−59
	Br	2227	2192 s	0.227	−35
	Br	2231^d	2194 s	0	−37
	BF_4		2194 s		−37
	ClO_4		2188 s		−43
	Br	2230^e	2198 s	−0.170	−32
			2199 m^f		−31
	BF_4	2217	2194 s	−0.268	−23
$-CH_3$	BF_4	2254^d	2239 s	. . .	−15
$-CD_3$	BF_4	2263^d	2244 s	. . .	−19

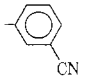
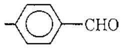
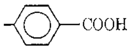
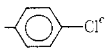
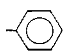
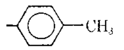
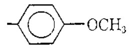
^{a} All spectra taken as KBr pellets unless noted. ^{b} Hammett substituent constant for benzonitrile substituents: K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, p 281. ^{c} Change in ν(CN) on coordination. ^{d} Neat. ^{e} In $CHCl_3$ solution. ^{f} In aqueous solution, Irtran liquid cell.

(III)–ammonia nitrogen stretching frequency. Values for $\nu(M{-}NH_3)$ of 474 w, 464 w, and 452 w cm^{-1} have been reported for $[Ru(NH_3)_6]Cl_3$.[11a] For $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_2$, one of the broad and weak absorptions at 415 or 345 cm^{-1} may represent $\nu(Ru{-}NH_3)$, either value being comparable to frequencies reported for $[Ru(NH_3)_5N_2]X_2$[6] or $[Ru(NH_3)_6]Cl_2$.[12] The spectra in the 200–300-cm^{-1} region (Figure 2) of both Ru(II) and Ru(III) species are quite similar and no absorption corresponding to the ruthenium–nitrile nitrogen stretch can be unequivocally identified. Frequencies in this region have been attributed to N–Ru–N bending modes for the complex $[Ru(NH_3)_5NO]Cl_3$.[13] We have determined that the spectrum of $[Ru(NH_3)_6]Cl_3$ also displays medium bands at 283, 260, and 225 cm^{-1} suggesting that at least most of the comparable bands in the nitrile complexes are probably N–Ru–N bending modes.

A prominent feature of the benzonitrile ir spectrum is the intense band at 2231 cm^{-1} assignable to ν(CN). Coordination to the $Ru(NH_3)_5{}^{2+}$ moiety shifts ν(CN) to lower frequency, 2188 cm^{-1}, while coordination to the $Ru(NH_3)_5{}^{3+}$ results in an increased ν(CN), 2267 cm^{-1}.

Table IV

C≡N Stretching Frequencies, ν(CN), in Cm^{-1}, for Pentaammineruthenium(III) Complexes of Organonitriles, $[Ru(NH_3)_5(RCN)]X_3$^{a}

-R	X	Free	Coordinated	$\Delta\nu$(CN)
	ClO_4	2234	2270 w	36
			2233 w	
	ClO_4	2229	2265 s, w	36
^{e}	Br	2231	2275 m	44
^{c}	ClO_4	2227	2267 sh	40
			2263 m	36
	ClO_4	2231^c	2267 s	36
	Br		2268 m	37
	BF_4		2272 m	41
	Br	2230^b	2261 s	31
			2263 w^d	33
	ClO_4	2217	2260 s	43
$-CH_3$	ClO_4	2254^c	2286 m	32
$-CD_3$	ClO_4	2263^c	2301 m	38

^{a} All spectra taken in KBr pellets unless noted. ^{b} In $CHCl_3$ solution. ^{c} Neat. ^{d} In aqueous solution, Irtran liquid cell. ^{e} Unrecrystallized product.

This pattern of frequency shifts is repeated over the entire series of substituted benzonitrile complexes (Tables III and IV) and is independent of either the identity of the anion of the salt (Tables III–V) or the spectrum medium (Table IV). The data presented in Table V show that for a particular complex both the anion and the spectral medium affect the absolute value of ν(CN) and consequently $\Delta\nu$(CN), the difference between the CN frequency of the coordinated ligand and that of the free ligand. The magnitude of these medium effects is comparable to differences in $\Delta\nu$(CN) observed between the various Ru(III) complexes, hence negating the significance of any small trends observable. In contrast, the $\Delta\nu$(CN) differences between the various substituted benzonitrile–ruthenium(II) complexes are large enough to show a definite trend toward more negative $\Delta\nu$(CN)'s with the more electron-withdrawing substituents.

Table V

Effect of Anion and of Spectral Medium on ν(CN) Measured for $[Ru(NH_3)_5(4\text{-}ClC_6H_4CN)]X_2$, in Cm^{-1}

X	Color	KBr pellet	H_2O soln	Halocarbon mull
Br	Yellow	2192	2194	2194
Cl	Light orange	2194		2196
BF_4	Light yellow	2188		2206
$^1/_2S_2O_6$	Dark orange	2188		2192

The spectra of the Ru(II) and the Ru(III) complexes of 1,3-dicyanobenzene both display two bands in the nitrile region (Tables III and IV). In each case, one band is shifted only slightly from the free-ligand frequency while the other occurs at lower frequency for the Ru(II) complex [$\Delta\nu$(CN) = −45 cm^{-1}] and at higher frequency for the Ru(III) complex [$\Delta\nu$(CN) =

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(12) M. B. Fairey and R. J. Irving, *Spectrochim. Acta*, **22**, 359 (1966).

(13) E. E. Mercer, W. A. McAllister, and J. R. Durig, *Inorg. Chem.*, **5**, 1881 (1966).

+36 cm^{-1}]. Presumably, it is the coordinated nitrile whose frequency is shifted from the free-ligand value while the remote (*i.e.*, uncoordinated) nitrile is little affected. In contrast to the 1,3-dicyanobenzene complexes, the 1,4-dicyanobenzeneruthenium(II) complex displays only a single nitrile band substantially shifted [$\Delta\nu$(CN) = −50 cm^{-1}] from the free-ligand value. Attempts to prepare isolable salts of the corresponding Ru(III) complex were unsuccessful.

The nitrile frequency shifts on Ru(II) or Ru(III) coordination are also observed for the acetonitrile complexes (Tables III and IV), although the band assignments are more ambiguous. The ir spectrum of free acetonitrile[14] has a doublet in the nitrile region, ν(CN) occurring at 2254 cm^{-1} and a combination band occurring at 2290 cm^{-1} which derives its intensity from proximity to ν(CN). In the Ru(II) complex [Ru(NH$_3$)$_5$(CH$_3$CN)][BF$_4$]$_2$ only a single, very intense nitrile-region band is observed (2239 cm^{-1}). The combination band is no longer evident either because of an accidental coincidence with ν(CN) or perhaps because the lowering of the CN frequency decreased the intensity enhancement of what would normally be a weak band. In acetonitrile, the combination band derives from δ(CH$_3$) at 1374 cm^{-1} (symmetrical CH$_3$ deformation) and ν(CC) at 919 cm^{-1} (C–C stretch).[14] In the Ru(II) complex, no absorption band is observed at 1375 ± 50 cm^{-1}, although a band at 955 cm^{-1}, probably ν(CC), is evident. If the latter assignment is correct, accidental coincidence of the combination band with ν(CN) would require a δ(CH$_3$) value of about 1300 cm^{-1} which does correspond approximately to an unassigned band in the spectrum (1290 cm^{-1}). However, a very similar band is observed in the spectrum of [Ru(NH$_3$)$_5$(CD$_3$CN)][BF$_4$]$_2$ which should have a significantly different value for δ(CD$_3$).[14]

The ir spectrum of the ruthenium(III)–acetonitrile complex [Ru(NH$_3$)$_5$(CH$_3$CN)][ClO$_4$]$_3$ does display two medium bands in the nitrile region, 2286 and 2313 cm^{-1}, as well as bands corresponding to δ(CH$_3$) at 1362 cm^{-1} and to ν(CC) at 941 cm^{-1}, the sum of which equals 2303 cm^{-1}. Previous workers[15] have noted that in Lewis acid–acetonitrile complexes the combination band frequency is often 5–10 cm^{-1} higher than the sum of the two component frequencies. Consequently, it is reasonable to assign the 2313-cm^{-1} band as the combination and the 2286-cm^{-1} band as ν(CN). To substantiate this conclusion, the perdeuterioacetonitrile complex [Ru(NH$_3$)$_5$(CD$_3$CN)][ClO$_4$]$_3$ was made. In this case, a single band at 2301 cm^{-1}, unequivocally ν(CN), is observed. Since free CD$_3$CN has a single nitrile region absorption at 2263 cm^{-1}, $\Delta\nu$(CN) for the Ru(III) complex is +38 cm^{-1}. The shift of the lower frequency and more intense nitrile-region band in the ir spectrum of [Ru(NH$_3$)$_5$(CH$_3$CN)][ClO$_4$]$_3$, $\Delta\nu$(CN) = +32 cm^{-1}, is the more consistent with $\Delta\nu$(CN) observed for the perdeuterioacetonitrile complex. The ir spectrum of the ruthenium(II)–perdeuterioacetonitrile complex [Ru(NH$_3$)$_5$(CD$_3$CN)][BF$_4$]$_2$ displays two bands in the nitrile region. The more intense band at 2244 cm^{-1} is assigned to ν(CN) since it it shifted only −19 cm^{-1} from the free-ligand ν(CN) compared with $\Delta\nu$(CN) = −15 cm^{-1} for the ruthenium(II)–acetonitrile complex. The less intense absorption at 2215 cm^{-1} may be the asymmetric C–D stretching frequency which is coincident with ν(CN) in the liquid spectrum of CD$_3$CN.[14] There are no obvious combinations in the spectrum of [Ru(NH$_3$)$_5$(CD$_3$CN)][BF$_4$]$_2$ leading to this frequency, although such a combination would be expected to gain intensity from proximity to the nitrile absorption. The far-infrared spectra of the CH$_3$CN- and CD$_3$CN–Ru(II) and –Ru(III) complexes are quite similar to those of the corresponding benzonitrile complexes.

TABLE VI

ν(CN) FOR TETRAAMMINEBIS(ORGANONITRILE)RUTHENIUM(II) COMPLEXES, IN CM^{-1}

Compound	ν(CN)	$\Delta\nu$(CN)
[*cis*-Ru(NH$_3$)$_4$(C$_6$H$_5$CN)$_2$][ZnBr$_4$]	2232 s	+1
	2219 vs	−12
[*cis*-Ru(NH$_3$)$_4$(C$_6$F$_5$CN)$_2$][B(C$_6$H$_5$)$_4$]$_2$	2231 s	−15
	2210 vs	−36
[*trans*-Ru(NH$_3$)$_4$(C$_6$H$_5$CN)$_2$][ClO$_4$]$_2$	2213 vs	−18

The tetraammineruthenium(II) complex salts [*cis*-Ru(NH$_3$)$_4$(C$_6$H$_5$CN)$_2$][ZnBr$_4$] and [*trans*-Ru(NH$_3$)$_4$(C$_6$H$_5$CN)$_2$][ClO$_4$]$_2$ were synthesized, respectively, from [*cis*-Ru(NH$_3$)$_4$Cl$_2$]Cl and from [*trans*-Ru(NH$_3$)$_4$Cl$_2$]Cl. The ir spectrum of the *cis* complex displays a doublet (2232 and 2219 cm^{-1}) in the nitrile region, the less intense band shifted little from the free-ligand frequency and the stronger band shifted −15 cm^{-1}. Both bands occur at higher frequency than that observed for the mononitrile complex [Ru(NH$_3$)$_5$(C$_6$H$_5$CN)][ClO$_4$]$_2$ (2188 cm^{-1}). A similar spectrum pattern is observed for the *cis*-bis(pentafluorobenzonitrile) complex (Table VI). In contrast to the *cis* complexes, [*trans*-Ru(NH$_3$)$_4$(C$_6$H$_5$CN)$_2$][ClO$_4$]$_2$ has a single sharp band in the nitrile region (2213 cm^{-1}). This absorption occurs at higher frequency than ν(CN) of [Ru(NH$_3$)$_5$(C$_6$H$_5$CN)][ClO$_4$]$_2$ but is slightly lower than either band in the *cis*-bis(benzonitrile) complex. (See Figure 3.) The *trans*-

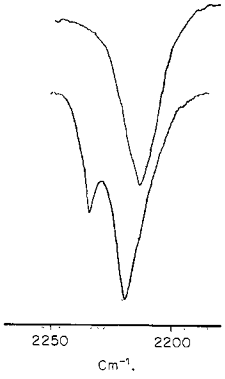

Figure 3.—Nitrile stretching bands for [*trans*-Ru(NH$_3$)$_4$(C$_6$H$_5$CN)$_2$][ClO$_4$]$_2$ (upper) and for [*cis*-Ru(NH$_3$)$_4$(C$_6$H$_5$CN)$_2$][ZnBr$_4$] (lower).

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(14) E. L. Pace and L. J. Noe, *J. Chem. Phys.*, **49**, 5317 (1968).

(15) J. Reedijk, A. P. Zuur, and W. L. Groeneveld, *Rec. Trav. Chim.*, **86**, 1127 (1967).

TABLE VII

VISIBLE–UV SPECTRA OF BENZONITRILE AND ACETONITRILE COMPLEXES[a]

Complex	Absorption maxima, nm (log ϵ_{max})
$Ru(NH_3)_5(C_6H_5CN)^{2+}$	376 (3.93), 347 sh (3.84), 249 (4.21), 226 (4.17)
cis-$Ru(NH_3)_4(C_6H_5CN)_2{}^{2+}$	344 (4.03), 226 (4.40)
trans-$Ru(NH_3)_4(C_6H_5CN)_2{}^{2+}$	362,[b] ~340 sh, ~240 sh, 231
$Ru(NH_3)_5(C_6H_5CN)^{3+}$	391 br (3.11), 312 (3.38), 283 sh (3.46), 246 (3.99), 230 (4.06)
$Ru(NH_3)_5(CH_3CN)^{2+}$	350 br (2.40), 229 (4.19)
$Ru(NH_3)_5(CH_3CN)^{3+}$	380 br (2.13), 295 br (2.76), 224 sh (2.97)

[a] Dilute solutions in H_2O, pH ~5. [b] Extinction coefficients not measured due to instability of compound; ratio of peak heights: 231 nm/362 nm = 1.33.

bis(benzonitrile) complex proved much less stable than the *cis*. Recrystallization of the *trans* under mild conditions (35°, aqueous methanol) gave a new complex having $\nu(CN) = 2185\ cm^{-1}$. This value is suggestive of a mononitrile such as *trans*-$Ru(NH_3)_4(H_2O)(C_6H_5CN)^{2+}$, a logical decomposition product. Under identical conditions, the *cis*-bis(benzonitrile) complex could be recrystallized in high yield.

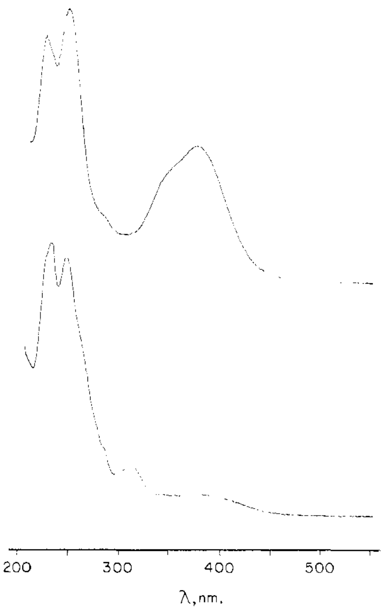

Figure 4.—Uv–visible spectra of $Ru(NH_3)_5(C_6H_5CN)^{2+}$ (upper, 5.6×10^{-5} *M*) and of $Ru(NH_3)_5(C_6H_5CN)^{3+}$ (lower, 8.0×10^{-5} *M*) in aqueous solution.

TABLE VIII

EFFECT OF SUBSTITUENTS ON THE POSITION OF THE LOW-ENERGY ABSORPTION BAND IN PENTAAMMINE-(SUBSTITUTED BENZONITRILE)RUTHENIUM(II) COMPLEXES

Substituent	σ^a	$\lambda_{max}{}^b$ (log ϵ)
4-CN	0.66	462
4-CHO	>0.5	446 (3.92)
4-CO_2H	0.406	428 (3.91)
Perfluoro	...	406 (3.78)
3-CN	0.56	403 (4.09)
4-CO_2	0.00	403 (3.94)
4-Cl	0.227	380 (3.91), 350 sh (3.83)
H	0.00	376 (3.93), 347 sh (3.84)
4-CH_3	−0.170	367 (3.86), 347 sh (3.83)
4-CH_3O	−0.268	365 sh (3.98), 344 sh (4.01)

[a] Hammett substituent constant: K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, p 281. [b] In nanometers.

Uv–Visible Spectra.—The electronic spectra of the ions $Ru(NH_3)_5(C_6H_5CN)^{2+}$ and $Ru(NH_3)_5(C_6H_5CN)^{3+}$ (Figure 4 and Table VII) are representative of the other substituted benzonitrile–pentaammine complexes. The longer wavelength absorption band(s) in the Ru(II) species is very responsive toward the nature of the phenyl ring substituents, the maxima varying from 462 nm for a *p*-cyano group to 365 nm (sh) and 344 nm for *p*-methoxy (Table VIII). The intensity of these bands (ϵ ~10^4) and the fact that the more electron-withdrawing groups, as estimated from the Hammett substituent constant σ, lead to longer wavelength maxima Table VIII) suggest a metal-to-ligand charge-transfer assignment. Intense metal-to-ligand charge-transfer bands showing similar sensitivity toward substituents have been observed with the pentaammineruthenium(II) complexes of substituted pyridines.[9] The electronic spectra of the tetraamminebis(benzonitrile)ruthenium(II) complex ions, *cis*- and *trans*-$Ru(NH_3)_4(C_6H_5CN)_2{}^{2+}$ (Table VII), are rather similar to that of $Ru(NH_3)_5(C_6H_5CN)^{2+}$. In both tetraammines, the visible-range charge-transfer absorption is shifted to higher energy.

The higher energy maxima occurring in the ultraviolet spectrum of $Ru(NH_3)_5(C_6H_5CN)^{2+}$ are paralleled by similar absorption bands in the spectrum of $Ru(NH_3)_5(C_6H_5CN)^{3+}$. Given that free benzonitrile also has absorption bands in this region which are of $\pi \rightarrow \pi^*$ origin (271 nm for the $^1A_{1g}$–$^1B_{2u}$ transition (log ϵ 3.00) and 224 nm for the $^1A_{1g}$–$^1B_{1u}$ transition (log ϵ 4.11)),[16] it is reasonable to suggest that the uv bands of the complexes are largely ligand in character with intensity and position perturbed somewhat by coordination.

The spectrum of $Ru(NH_3)_5(CH_3CN)^{2+}$ exhibits a broad absorption at ~350 nm and a much stronger one at 229 nm (Table VII). It is likely that the 350-nm band is a d–d transition as hexaammineruthenium(II) and -(III) spectra display ligand field absorptions in the range 275–400 nm of comparable intensity.[17,18] In contrast to the benzonitrile complexes, the strong 229-nm band of $Ru(NH_3)_5(CH_3CN)^{2+}$ is not paralleled by any features in the free-ligand spectrum, the longest wavelength absorptions in alkylnitriles occurring in the vacuum ultraviolet region (~170 nm).[19] The position and intensity of the 229-nm band are comparable to an absorption observed in the spectrum of $Ru(NH_3)_5N_2{}^{2+}$ (221 nm, log ϵ 4.12)[20] and it is conceivable that both are metal-to-ligand charge transfers.

Cyanobenzoic Acid and Cyanobenzoate Complexes.—Reaction of aquopentaammineruthenium(II) with 4-cyanobenzoic acid (see Experimental Section) gives an

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[16] H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, p 257.

[17] T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

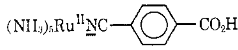
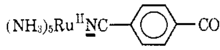
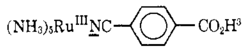
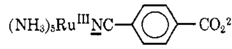
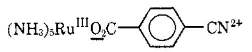
[18] H. H. Schmidtke and D. Garthoff, *Helv. Chim. Acta*, **49**, 2039 (1966).

[19] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 455.

[20] D. E. Harrison and H. Taube, *J. Am. Chem. Soc.*, **89**, 5706 (1967).

TABLE IX

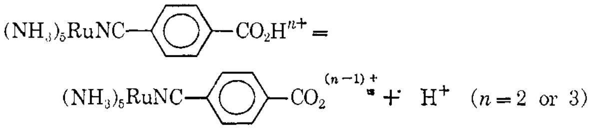
VISIBLE–UV SPECTRA OF 4-CYANOBENZOIC ACID AND 4-CYANOBENZOATE COMPLEX IONS

Complex ion[a]	λ_{max}[b] (log ϵ)
	428 (3.91), 242 (4.33)
	403 (3.94), 243 (4.29)
	380 br (3.38), 313 sh (3.43), 240 (4.15)
	394 (3.58), 325 (3.52), 238 (4.10)
	285 (3.76), 239 (4.28)

[a] Coordination site underlined. [b] In nanometers.

isolable Ru(II) complex displaying a visible–uv spectrum analogous to that of the benzonitrile complex. The positions of the absorption maxima are different at low pH from those at high pH indicating that an acid and a base form of the complex can exist in solution (Table IX). The ir spectrum shows ν(CN) decreased from the free-ligand value ($\Delta\nu$(CN) = 59 cm^{-1}, Table III) and a well-defined carbonyl absorption at 1708 cm^{-1}, consistent with an aryl carboxylic acid. Oxidation of the Ru(II) gives an isolable Ru(III) salt also having a pH-sensitive visible–uv spectrum. The ir spectrum of the Ru(III) species shows a positive $\Delta\nu$(CN) (+44 cm^{-1}, Table IV) and a carbonyl frequency of 1700 cm^{-1}. In the preliminary communication of this work,[2] a second nitrile-region band having a negative $\Delta\nu$(CN) was reported for the Ru(III) species. It has been found that a second, but weak, band having $\Delta\nu$(CN) $\approx$ −50 cm^{-1} occurs in occasional preparations of this complex; however, the exact position and intensity relative to the stronger nitrile absorption are not reproducible. Since ν(CN) is much more intense for the Ru(II) complex than for the Ru(III) species, it is probable that the weak, second band represents trace impurities of Ru(II). On the basis of the observed ν(CN) shifts and the carbonyl frequencies, we conclude that these two complexes are both nitrile coordinated rather than the possible alternative carboxylate coordinated isomers.

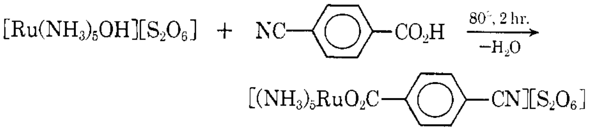
The differences in the visible–uv spectra (Table IV) of the acid and base forms potentially allow determination of the equilibrium constant for eq 2. The pK_a's determined in this manner were 3.5 ± 0.2 for n = 2 and



(2)

3.8 ± 0.5 for n = 3. These determinations were subject to large experimental uncertainty owing to the rather small differences in the spectra of the respective acid and base forms and to the instability of the Ru(III) species in basic media. The values so determined are perturbed only slightly from the pK_a of the free ligand, 3.57, the three values being indistinguishable within the limits of experimental uncertainty.

The reaction of 4-cyanobenzoic acid with hydroxopentaammineruthenium(III) dithionate (eq 3; see Experimental Section) leads to a new complex salt (A)

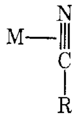


A (3)

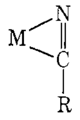
having a pH-insensitive visible–uv spectrum substantially different from either the acid or the base forms of the previously described ruthenium(III)–4-cyanobenzoic acid complex (Table IX). The ir spectrum of this salt displays a ν(CN), 2229 cm^{-1}, essentially unchanged from the free-ligand value, 2231 cm^{-1}, has no CO stretching band in the region of 1700 cm^{-1}, but does have a new band at 1550 cm^{-1} which could represent a coordinated carboxylate. On the basis of the spectral evidence, we conclude that A is carboxylate-coordinated 4-cyanobenzoatopentaammineruthenium(III) dithionate.

Discussion

The most dramatic effect of pentaammineruthenium(II) coordination on the properties of organonitriles is the ν(CN) decrease from the free-ligand frequencies. With very few exceptions, nitrile coordination to other metals results in ν(CN) increases[5a] in the manner observed with the pentaammineruthenium(III) complexes. The exceptions either involved ambidentule ligands coordinated at positions other than the nitrile or involve a π-complex configuration (B). Examples of



B



C

D

the former include various complexes of acrylonitrile which purportedly are coordinated *via* the double bond and show small negative shifts in ν(CN). The ir spectrum of the recently reported[21] $RuCl_2(P(C_6H_5)_3)_2(CH_2{=}CHCN)_2$ displays a CN frequency of 2215 cm^{-1}, about 13 cm^{-1} lower than that of free acrylonitrile. However, in this example, shifts in other characteristic ir frequencies and some nmr data were interpreted as suggesting coordination *via* the olefinic function. Similarly, a negative $\Delta\nu$(CN) (−14 cm^{-1}) was observed[4] for $W(CO)_3(CH_2{=}CHCN)_3$ although a positive $\Delta\nu$(CN) (+6 cm^{-1}) was found for the analogous acetonitrile species, $W(CO)_3(CH_3CN)_3$. Again, nmr data and shifts in other ir frequencies were used to assign an olefin-coordinated structure to the tris(acrylonitrile) complex. We have synthesized the pentaammineruthenium(II)- and pentaammineruthenium(III)-acryl-

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[21] A. Misono, Y. Uchida, M. Hidai, and I. Inomata, *Chem. Commun.*, 705 (1968).

onitrile derivatives but have concluded that the products are primarily the nitrile-coordinated isomers.[22] The spectra of some Ni(II), Pd(II), and Pt(II) complexes of the ambident 4-cyanopyridine also display small negative $\Delta\nu$(CN)'s.[23] In these cases it was argued that the ir spectra and especially the unusual decreased ν(CN) indicates coordination at the pyridine nitrogen. In agreement with this rationale is the observation that coordination of monodentate alkyl- and arylnitriles to the same metal centers results in large ν(CN) increases.[24]

The present work reports two $Ru(NH_3)_5{}^{3+}$ complexes having nitrile groups remote from the coordination site. Both the 1,3-dicyanobenzene [$\Delta\nu(CN) = +36$ cm^{-1}, $\Delta\nu(CN)' = -1$ cm^{-1}] and the carboxylate-coordinated 4-cyanobenzoate [$\Delta\nu(CN) = -2$ cm^{-1}] show very small decreases in ν(CN) for the remote nitrile, confirming the observation that coordination at another site can decrease the CN frequency of ligand nitrile.

The few characterized examples of nitrile π complexes[25] (B) show very large decreases in ν(CN). One of these involves the bidentate ligand succinonitrile[25d] which in the complex $Mn(CO)_3(NCCH_2CH_2CN)X$ [X = Cl, Br, or I, $\Delta\nu(CN) = -185$ cm^{-1}] must assume the π configuration (B) in order to coordinate both nitrile groups. Another purported organonitrile π complex is $Pt(CF_3CN)(P(C_6H_5)_3)_2$ which is the product from the reaction of bis(triphenylphosphine)platinum–*trans*-stilbene with excess trifluoroacetonitrile.[25b] The product has an intense ir absorption at 1734 cm^{-1} [$\Delta\nu(CN) = -535$ cm^{-1}] which is presumed to represent C=N in a structure such as C.

Despite the abnormal negative $\Delta\nu$(CN), we believe that the Ru(II) species reported in this article are of the more typical linear structure D as is the N_2 complex $[Ru(NH_3)_5N_2]Cl_2$.[26] The reasoning is based upon several considerations. First, the magnitudes of the ν(CN) negative shifts are markedly smaller than in the previous examples of π coordination. Second, examination of space filling models indicates some steric crowding in the B configuration of the octahedral ruthenium(II)–ammine complexes, especially the *cis*-bis(benzonitrile) species. Third, nearly all the Ru(II) species can be oxidized easily and reversibly with aqueous Ag(I) to form Ru(III) analogs whose spectra display the positive $\Delta\nu$(CN) normally expected for structure type D. While an oxidation-induced rearrangement from a B structure to a D structure is not inconceivable, the more consistent explanation is that both the ruthenium(II)- and the ruthenium(III)–ammine–benzonitrile complexes conform to structure type D. If so, the Ru(II) species are to our knowledge the only cationic metal complexes reported for which ν(CN) of a coordinated monodentate organonitrile shows a decrease from the free-ligand value.

The increase of ν(CN) on organonitrile coordination of type D has been previously described in terms of two perturbations: (1) a kinematic coupling of the C–N and M–N stretching vibrations[27] and (2) an increase in the CN bond force constant resulting from hybridization changes in the coordinated RCN.[28] The size of $\Delta\nu$(CN) ranges up to +105 cm^{-1} (for $C_6H_5CNBF_3$),[5a] the magnitude of $\Delta\nu$(CN) for $Ru(NH_3)_5{}^{3+}$ coordination (31 to 43 cm^{-1}) being typical for transition metal complexes.

The negative $\Delta\nu$(CN) on coordination to $Ru(NH_3)_5{}^{2+}$ undoubtedly results from a lowered CN bond order caused by metal d-electron back-bonding into the nitrile π^* orbitals. The magnitude of the back-bonding effect is particularly impressive when one considers the benzonitrile coordination to a second-row transition metal in the +2 oxidation state would be expected substantially to increase ν(CN), *e.g.*, for $Pd(C_6H_5CN)_2Cl_2$, $\Delta\nu(CN) = +56$ cm^{-1}.[24] Consonant with this explanation is the observation that $Ru(NH_3)_5{}^{2+}$ complexes of benzonitriles having electron-withdrawing substituents display the most negative $\Delta\nu$(CN)'s (Table III). In contrast, the fact that the $Ru(NH_3)_5{}^{3+}$ complexes of these substituted benzonitriles, which are weaker Lewis bases but stronger π acids than benzonitrile, proved unstable indicates that π back-bonding is at most a minor contributor to the ruthenium(III)–nitrile bond strength.

In a recent communication, the ir spectrum of the uncharged species $CoH(CH_3CN)(P(C_6H_5)_3)_3$ was also shown to have a negative $\Delta\nu$(CN).[29] It is not entirely coincidental that this compound is also an analog of a molecular nitrogen complex, $CoH(N_2)(P(C_6H_5)_3)_3$. All of the metal species known to be capable of forming stable metal–N_2 bonds are low valent and capable of substantial back-bonding as evidenced by the large decreases in the N_2 stretching frequencies in each of these compounds.[30] The ν(CN) decreases of the analogous organonitrile species show that, in terms of the experimental parameter ν(CN), back-bonding from the Ru(II) or Co(I) centers predominates over the expected electrostatic effect of coordination. The opposite is true of $Ru(NH_3)_5{}^{3+}$ organonitrile compounds, an observation which is matched with the apparent instability of Ru(III)–N_2 complexes.[20] For comparison, Table X summarizes the infrared stretching frequencies ν(XY) for several complexes of the type $(NH_3)_5RuX{\equiv}YR$. In each case, substantial back-bonding from the Ru(II) is demonstrated by relatively large decreases in ν(XY).

The nitrile region spectrum of [*cis*-$Ru(NH_3)_4(C_6H_5CN)_2$][$ZnBr_4$] is quite similar to the N–N stretching region of the dinitrogen complexes $[Ru(NH_3)_4(N_2)_2]Br_2$[3c]

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TABLE X
SHIFTS IN ν(XY) (IN cm^{-1}) FOR COMPLEXES OF THE TYPE $(NH_3)_5Ru^{II}X{\equiv}YR$

RY≡X	ν(free ligand)	ν(coord ligand)	$\Delta\nu$	Ref
N_2	2330	2129[a]	−201	*f*
CO	2143	1955[a]	−188	*g*
NO^+	2220	1903[b]	−317	*e, h*
C_6H_5CN	2231	2194[c]	−37	
CH_3CN	2254	2239[c]	−15	
CH_3NC	2166	2095[d]	−71	*i*

[a] I_2 salt. [b] Cl_3 salt. [c] Br_2 salt. [d] $(ClO_4)_2$ salt. [e] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 72. [f] Reference 6. [g] C. H. Campbell, A. R. Dias, M. L. H. Green, T. Saito, and M. Swanwick, *J. Organometal. Chem.* (Amsterdam), **14**, 349 (1968). [h] Reference 13. [i] Reference 22.

and $[Ru(en)_2(N_2)_2][B(C_6H_5)_4]_2$.[3b] Two bands are observed, both occurring at higher frequency than the ν(CN) of $[Ru(NH_3)_5(C_6H_5CN)][ClO_4]_2$ (Tables III and VI). The spectrum of [*trans*-$Ru(NH_3)_4(C_6H_5CN)_2][ClO_4]_2$ showed the expected single ν(CN) higher than the monobenzonitrile complex. This frequency is slightly less than the lower and more intense nitrile band of the *cis*-bis(benzonitrile) complex. The difference is apparently of little significance in terms of the metal–nitrile bond stability since the *trans* salt proved to be the less stable in aqueous methanol solution, presumably because of the competition between the *trans*-nitriles for the same sets of metal π electrons.

The different pathways leading to the formation of 4-cyanobenzoatopentaammineruthenium(III) linkage isomers illustrate basic differences between $Ru(NH_3)_5^{2+}$ and $Ru(NH_3)_5^{3+}$. The reaction of $Ru(NH_3)_5H_2O^{2+}$ [generated by Zn(Hg) reduction of $Ru(NH_3)_5Cl^{2+}$] with 4-cyanobenzoic acid gives exclusively the cyano-coordinated $Ru(NH_3)_5$(4-cyanobenzoic acid)$^{2+}$. This product was anticipated on the basis of the lability of $Ru(NH_3)_5^{2+}$ carboxylate complexes[31] and of the relative inertness of the benzonitrileruthenium(II) species (above). Oxidation to ruthenium(III) apparently does not perturb the coordination sphere as the product showed the increased ν(CN) typical of the ruthenium(III)–nitrile coordination. The carboxylate coordinated isomer is formed by the reaction of $[Ru(NH_3)_5OH][S_2O_6]$ with 4-cyanobenzoic acid in an aqueous slurry. No absorption at 2275 cm^{-1}, characteristic of the nitrile-coordinated isomer, is observed in the ir spectrum of the product, indicating that the reaction is specific for the carboxylate-coordinated isomer. The specificity may be the result either of kinetic (mechanistic) control or of thermodynamic bond stability. Insufficient information is available to discriminate between these possibilities although it is likely that the carboxylate–ruthenium(III) bond is thermodynamically favored over the nitrile–ruthenium(III) linkage owing to the relative "hardness" of Ru(III) and of the $-CO_2^-$ compared to the relative "softness" of RCN. Such a qualitative description is, however, subject to incalculable assumptions as alkylnitriles are known to form quite stable complexes with other tripositive second- and third-row transition metal ions.[32]

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CONTRIBUTION FROM THE MATERIALS RESEARCH LABORATORY AND NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Cobalt-59 Nuclear Quadrupole Resonance Spectra of Tetracarbonylcobalt–Tin Compounds[1]

BY DIANE D. SPENCER,[2] JOSEPH L. KIRSCH, AND THEODORE L. BROWN

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The ^{59}Co nuclear quadrupole resonance frequencies are reported for compounds of the form $X_nSn[Co(CO)_4]_{4-n}$, where X = Cl, Br, or CH_3, and n = 0, 1, 2, or 3. The nqr frequencies increase with increased halogen substitution and decrease upon methyl substitution. The results support the hypothesis that the populations of the cobalt $3d_{z^2}$ and d_{xz}, d_{yz} orbitals are lower than for the $d_{x^2-y^2}$, d_{xy} orbitals. Cobalt-59 nqr frequencies are reported also for $Cl_2Ge[Co(CO)_4]_2$ and $Hg[Co(CO)_4]_2$.

Studies of the ^{59}Co nqr spectra of tetracarbonylcobalt compounds of the form $Co(CO)_4L$ have shown[3] that the quadrupole resonance frequencies are quite sensitive to the nature of the group L. Analysis of the results was based on the simplifying assumption that the field gradient at cobalt is determined primarily by the 3d orbital populations on the metal, so that q_{zz} is of the form

$$q_{zz} = q_{320}[N_{d_{z^2}} + {}^1/_2(N_{d_{xz}} + N_{d_{yz}}) - (N_{d_{xy}} + N_{d_{x^2-y^2}})] \quad (1)$$

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(2) University of Illinois Fellow, 1965–1968; Standard Oil Co. of California Chevron Fellow, 1968–1969.

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