The preparation of $NaCo(CO)_4$ by the reaction of powdered NaOH with $Co_2(CO)_8$ in dry THF has a number of desirable features. It is rapid and yields a clean product. The solid salt is readily obtained and its dissolution in dry solvents yields dry solutions. It avoids the preparation and handling of quantities of Na amalgam while eliminating the formation of $Hg[Co(CO)_4]_2$, an impurity often found in the preparations with amalgam.[8,9]

Hieber and coworkers[10] have studied the reaction of $Co_2(CO)_8$ with alcoholic and aqueous hydroxide. The reaction outlined here for the preparation of $NaCo(CO)_4$ probably proceeds in a similar manner. The objections which have been raised to the use of alcoholic or aqueous hydroxide for the preparation of the salt when employed in the synthesis of other materials relate to the fact that a hydrolytic solvent is used and that the solubility of the hydroxide results in the presence of excess hydroxide in the final solution. Neither of these objections applies to the preparation outlined here. Note that the only reaction product soluble in dry THF is $NaCo(CO)_4$.

The basic method of preparation outlined here can be expected to be general for the alkali metal salts of metal carbonylate anions. We have used it to date to prepare THF solutions of $LiCo(CO)_4$ and $KCo(CO)_4$ as well as those of $NaCo(CO)_4$.

Experimental Section

Preparation of $NaCo(CO)_4$ with NaOH.—For these experiments, the THF was dried and deoxygenated by a sequential procedure involving storage over Na ribbon, distillation in a stream of dry N_2, deaeration on a vacuum line, and distillation *in vacuo* onto Linde 4A Molecular Sieves. Prior to use, the sieves were activated by heating to at least 300° and pumping on the vacuum line. Excess NaOH (Mallinckrodt analytical reagent) was quickly powdered and put in a 100-ml round-bottom flask which was placed at once on a vacuum line and pumped. After thorough evacuation, the flask was opened in an N_2-filled polyethylene bag and charged with 1.66 g of $Co_2(CO)_8$. *Caution! Then, 40 ml of THF was added slowly.* Care must be exercised in the addition of THF since considerable ebullition can take place at this point. The flask was attached to a vacuum line by means of a fitting which allowed the transfer from the N_2-filled bag to the vacuum line without admission of air to the sample. After evacuation, the line was filled with N_2, the flask was opened to the line, and stirring was begun by means of a Teflon-coated magnetic stirring bar, while a gentle stream of N_2 was maintained. After the solution had stirred for 1–2 hr, a pinkish purple precipitate had formed. The light yellow solution which remained was separated from the precipitate by centrifuging, and the precipitate was washed with THF. This wash was combined with the solution.

In typical preparations, the solution was returned to the vacuum line and the solvent removed by pumping. The white salt which resulted was stored in the absence of air and light until use.

Analysis.—Aliquots of the $NaCo(CO)_4$ solutions were allowed to decompose in the air and were then treated with sufficient 3% H_2O_2 to ensure complete decomposition of the metal carbonyl. After the residue had been dissolved in concentrated HNO_3, the resulting solutions were diluted with a small amount of H_2O and heated until evolution of brown fumes ceased. Analysis of a typical $NaCo(CO)_4$ solution prepared as above gave 7.19×10^{-2} and 7.25×10^{-2} mol/l. for Co and Na, respectively. This result corresponded to a 75% conversion of $Co_2(CO)_8$ to $Co(CO)_4^-$ and showed the presence of no detectable amount of NaOH in the THF solution of the salt.

Unsuccessful Preparation Using Sodium Amalgam.—A 1% amalgam was prepared in a 500-ml, three-necked, round-bottom flask which was provided with a dropping funnel in one inlet, a connection suitable for attachment to a vacuum line without exposure to the air in a second inlet, and a glass stopper in the third inlet. The flask was placed on a vacuum line and thoroughly flamed. After cooling, it was placed in an N_2-filled polyethylene bag where 10 ml of Hg was added to the dropping funnel. After the oxide and hydroxide coating had been removed from a piece of Na (1.73 g) in the N_2-filled bag, it was placed in the flask. The flask was then replaced on the vacuum line, the line was filled with dry N_2, and a few milliliters of Hg was run into the flask. The sodium was then heated until amalgamation began. Then, the remainder of the Hg was added at such a rate that amalgamation proceeded smoothly. The resulting amalgam was a liquid.

After the flask had cooled, it was once again placed in an N_2-filled polyethylene bag and the dropping funnel was replaced by a straight-bore stopcock through which samples could be removed. Twenty milliliters of THF, treated as indicated above, was added and then 6.35 g of $Co_2(CO)_8$ was added followed by a wash of an additional 10 ml of THF. The flask was placed on an N_2-filled vacuum line and stirring by means of a Teflon-coated magnetic stirring bar was begun. After several weeks of stirring, the solution still retained its original brown color. The infrared spectrum of the solution, however, showed only those bands associated with the $Co(CO)_4^-$ ion in the 5-μ region.

Acknowledgment.—Thanks are due to the Advanced Research Projects Agency for the support of this work through the Purdue IDL Program.

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

Spectroscopic Characterization of Pentaammineruthenium Complexes of Acrylonitrile

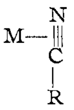
BY PETER C. FORD,[1] RICHARD D. FOUST, JR.,
AND RICHARD E. CLARKE

Received February 2, 1970

A recent contribution[2] from these laboratories described the syntheses and properties of substituted benzonitrile and acetonitrile complexes of ruthenium(II) and ruthenium(III) ammines. In that article, it was concluded that the "abnormal" decrease in the C≡N stretching frequency, ν(CN), observed for the pentaammineruthenium(II)-coordinated nitriles was the result of ruthenium-to-nitrile π back-bonding in a linear metal–nitrogen–carbon array (A) rather than the result of a perpendicular π-bond configuration (B). We

$$M—N{\equiv}C—R$$

A



$$M—\begin{matrix}N\\ \|\!| \\ C\\ | \\ R\end{matrix}$$

B

---

[8] S. V. Dighe and M. Orchin, *Inorg. Chem.*, **1**, 965 (1962).

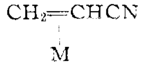
[9] R. B. King, *J. Inorg. Nucl. Chem.*, **25**, 1296 (1963).

[10] W. Hieber, J. Sedlmeier, and W. Abeck, *Chem. Ber.* **86**, 700 (1953).

[1] Author to whom inquiries should be addressed.

[2] R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970).

have also been interested in the ligand properties of organonitriles having a second functional group which could act as a coordination site or display some physical or chemical property which might be perturbed by coordination to the nitrile. These potentially ambident ligands include the cyanobenzoic acids,[2] dicyanobenzenes,[2] cyanopyridines,[3] and acrylonitrile (AN), the subject of this note. Acrylonitrile complexes conforming to structure A as well as other compounds involving a metal–olefin π bond (C) are known.[4,5]


$$\underset{\text{M}}{\overset{\vert}{\text{CH}_2\text{=CHCN}}}$$

C

Furthermore, chlororuthenium– and phosphineruthenium–acrylonitrile complexes have been shown to be important in certain catalytic polymerizations of this ligand.[6] Described here are the pentaammineruthenium(II) and -(III) complexes of acrylonitrile, $[\text{Ru}(\text{NH}_3)_5(\text{CH}_2\text{=CHCN})]\text{X}_n$, where X is a uninegative ion and $n = 2$ or 3.

Experimental Section

Synthesis.—The pentaammineruthenium(II) and -ruthenium(III) acrylonitrile complex salts $[\text{Ru}(\text{NH}_3)_5(\text{AN})]\text{X}_2$ and $[\text{Ru}(\text{NH}_3)_5(\text{AN})\text{X}_3$ ($\text{X}^- = \text{Br}^-$, ClO_4^-, or BF_4^-) were synthesized in good yields from $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ *via* procedures identical with those used to prepare the analogous benzonitrile and acetonitrile complexes.[2] The perdeuterioammine complexes were synthesized from $[\text{Ru}(\text{ND}_3)_5\text{Cl}]\text{Cl}_2$, prepared by repetitive recrystallization of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ from D_2O.[3] In these cases, all reactions and recrystallizations were carried out in D_2O.

Analyses.—Elemental analyses of the pentaammine(acrylonitrile)ruthenium salts were done by Elek Microanalytical Laboratories, Torrance, Calif. Some difficulty was experienced in obtaining a sample of the ruthenium(III) salt sufficiently pure for analysis, as recrystallization from 50° water led to partial reduction to the Ru(II) species as evidenced both by its ir spectrum and by a high carbon analysis. This difficulty was circumvented by adding a few drops of acidic hydrogen peroxide solution to the recrystallization mixture. *Anal.* Calcd for $[\text{Ru}(\text{NH}_3)_5(\text{CH}_2\text{=CHCN})][\text{BF}_4]_2$ ($\text{C}_3\text{H}_{18}\text{B}_2\text{F}_8\text{N}_6\text{Ru}$): C, 8.72; H, 4.40; N, 20.36. Found: C, 8.99; H, 4.59; N, 20.46. Calcd for $[\text{Ru}(\text{NH}_3)_5(\text{CH}_2\text{=CHCN})][\text{ClO}_4]_3$ ($\text{C}_3\text{H}_{18}\text{Cl}_3\text{O}_{12}\text{N}_6\text{Ru}$): C, 6.70; H, 3.37; N, 15.64. Found: C, 6.52; H, 3.55; N, 15.79.

Spectra.—All uv–visible spectra were recorded on a Cary 14 spectrophotometer in aqueous solution, 25°. Electronic spectra features [$\lambda_{\max}$ ($\log \epsilon$)] of $\text{Ru}(\text{NH}_3)_5(\text{AN})^{2+}$ are 372 nm (3.72), 352 nm (sh, 3.66), and 249 nm (3.95) and of $\text{Ru}(\text{NH}_3)_5(\text{AN})^{3+}$ are 361 nm (br, 2.56), 300 nm (sh, 3.01), and 243 nm (3.63).

Infrared spectra were obtained as KBr disks on a Perkin-Elmer Model 225 recording spectrophotometer. With sharp peaks, frequencies of absorption maxima were reproducible within ±1 cm^{-1}.

Proton magnetic resonance spectra were obtained using deoxygenated D_2O solutions saturated with the complex salt at normal probe temperature (24°) on a Jeolco Model C60-H, 60-MHz nmr spectrometer using acetonitrile as the internal standard. Chemical shifts are reported as δ values downfield from tetramethylsilane (TMS).

Results

Distinguishable ir spectral bands of the pentaammine(acrylonitrile)ruthenium(II) and -(III) salts are summarized in Table I. Assignments were made in analogy to spectra of other pentaammineruthenium complexes,[2,3] of free acrylonitrile,[7] and of acrylonitrile complexed to Lewis acids.[8] A prominent feature in each spectrum is the C≡N stretch, ν(CN), which occurs at 2267 cm^{-1} for the ruthenium(III) compound and at 2184 cm^{-1} for the ruthenium(II) compound. The increase in ν(CN) from the free ligand value (2228 cm^{-1}) would be expected for nitrile coordination to $\text{Ru}(\text{NH}_3)_5{}^{3+}$ and the ν(CN) decrease ($\Delta\nu(\text{CN}) = -44$ cm^{-1}) on coordination to $\text{Ru}(\text{NH}_3)_5{}^{2+}$ parallels decreases observed for the monodentate nitrile complexes of this species.[2] However, ν(CN) decreases have been observed for other acrylonitrile complexes in which cases a ν(CN) decrease has been interpreted as indicating an olefin-coordinated species.[5] Notable in both spectra in Table I are the bands assignable to the CH_2 in-plane deformation, to the vinyl wag, to the vinyl twist, and to the carbon–carbon single-bond stretch at frequencies not markedly shifted from the corresponding free acrylonitrile values. In previous examples, nitrile coordination has been shown to perturb these four bands only slightly,[8] while π coordination to the olefinic function apparently leads to the disappearance of the vinyl wag and twist frequencies.[5] In these spectra, the strong absorption assigned to the degenerate deformation of the coordinated ammonias (~1625 cm^{-1}) obscures the region where an acyrlonitrile carbon–carbon double-bond stretch would be expected. To circumvent this problem, the perdeuterioammine complexes $[\text{Ru}(\text{ND}_3)_5(\text{AN})]\text{Br}_2$ and $[\text{Ru}(\text{ND}_3)_5(\text{AN})]\text{Br}_3$ were prepared. The spectra of both salts displayed sharp, medium-intensity bands in the ν(C=C) region, 1592

TABLE I

IR SPECTRA OF ACRYLONITRILE COMPLEXES (CM^{-1})

$[\text{Ru}(\text{NH}_3)_5(\text{CH}_2\text{=CHCN})][\text{ClO}_4]_3$	$[\text{Ru}(\text{NH}_3)_5(\text{CH}_2\text{=CHCN})][\text{ClO}_4]_2$	Assignment
3450 br, s	3430 br, s	
3200 br, vs	3300 br, vs	N—H str
	3165 sh, s	
2267 m	2184 s	C≡N str
1625 br, s	1625 br, s	NH_3 degen def
1403 w	1394 w	$\delta(\text{CH}_2)$ in plane
1350 br, sh, m		
1312 s	1268 s	NH_3 sym def
~1100 vbr, vs	~1100 vbr, vs	ClO_4^-
984 br, m	973 br, m	Wag, δ(vinyl) out of plane
940 m	938 m	Twist, δ(vinyl) out of plane
~890 w	~900 w	C—C str
820 br, s	768 br, s	NH_3 rocking mode
665 w	665 w	C=C torsion
636 vs	633 s	ClO_4^-
626 vs	625 s	
564 br, m	552 w	
465 br, m		Ru(III)–NH_3 str

---

[3] R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 495 (1970).

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

[5] (a) G. N. Schrauzer, *J. Amer. Chem. Soc.*, **81**, 5310 (1959); (b) A. G. Massey, *J. Inorg. Nucl. Chem.*, **24**, 1172 (1962); (c) R. J. Kern, *ibid.*, **25**, 5 (1963).

[6] (a) E. Billig, C. B. Strow, and R. L. Pruett, *Chem. Commun.*, 1307 (1968); (b) J. D. McClure, R. Owyang, and L. H. Slaugh, *J. Organometal. Chem.*, **12**, P8 (1968).

[7] F. Halverson, R. F. Stamm, and J. J. Whalen, *J. Chem. Phys.*, **16**, 808 (1948).

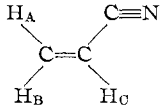
[8] M. F. Farona and G. R. Tompkin, *Spectrochim. Acta, Part A*, **24**, 788 (1968).

cm^{-1} for the ruthenium(II) complex and 1596 cm^{-1} for the ruthenium(III) complex. Observation of the vinyl wag and twist and the ν(C═C) frequencies leaves little doubt that pentaammine(acrylonitrile)ruthenium(II) and the corresponding ruthenium(III) complex are both largely the nitrile-coordinated isomers.

The proton magnetic resonance spectrum of [Ru(NH$_3$)$_5$(AN)]Br$_2$ in D$_2$O showed an 11-line multiplet at δ 5.72–6.17 (ppm downfield from TMS), having a signal-to-noise ratio of about 20. Only one other broad resonance (singlet) at δ 2.8, a value consistent with that reported[9] for the coordinated ammonias of $Ru(NH_3)_5$-CO^{2+}, was observed with freshly prepared samples. Older solutions did not display this resonance apparently because of slow H–D exchange between coordinated NH$_3$ and solvent D$_2$O. The pmr spectrum of the acetonitrile complex [Ru(NH$_3$)$_5$(CH$_3$CN)]Br$_2$ was also obtained and shows a sharp singlet for the methyl group ($\delta(H_{CH_3})$ 2.48 ppm) occurring 0.48 ppm downfield from the free acetonitrile singlet.

The 11-line complexed acrylonitrile multiplet was analyzed by assuming a three-proton ABC system and using a modified version of the magnetic equivalence factoring computer program of Ferguson and Marquardt[10] to fit iteratively a theoretical spectrum to the experimental spectrum. By this procedure, proton chemical shifts and coupling constants were calculated (Table II) which lead to a nearly perfect match of line positions and intensities between the theoretical and experimental spectra. Comparison of the calculated chemical shifts for the complex with the chemical shifts observed for free acrylonitrile supports the conclusion from the infrared spectra that $Ru(NH_3)_5(AN)^{2+}$ has the nitrile-coordinated structure. Clearly, the environment of proton H$_C$ is changed in a manner different from that of either H$_A$ or H$_B$, an observation not consistent with structure C but consistent with A.

TABLE II
COMPUTED NMR SPECTRAL PARAMETERS FOR $Ru(NH_3)_5(CH_2CHCN)^{2+}$ AND FREE ACRYLONITRILE IN D$_2$O



	Ru(NH$_3$)$_5$-(CH$_2$═CHCN)$^{2+}$ [a]	CH$_2$═CHCN [b]	Δ[c]
$\delta(H_A)$, ppm	6.05[d]	6.21[d]	−0.16
$\delta(H_B)$, ppm	5.82	6.07	−0.25
$\delta(H_C)$, ppm	5.93	5.69	+0.24
J_{AB}, cps	0.91	0.91	0.00
J_{AC}, cps	15.49	17.92	−2.43
J_{BC}, cps	10.03	11.75	−1.72

[a] Br$^-$ salt. [b] These values computed for acrylonitrile in D$_2$O compare favorably to parameters calculated for acrylonitrile in CCl$_4$: R. T. Hobgood, Jr., R. E. Mayo, and J. H. Goldstein, *J. Chem. Phys.*, **39**, 2501 (1963). [c] Δ = parameter (complex) − parameter (acrylonitrile). [d] Downfield from TMS. CH$_3$CN used as internal standard.

Discussion

The pmr and ir spectra of the $Ru(NH_3)_5(AN)^{2+}$ salts and the ir spectra of the $Ru(NH_3)_5(AN)^{3+}$ salts indicate that each of these complexes conforms to the nitrile-coordinated structure A. However, neither spectroscopic technique is sufficiently quantitative to exclude the possibility that 5–10% of the ruthenium(II) complex in configuration C might go undetected, although the sharpness of the nmr lines in the complexed acrylonitrile multiplet does demonstrate that A is not undergoing rapid interchange with another significant structural isomer. Unsuccessful attempts were made in this laboratory to synthesize the $Ru(NH_3)_5^{2+}$ complex of acrolein (CH$_2$═CHCHO) with the procedures used to prepare $Ru(NH_3)_5(AN)^{2+}$. Since the electron-withdrawing nature of the –CHO group is comparable to that of –CN, the failure to isolate a ruthenium(II)–acrolein complex is an indication that a $Ru(NH_3)_5^{2+}$–olefin bond of this type is not sufficiently stable to survive under the reaction conditions.

The chemical shifts calculated for the $Ru(NH_3)_5^{2+}$-complexed acrylonitrile (Table II) are particularly interesting. The appearance of $\delta(H_C)$ downfield from the free-ligand value (Δ = +0.24 ppm) can be interpreted as H$_C$ deshielding by cation coordination to the adjacent nitrile and is paralleled by the similar change in $\delta(H_{CH_3})$ observed for $Ru(NH_3)_5(CH_3CN)^{2+}$. In contrast the complexed acrylonitrile geminal hydrogens, H$_A$ and H$_B$, each appear upfield from the corresponding free-ligand hydrogens suggesting that enhanced electron density at the methylene carbon results from coordination. In an earlier study of a tungsten(0)–acrylonitrile complex, W(CO)$_4$(AN)$_2$, Ross, *et al.*,[4] observed that $\delta(H_C)$ appeared 0.13 ppm downfield from the free-ligand value while the geminal hydrogens were essentially unchanged. In this context, the decrease in $\delta(H_A)$ and $\delta(H_B)$ on acrylonitrile coordination to the ruthenium(II) cation is striking and perhaps reflects the metal-to-ligand π back-bonding apparently also responsible for the decrease in the C≡N frequency, ν(CN), and such chemical effects as the basicity enhancement of $Ru(NH_3)_5^{2+}$ nitrile-coordinated cyanopyridines.[3] The increases in $\delta(H_C)$ and in $\delta(H_{CH_3})$ (acetonitrile complex) suggest that at the adjacent carbon the deshielding resulting from cationic coordination is more important than any opposite effect from back-bonding. We believe that the pmr parameter analyses display excellent potential as a probe into the intimacies of metal–ligand π interactions and are extending these studies into more complicated systems such as the ruthenium(II)–benzonitrile complex[2] with the anticipation that chemical shift data may be correlated with the preiously observed chemical phenomena.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We thank Professor J. T. Gerig of this department for his patient help in the analysis of the nuclear magnetic resonance spectra.

---

(9) A. D. Allen, T. Eliades, R. O. Harris, and P. Reinsalu, *Can. J. Chem.*, **47**, 1605 (1969).

(10) R. C. Ferguson and D. W. Marquardt, *J. Chem. Phys.*, **41**, 2087 (1964).