g) was eluted with 0.01 M NaCl. The initial fractions taken were about 3 ml each.

Spectra.—The circular dichroism (CD) spectra were recorded on a Roussel–Jouan Dichrographe and a Jasco Model ORD–UV-5 with CD attachment. Concentrations of the solutions (10^{-3}–10^{-2} M) were determined through their absorption spectra recorded on a Cary Model 14 spectrophotometer. The proton nmr spectra were obtained in D_2O on a Varian A-60 spectrometer.

Acknowledgment.—The authors wish to thank Mr. J. A. Weyh and Mr. P. F. Coleman for preparing the anionic complexes.

CONTRIBUTION FROM THE PHYSICAL RESEARCH LABORATORY,
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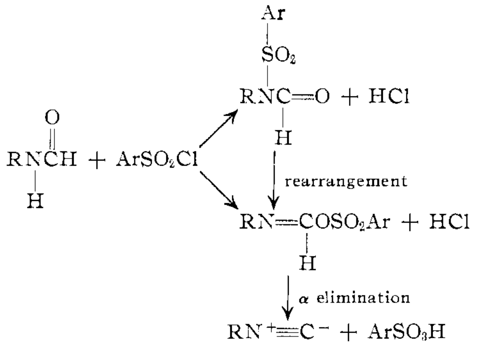
Preparation and Properties of Metal(II) Complexes of N-Methylformamide

BY RAYMOND A. MACKAY AND EDWARD J. POZIOMEK

Received December 6, 1967

In a recent review Ugi, *et al.*,[1] describe experiments in which N-alkylformamides are dehydrated easily by various electrophiles, including arylsulfonyl chlorides, to produce isocyanides. The probable mechansim of this reaction involves electrophilic attack at formamide oxygen (eq 1b).[1] However, initial attack at formamide nitrogen (eq 1a) followed by rapid rearrangement has not been eliminated. In fact, reaction of various alkylformamides with acetyl chloride leads to stable N-acetylated derivatives.[2]



(1a)

(1b)

(2)

We have undertaken a study of the effect of metal ion complexation on the reactivity of N-substituted formamides. We report here the preparation and chemical and physical properties of a series of N-methylformamide (NMF) complexes. The colors, methods of preparation, and analytical results are listed in Table I. A number of physical properties, including carbonyl stretching frequencies, magnetic moments, and molar conductances, are presented in Table II. The electronic absorption spectra are given in Table III. None of the perchlorate complexes on treatment with p-toluenesulfonyl chloride (TsCl) in nitromethane produced isocyanide, whereas NMF itself did. The nitrate complexes in nitromethane gave a weak isocyanide test. The complexes are generally soluble in highly polar solvents (*e.g.*, CH_3NO_2, alcohols, NMF) and insoluble in less polar solvents (*e.g.*, $CHCl_3$, CH_2Cl_2, ether, ethyl acetate). The complexes hydrolyze in water. Though the preparation and physical properties of a number of metal–amide complexes have been described,[3–6] we do not believe that there has been any comprehensive study of the metal complexes of N-monosubstituted formamides.

Physical Properties.—The shift of the C=O stretching band to lower frequency (relative to NMF) indicates that the formamide is coordinated to the metal *through the oxygen atom*, although the shifts (∼10–20 cm^{-1}) are less than those usually found for metal–amide complexes (∼30–70 cm^{-1}).[3,5] The electronic spectra of the Co and Ni complexes (Table III) in NMF and CH_3NO_2 are characteristic of the high-spin octahedral complexes, and their magnetic moments (Table II) are within the ranges observed for these complexes. The ligand field parameters were calculated using the matrix elements given by Orgel.[7] The calculated and observed values of ν_2 are in good agreement, substantiating the assignment of octahedral configuration for Ni and Co (Table IV).

The observed value for Ni given in Table IV is the average of the two maxima in the doublet. The value of Dq for the nickel perchlorate salt in NMF is in good agreement with that obtained by Drago, *et al.*[4] (838 cm^{-1}). However, it is evident from the data in Table IV that the value of Dq is somewhat dependent on both the solvent and the anion. For the $Ni(NMF)_6{}^{2+}$ species ($ClO_4{}^-$ or $NO_3{}^-$ anion, NMF and CH_3NO_2 as solvent) the value of Dq ranges from 840 to 859 cm^{-1}.

The electronic spectrum of $[Cu(NMF)_4](ClO_4)_2$, for both the solid (Nujol mull) and the NMF solution, consists of a broad band at 14,000 cm^{-1} which probably contains two or more overlapping bands. The ratio of the principal ligand field band of Cu to that of Ni (σ_{Cu}/σ_{Ni}) is 1.67, indicating a highly tetragonal complex.[8] The ir spectrum (4000–250 cm^{-1}) of the solid shows no evidence for coordinated perchlorate (*i.e.*, no splitting of ν_3 or ν_4 and a weak ν_1). However, the high melting point of the Cu complex (210–211° dec) would tend to indicate a stronger interaction between the anion and cation than in the $[M(NMF)_6](ClO_4)_2$ complexes. In any event, it is clear that the $Cu(NMF)_4{}^{2+}$ moiety is square planar rather than pseudo-tetrahedral.[9]

The stoichiometry, the similarity of melting points, and the presence of only one C=O stretching band in-

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TABLE I

METAL SALT COMPLEXES OF N-METHYLFORMAMIDE

Compound[a]	Color	Synthetic method	% calcd C	% calcd H	% calcd N	% calcd Cl	% calcd Metal	% found C	% found H	% found N	% found Cl	% found Metal
$[Mg(NMF)_6](NO_3)_2 \cdot 2H_2O$	White	B	26.8	6.3	20.8	...	...	26.8	6.3	20.4	...	...
$[Mn(NMF)_6](ClO_4)_2$	White	C	23.7	4.9	13.8	11.7	...	24.0	4.9	13.8	11.9	...
$[Co(NMF)_6](NO_3)_2 \cdot 2H_2O$	Pink	A	25.1	5.9	19.5	...	10.3	24.8	6.0	18.8	...	10.3
$[Ni(NMF)_6](NO_3)_2$	Light green	A	26.8	5.6	20.8	...	11.0	27.0	5.7	20.8	...	11.1
$[Cu(NMF)_4](ClO_4)_2$	Light blue	B	19.3	4.0	11.2	14.2	12.8	19.3	4.1	11.2	14.5	13.0
$[Zn(NMF)_6](ClO_4)_2$	White	C	23.2	4.9	13.6	11.5	10.6	23.1	5.0	12.8	11.7	10.6
$[Co(NMF)_6](ClO_4)_2$	Pink	A	23.6	4.9	13.7	11.6	9.6	23.6	4.7	13.9	11.9	9.8
$[Ni(NMF)_6](ClO_4)_2$	Light green	A	23.6	4.9	13.7	11.6	9.6	23.8	5.2	13.4	12.0	9.7
$[Mg(NMF)_6](ClO_4)_2$	White	C	...	...	...	12.3	4.2	...	...	...	12.5	4.3

[a] Repeated attempts to prepare $[Fe(NMF)_6](ClO_4)_2$ gave an amber solid with poor elemental analysis.

TABLE II

PHYSICAL PROPERTIES

Compound	Hygroscopic	$\nu_{C=O}$, cm^{-1}	$\Delta\nu_{C=O}$,[a] cm^{-1}	μ_{eff},[b] BM	Mp,[c] °C	Λ[d]	$10^5\chi_M$,[b] cgs units
$[Mg(NMF)_6](NO_3)_2 \cdot 2H_2O$	No	1657	−10	...	74–77	14	...
$[Mg(NMF)_6](ClO_4)_2$	Yes	1662	−5	...	103–107	149	...
$[Mn(NMF)_6](ClO_4)_2$	Yes	1653	−14	5.90[e]	82–84	154	1357
$[Co(NMF)_6](NO_3)_2 \cdot 2H_2O$	No	1648	−19	4.97	78–80	13	943
$[Co(NMF)_6](ClO_4)_2$	No	1652	−15	5.20	125–127	149	1024
$[Ni(NMF)_6](NO_3)_2$	No	1648	−19	3.26	104–108	9	407
$[Ni(NMF)_6](ClO_4)_2$	No	1650	−17	3.17	148–149	156	380
$[Cu(NMF)_4](ClO_4)_2$	No	1635	−32	1.88	210–211 dec	176	134
$[Zn(NMF)_6](ClO_4)_2$	Yes	1645	−22	...	101–105	169	...

[a] $\Delta\nu = \nu_{NMF} - \nu_{complex}$; error on frequencies is *ca.* ±5 cm^{-1}. [b] At 302°K; error on μ_{eff} is ±0.1 BM; χ_M is corrected for diamagnetic susceptibility. [c] Uncorrected. [d] Molar conductance in cm^2 mho mol^{-1} in CH_3NO_2 at 25°, corrected for solvent conductivity. [e] In CH_3NO_2. In NMF (CH_2Cl_2), $\chi_M = 1260 \times 10^{-5}$ cgs unit, $\mu_{eff} = 5.8 \pm 0.1$ BM.

TABLE III

ELECTRONIC SPECTRA[a]

	$[Ni(NMF)_6](ClO_4)_2$			$[Co(NMF)_6](ClO_4)_2$	
	NMF		CH$_3$NO$_2$	NMF	CH$_3$NO$_2$
	ν_{max} (ϵ_{max})		ν_{max} (ϵ_{max})	ν_{max} (ϵ_{max})	ν_{max} (ϵ_{max})
	25.20 (11.9)		25.20 (11.9)	19.12 (16.1)	19.20 (18.1)
b	14.83 (4.19)	b	14.92 (4.53)	...	...
	13.80 (3.68)		13.72 (3.76)	7.80 (3.45)	7.94 (4.50)
	8.40 (5.16)		8.56 (5.58)		

	$[Ni(NMF)_6](NO_3)_2$			$[Co(NMF)_6](NO_3)_2 \cdot 2H_2O$	
	NMF		CH$_3$NO$_2$	NMF	CH$_3$NO$_2$
	ν_{max} (ϵ_{max})		ν_{max} (ϵ_{max})	ν_{max} (ϵ_{max})	ν_{max} (ϵ_{max})
	25.10 (12.9)		24.90 (31.2)	19.15 (17.8)	18.60 (87.2)
b	14.90 (5.10)	b	14.75 (11.1)	16.75 sh[c]	...
	13.50 (4.20)		12.97 (6.34)	7.79 (3.90)	8.35 (10.5)
	8.59 (5.40)		8.45 (5.51)		

$[Cu(NMF)_4](ClO_4)_2$	
NMF	Nujol
ν_{max} (ϵ_{max})	ν_{max} (ϵ_{max})
14.00 (57.2)[d]	14.08 (· · ·)[d]

[a] ν_{max} given in kK (1 kK = 1000 cm^{-1}); ϵ_{max} given in l. mol^{-1} cm^{-1}. [b] Doublet: A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6,** 134 (1959). [c] Shoulder on 19.15-cm^{-1} band. [d] Broad.

TABLE IV

Compound	Solvent	*Dq*, cm^{-1}	β, %	ν_2, cm^{-1} Calcd	ν_2, cm^{-1} Found
$[Co(NMF)_6](NO_3)_2 \cdot 2H_2O$	NMF	894	14.0	16,800	16,750
$[Ni(NMF)_6](NO_3)_2$	NMF	859	13.8	14,300	14,200
$[Ni(NMF)_6](NO_3)_2$	CH$_3$NO$_2$	845	14.0	14,020	13,860
$[Ni(NMF)_6](ClO_4)_2$	NMF	840	11.4	14,000	14,320
$[Ni(NMF)_6](ClO_4)_2$	CH$_3$NO$_2$	856	13.1	14,200	14,320

dicate that the Mg, Mn, and Zn complexes are also octahedrally coordinated. The magnetic moment of the Mn complex is the spin-only value usually found for high-spin Mn(II).

The molar conductances (Table II) of the perchlorate complexes in nitromethane are consistent with their formulation as 2:1 electrolytes. However, the nitrate complexes appear to be nonelectrolytes. A similar behavior for Co(II) and Ni(II) complexes of some primary amides was recently observed by Ragsdale and Cunningham,[10] who ascribe it to nitrate interaction.

We propose that a nitrate interaction is also responsible in this case, according to the reaction

$$\underset{\text{solid}}{[ML_6](NO_3)_2} \xrightarrow{CH_3NO_2} \underset{\text{solution}}{ML_4(NO_3)_2 + 2L} \qquad (3)$$

This explanation is supported by the spectral data (Table III). A comparison of the spectra of the nitrate and perchlorate salts shows that octahedral species are present in both NMF and CH_3NO_2. However, for the nitrate salts in CH_3NO_2, the extinction coefficients are at least twice as large for Ni and over four times as large for Co, which is consistent with replacement of two NMF ligand molecules with nitrate ions.

Chemical Properties.—*p*-Toluenesulfonyl chloride (tosyl chloride) and other arylsulfonyl chlorides react with formamides (in nitromethane and numerous other solvents) to produce isocyanides. Base catalysts such as quinoline are usually added to effect high yields. As mentioned in the introduction, the mechanism in the dehydration of formamides by an electrophile (EX) is undoubtedly a nucleophilic attack by the

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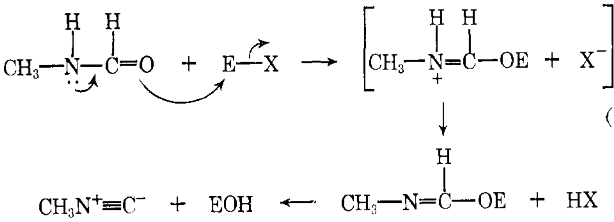
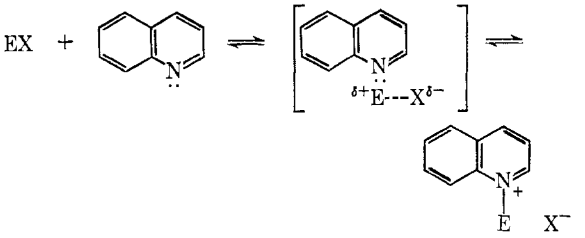
(10) R. O. Ragsdale and W. K. Cunningham, paper presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

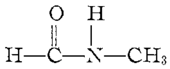
formyl oxygen followed by an α elimination (eq 4), though initial attack at the nitrogen atom has never been eliminated.


(4)

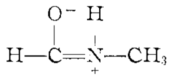
The proton loss in eq 4 is illustrated as occurring after the initial step but may occur otherwise. The presence of a base such as quinoline may enhance the reaction by aiding proton dissociation and/or by increasing the electron-deficient character of the electrophile (eq 5). The NMF itself could act as a base and may do so in reactions with tosyl chloride. Whether reaction occurs at all depends on the nucleophilic strength of the formyl oxygen and the electron-deficient character of the electrophile.


(5)

We have been interested in how metal ions might influence NMF dehydration. All of the NMF–metal complexes synthesized show coordination through formamide oxygen to metal. This should weaken the C–O bond and also cause the oxygen to become more negative, since coordination will increase the importance of resonance form II relative to I. Additionally, the acidity of the proton on nitrogen will be increased. However, none of the perchlorate complexes prepared in the present study produced methyl isocyanide. This was checked by air-sampling techniques[11] and also by infrared examination of the reaction solution.


$H{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}CH_3$

I


$H{-}\overset{O^-}{\overset{|}{C}}{=}\underset{+}{\overset{H}{\overset{|}{N}}}{-}CH_3$

II

Addition of quinoline to the metal complex and tosyl chloride mixture led to a positive test for methyl isocyanide. A control experiment indicated that this was due to reaction with uncoordinated NMF since addition of quinoline to the complex alone gave decomposition. A weak test for isocyanide using the nitrate complexes in nitromethane is thought to be due to the reaction of uncoordinated NMF with tosyl chloride. The NMF arises from the nitrate interaction (eq 3).

Inspection of molecular models showed that in octahedral complexes, attack at the oxygen is hindered sterically. In fact, it is impossible for the sulfur atom in tosyl chloride to approach closely the formamide oxygen atom. This would easily explain the lack of isocyanide formation from the octahedral complexes *if the initial attack is on oxygen.* However, in the case of the Cu complex, which has essentially a square-planar geometry, its lack of chemical reactivity cannot be explained on the basis of steric hindrance. If initial attack is on the formamide nitrogen then metal complexation would inhibit reactivity by decreasing the nitrogen basicity (resonance form II).

It is not completely clear at this time why high yields of methyl isocyanide were not obtained from the reaction of tosyl chloride with metal complexes of NMF. Work is continuing to determine more precisely the effect of metal ions on the reactivity of formamides.

Experimental Section

Preparation of Complexes.—The appropriate hydrated metal salt (0.01 mol) is dehydrated by dissolution in excess ethyl orthoformate (0.12 mol). A small excess of NMF (0.10 mol) is added and the complex is isolated by treatment with ether. Slight variations of this general method, depending on the metal salt, are employed and are given below.

(A) The hydrated metal salt is dissolved with stirring (magnetic) in ethyl orthoformate (EOF), the NMF is added, and the solution is stirred for about 10 min. Upon addition of 50 ml of ether a precipitate is obtained which is allowed to settle; it is then filtered, washed well with ether, and dried in a vacuum desiccator.

(B) This is the same as method A except that the hydrated metal salt is dissolved in EOF with gentle heating.

(C) This is the same as method A except that an oil is obtained upon addition of ether. A solid is obtained by extracting the oil two or three times with 50-ml portions of ether.

Physical Measurements. (1) **Infrared Spectra.**—Spectra of the solid complexes from 250 to 4000 cm^{-1} were obtained on a Perkin-Elmer 521 grating spectrophotometer as Nujol mulls between KRS-5 (TlBr–I) windows. Polystyrene was employed for the frequency calibration in the carbonyl stretching region (1600 cm^{-1}).

(2) **Electronic Spectra.**—Absorption spectra of the metal complexes in the 300–1500-mμ region were obtained on a Cary 14 spectrophotometer. The spectra of the solutions were measured in 10-mm quartz cells with the solvent as reference. The solutions were prepared by dissolving the complexes in NMF. In a few instances, spectra were also obtained in nitromethane solution.

(3) **Magnetic Measurements.**—The magnetic susceptibilities were measured using a Varian A-60 nmr spectrometer according to the method described by Evans.[12] The solutions were made by dissolving the complexes in NMF containing about 5% of an inert solvent. The inert solvents employed were *p*-dioxane, $CHCl_3$, and CH_2Cl_2. In a few instances, the measurements were also performed on solutions of the complexes in CH_3NO_2, for which no additional inert solvent is needed. The susceptibilities were corrected for diamagnetic contributions as outlined by Figgis and Lewis.[13]

(4) **Conductivity Measurements.**—Conductances were measured using a dip cell and a Serfass conductance bridge operating at 1000 cps. All measurements were made at 25° in 10^{-3}–10^{-4} *M* nitromethane solutions.

Reaction Studies.—Semiquantitative studies of the reaction of the metal complexes with *p*-toluenesulfonyl chloride were carried out in nitromethane solution. These studies were performed in the apparatus employed by Crabtree, Poziomek, and Hoy[11] for the colorimetric detection of alkyl isocyanides. The

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[11] E. V. Crabtree, E. J. Poziomek, and D. J. Hoy, *Talanta*, **14**, 857 (1967).

[12] D. F. Evans, *J Chem. Soc.*, 2003 (1959).

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reagents were mixed and allowed to react at room temperature for specified lengths of time, usually 1–10 min. The presence of isocyanide is indicated by a white to blue color change in the detector tube.[11] The yields of isocyanide can be semiquantitatively estimated from the intensity of the color. The lowest amount of methyl isocyanide detectable is approximately 0.1 μg.

Analyses.—All elemental analyses were performed by the Analytical Research Department, Chemical Research Laboratory, Edgewood Arsenal, Md.

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CONTRIBUTION FROM THE LABORATORIUM FÜR
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The Preparation of Rare Rarth Nitrides from Amalgams

BY B. MAGYAR

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Many transition and rare earth metal compounds have been examined as new ferromagnetic semiconductors, but this important property has so far been demonstrated conclusively only in some compounds of europium(II)[1,2] and chromium(III).[3,4] Investigations of the rare earth nitrides have not been definitive, since the samples which have been prepared either by direct combination of the elements[5–7] or by reaction of the hydride and nitrogen[8] have contained amounts of nitrogen to metal in less than the stoichiometric ratio. The samples contained either unreacted metal or a second anion, presumably O^{2-}. If air is carefully excluded during preparation of the nitride, any oxygen present must have preexisted in the metal as an impurity. Such oxygen can probably not be removed by outgassing the metal, since, at the elevated temperatures required for outgassing, oxygen is chemically bound by the metal. Since the oxygen content of commercially available metals is in the range 0.1–1.0 mol %, products with a nitrogen/metal ratio of 0.99 are to be expected. Lower ratios than this must be attributed to incomplete reaction of the metal with nitrogen. The incomplete reaction of the metal with nitrogen presumably occurs for kinetic reasons. During the reaction the metal particles become coated with nitride, and the diffusion of both metal and nitrogen through this layer appears to be slow. In order to complete the reaction, the nitridation would have to be continued for an impracticably long period. This problem might be overcome by continuous pulverization during the reaction or by carrying out the reaction with the metal in the gaseous, molten, or dissolved state. From the kinetic standpoint, combination of the molten metal with nitrogen, atomized in an electric arc, would perhaps be the best method.[9] Some nitrides of the transition metals have already been obtained by treatment of liquid amalgams with ammonia,[10] but the products were obtained in highly disperse state and were not easily separable from the large amounts of mercury present. For preparative purposes, it is preferable to use solid amalgams having a higher content of rare earth. The solubility[11] of the rare earth metals in mercury is very small. "Amalgams" with a higher rare earth content are suspensions of different solid intermetallic compounds in mercury. These compounds are of the type $LnHg_x$, where $x = 1–4$, and have a moderate thermal stability.[12] Their decomposition temperatures are well below the melting points of the rare earth metals. Therefore, the thermal decomposition of the amalgams yields solid rare earths in a highly dispersed form, thus offering good conditions for direct union with nitrogen. The following scheme was found to yield stoichiometric rare earth nitrides

$$LnHg_x(s) + 0 \cdot 5N_2(g) \xrightarrow{500–1000°} LnN(s) + Hg(g)$$

where $x = 1–4$ and Ln = La, Pr, Nd, Gd, or Tm. Table I contains the stoichiometric ratio and the lattice constants of some nitrides obtained by the amalgam method. The composition of the amalgam seemed to have no influence upon the composition of the obtained nitride. There appeared to be little advantage in using a nitrogen–ammonia mixture for the nitridation as the reaction with nitrogen alone was sufficiently rapid. This method readily afforded mixed crystals of rare earth nitrides at a relatively low temperature. This represents a considerable advantage over the more usual method of heating the two nitrides together, requiring a high temperature, presumably owing to slow diffusion in the nitride phase. The systems $Gd_{1-x}Pr_xN$ and $Gd_{1-x}La_xN$ were studied. The mutual solubility of the nitrides was readily estimated from a plot of the unit cell dimensions against the chemical composition (see Figure 1). At 1000°, the PrN-rich phase dissolved 46 mol % of GdN, whereas the GdN-rich phase dissolved up to 7 mol % of PrN only. Upon nitridation, mixed amalgams of the composition $Pr_{1-x}Gd_xHg_y$ yielded two phases, both having the NaCl structure, when x had a value between 0.07 and 0.54. The $Gd_{1-x}La_xN$ system behaved similarly, where the solubility gap extended from $x = 0.00$ to $x = 0.60$.

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