are compatible with those of previous workers for other symmetries.[10] The authors will be pleased to furnish larger versions of the figures upon request.

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(10) (a) R. D. Dowsing, J. F. Gibson, D. M. L. Goodgame, and P. J. Hayward, *Nature (London)*, 1037 (1968); (b) R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, **50**, 294 (1969); (c) R. D. Dowsing, J. F. Gibson, M. Goodgame, and P. J. Hayward, *J. Chem. Soc. A*, 188 (1969).

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Reaction of Electrophiles with Metal(II) Complexes of Formamides

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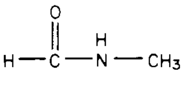
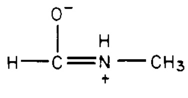
A number of years ago, we reported the preparation of metal(II) complexes of *N*-methylformamide (NMF).[1] These were perchlorate and/or nitrate complexes of Mg, Mn, Co, Ni, Cu, and Zn. All are octahedral except Cu which is approximately square planar, and none contain coordinated anion. The ligand is coordinated to the metal via the oxygen, which will increase the importance of resonance from II relative to I.



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

I



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

II

Since NMF can be dehydrated by various electrophiles to produce isocyanides,[2] it was anticipated that metal complexes of NMF should be more reactive than the free ligand. This was not the case, however. None of the complexes reacted with tosyl chloride, which does react with NMF itself. Although the lack of reactivity of the octahedral complexes could be explained on the basis that attack at oxygen is sterically hindered, such is not the case for the Cu complex. therefore, work was continued in order to determine more precisely the effect of metal ions on the reactivity of formamides, and we report here the results of those studies.

Experimental Section

Preparation of Formamide Complexes. The synthesis of all of the metal chloride complexes of NMF as well as the ZnI_2 complex has been previously reported.[3] The preparation of the nitrate and perchlorate complexes is described in ref 1. The NMF complex of $ZnBr_2$ was prepared by dissolving 0.01 mol of the hydrated metal salt in 5 mL of NMF, then adding 5 mL of ethylorthoformate (EOF), and stirring about 1 h. Addition of 50 mL of ether produced an oil. The ether was decanted off, and the oil was triturated with another 50 mL of ether and then 25 mL of petroleum ether (30–60 °C), resulting in the formation of a white paste. After decantation the paste was dissolved in 2 mL of 1-butanol, followed by addition of 50 mL of ether. Upon stirring, the white, cloudy oil phase became a sticky solid and finally a fine white powder. The solid was filtered, washed with ether, and dried in a vacuum desiccator over P_2O_5. Anal. Calcd for $ZnBr_2(NMF)_{2.3}$: C, 15.4; H, 3.2; N, 8.9; Br, 44.2; Zn, 18.1. Found: C, 14.8; H, 3.2; N, 9.1; Br, 43.0; Zn, 17.1.

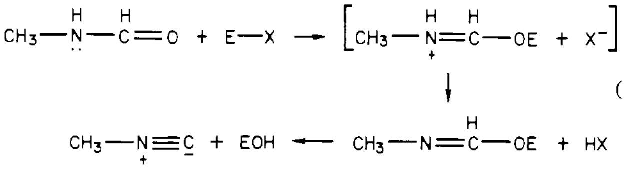
Preparation of Thioformamide $ZnCl_2$ Complexes. The *tert*-butylthioformamide (TBTF) was prepared by dissolving 5.0 mL of *tert*-butylformamide in 50 mL of benzene, adding 20 g of P_2S_5, and refluxing for 1 h with vigorous stirring. The benzene was stripped off, the remaining yellow solid treated with 50 mL of cold 5% NaOH, and the suspension stirred for 1 h in an ice bath. An additional 1 mL of cold 10% NaOH was added, and the solid was filtered off, washed with water, and dried in a vacuum desiccator. The product was recrystallized from 200 mL of hexane–benzene and separated as 2.5 g of fine white needles, mp 121–122 °C (reported value, 124–125 °C).[4] Anal. Calcd for $C_5H_{11}NS$: C, 50.9; H, 9.4; S, 27.2. Found: C, 51.1; H, 9.4; S, 27.1. The *N*-methylthioformamide (NMTF) was prepared according to the procedure of Willstatter and Wirth.[5] Hydrated $ZnCl_2$ (3 mmol) was dissolved in 5 mL of ethanol and 1 mL of EOF. After stirring for 1 h, thioformamide (10 mmol) was added, the solution stirred for a few hours and filtered, and 25 mL of ether added to the filtrate. After stirring for 1 h, the white solid was filtered off, washed with ether, and dried as above. Anal. Calcd for $ZnCl_2(NMTF)_2$: C, 16.8; H, 3.5; N, 9.8; Cl, 24.8; Zn, 22.8; S, 22.3. Found: C, 17.2; H, 3.6; N, 9.5; Cl, 24.5; Zn, 22.5; S, 22.1. Anal. Calcd for $ZnCl_2(TBTF)_2$: C, 32.4; H, 5.9; N, 7.6; Cl, 19.1; Zn, 17.7; S, 17.3. Found: C, 30.1; H, 5.7; N, 7.0; Cl, 21.8; Zn, 19.4; S, 14.9.

Reaction Studies. Semiquantitative studies of the reaction of the metal complexes with the various electrophiles were performed in the apparatus employed by Crabtree, Poziomek, and Hoy[6] for the colorimetric detection of alkyl isocyanides. The reagents were mixed and allowed to react at room temperature, and the presence of isocyanide was determined by a white to blue color change in the detector tube. The yield of isocyanide can be semiquantitatively estimated from the intensity of the color. The lowest detectable amount of methyl isocyanide is approximately 0.1 μg.

Analyses. All elemental analyses were performed by the Analytical Branch, Chemical Systems Laboratory, Aberdeen Proving Ground, MD.

Results and Discussion

The mechanism in the dehydration of the formamide by an electrophile (EX) is undoubtedly a nucleophilic attack by the formyl oxygen followed by an elimination (eq 1). Coordination of the formamide oxygen by metal, as mentioned above, should increase the importance of resonance form II relative to I. This should weaken the C–O bond and also cause the oxygen to become more negative, causing an enhancement in reactivity. However, the reverse was observed.[1] The octahedral nitrate and perchlorate salts of $M(NMF)_6{}^{2+}$ did not react with tosyl chloride, which itself does react directly with NMF. The lack of reactivity of the octahedral complexes can be attributed to steric hindrance of the approach of the sulfur atom of the tosyl chloride to the formamide oxygen. However, in the (approximately) square-planar copper complex,[1] no such hindrance exists.



$$CH_3-\underset{\cdot\cdot}{\overset{H}{N}}-\overset{H}{C}=O + E-X \longrightarrow \left[CH_3-\underset{+}{\overset{H}{N}}=\overset{H}{C}-OE + X^-\right]$$

$$CH_3-\underset{+}{N}\equiv\underset{-}{C} + EOH \longleftarrow CH_3-N=\overset{H}{C}-OE + HX \qquad (1)$$

Following the preparation of the nitrate and perchlorate complexes of NMF, a number of chloride complexes were

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(1) R. A. Mackay and E. J. Poziomek, *Inorg. Chem.*, **7**, 1454 (1968).
(2) I. Ugi, U. Fetzer, M. Knupfer, and K. Offerman, *Angew. Chem., Int. Ed. Engl.*, **4**, 472 (1965).
(3) R. A. Mackay and E. J. Poziomek, *J. Chem. Eng. Data*, **14**, 271 (1969).
(4) P. L. DeBennevile, J. S. Strong, and V. T. Elkind, *J. Org. Chem.*, **21**, 772 (1956).
(5) R. Willstatter and T. Wirth, *Ber, Dtsch. Chem. Ges.*, **42**, 1908 (1909).
(6) E. V. Crabtree, E. J. Poziomek, and D. J. Hoy, *Talanta*, **14**, 857 (1967).

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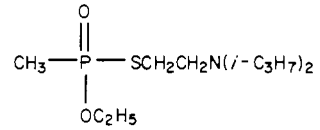
Table I. Reaction of Zinc(II)–NMF Complexes with *O*-Ethyl *S*-[(Diisopropylamino)ethyl]methylphosphonothioate in NMF

compd	result[a]	compd	result[a]
$Zn(NMF)_6(ClO_4)_2$	neg	$ZnCl_2 \cdot nH_2O$	++
$ZnCl_2(NMF)_2$	+++	10% aqueous $ZnCl_2$	+
$ZnBr_2(NMF)_{2.3}$	++++	$Zn(ClO_4)_2$ + NaI	++++
$ZnI_2(NMF)_2$	+++++	$Zn(ClO_2)_2$ + KF	+

[a] The intensity is indicated by the number of + signs. The test was performed after a reaction time of 1 min.

synthesized,[3] and it was discovered that the $ZnCl_2(NMF)_2$ complex did in fact react with tosyl chloride in 1-butanol. Since some of the complexes tend to dissociate to various extents when dissolved in solvents such as butanol or nitromethane and since NMF reacts directly with tosyl chloride, the results were questionable. Therefore, another electrophile was chosen which does not react directly with the free ligand. This electrophile is *O*-ethyl *S*-[(diisopropylamino)ethyl]methylphosphonothiolate (III).



$$CH_3-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{O}{\|}}{P}}-SCH_2CH_2N(i\text{-}C_3H_7)_2$$

III

A number of metal chloride complexes of NMF were allowed to react with III without solvent in one case and in NMF in the other. These are $MgCl_2(NMF)_4{\cdot}2H_2O$, $MnCl_2(NMF)_2$, $FeCl_2(NMF)_{2.5}$, $CoCl_2(NMF)_3$, $NiCl_2(NMF)_4$, $CuCl_2(NMF)_2$, and $ZnCl_2(NMF)_2$. (It should be noted that III does not react with any of the octahedral nitrate or perchlorate salts or the copper perchlorate salt.) Again, there is no reactivity of any of the (psuedo) *octahedral* chloride complexes or of the copper complex. However, the zinc complex, which is presumably tetrahedral, promotes the dehydration of NMF by III. The only other positive result, albeit weak, is for $CoCl_2(NMF)_3$ in NMF. In the solid, this compound has the structure $[Co(NMF)_6][CoCl_4]$,[3] and its lack of reactivity is therefore not surprising. In nitromethane, conductance data indicate that disproportionation to a tetrahedral species is occurring (eq 2). Dissolution in NMF leads to $Co(NMF)_6^{2+}$

$$\underset{\text{solid}}{[Co(NMF)_6][CoCl_4]} \xrightarrow{CH_3NO_2} \underset{\text{tetrahedral}}{2[Co(NMF)_2Cl_2]} + 2NMF \tag{2}$$

in dilute solution and a mixture containing some tetrahedral species $[Co(NMF)_xCl_{4-x}]^{2-x}$ in more concentrated solution.[3] This again leads to the conclusion that a tetrahedral species is a necessary (but not sufficient) condition for reaction.

Zinc Halide Complexes. Since only the zinc chloride complex exhibited appreciable reactivity, attempts were made to synthesize the set of complexes $ZnX_2(NMF)_2$ (X = F, Cl, Br, I) in order to gain additional information on the reaction mechanism. The iodide and bromide complexes were prepared, the latter apparently containing some lattice NMF. Attempts to isolate a fluoride complex were unsuccessful. The results of the reaction of the zinc halide compounds with III in NMF are given in Table I. A few points are immediately evident. First, the order of reactivity, perhaps initially somewhat surprising, is I > Br > Cl. Second, formation of a complex in situ by adding the ZnX_2 salt directly to NMF gives essentially the same result. This indicates that the complete order is I > Br > Cl > F. Third, increasing the water content decreases the reactivity. Presumably this is a result of displacement of ligand by water.

Reaction Mechanism. The above results permit us to draw some conclusions concerning the mechanism of the reaction between electrophile and coordinated (NMF) ligand. We consider the following three principal mechanisms: (i) direct attack on (formamide) oxygen; (ii) coordination to zinc, followed by attack on oxygen; (iii) coordination to zinc by displacement of halide, followed by attack on oxygen. Mechanism i should result in enhanced reactivity with increasing electronegativity of X (F > Cl > Br > I), while the reverse order is observed. Also, it does not explain the lack of reactivity of the copper complexes. Mechanism ii is consistent with the latter, since coordination of a fifth (weak) ligand is not expected. However, for the zinc complexes, this would lead to a five-coordinate complex which from both electronic and steric considerations should become more reactive as the halide becomes more electronegative. Thus, mechanism iii seems to be the best candidate at present since it is consistent not only with the copper result but also with the expected ease of displacement of the halide leaving group.

Thioformamide Complexes. The two thioformamide $ZnCl_2$ complexes are coordinated via the sulfur atom as shown by their infrared spectra. The spectra are consistent with those expected for N-substituted thioformamides.[7,8] The observed shift of the C=S bond is from 957 ± 4 cm^{-1} in free TBTF to 915 ± 4 cm^{-1} in the complex. Similar directional shifts have been reported for transition metal–thioacetamide complexes.[8] Thioformamides are weaker nucleophiles and even complexation does not lead to reactivity of either the TBTF or the NMTF complex with III. The NMTF does react with tosyl chloride but not to produce isocyanide. However, the $ZnCl_2(NMTF)_2$ complex in DMF does react with tosyl chloride to produce some isocyanide.

In summary, a number of metal nitrate, perchlorate, and chloride complexes (M = Mg, Mn, Co, Ni, Cu, Zn) of *N*-methylformamide have been reacted with the electrophile *O*-ethyl *S*-[(diisopropylamino)ethyl]methylphosphonothioate (III). Only the $ZnCl_2$ complex reacted to produce isocyanide. For the series of $ZnX_2(NMF)_2$ complexes (X = halogen) the order of reactivity was I > Br > Cl > F. It is concluded that the mechanism of reaction involves coordination of the electrophile with displacement of the halide, followed by reaction of the two coordinated ligands.

Registry No. III, 50782-69-9; $ZnBr_2(NMF)_2$, 32371-45-2; $ZnCl_2(NMF)_2$, 26250-62-4; $ZnI_2(NMF)_2$, 26250-63-5; $ZnF_2(NMF)_2$, 77827-60-2; $ZnCl_2(NMTF)_2$, 77827-61-3; $ZnCl_2(TBTF)_2$, 77827-62-4; TBTF, 20278-31-3; *tert*-butylformamide, 2425-74-3.

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(7) C. N. R. Rae, R. Venkataraghavan, and T. R. Kasturi, *Can. J. Chem.*, **42**, 36 (1964).

(8) Isao Suzuki, *Bull. Chem. Soc. Jpn.*, **35**, 1456 (1962).

(9) C. D. Flint and M. Goodgame, *J. Chem. Soc A*, 750 (1968).

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Formation of $[Co(en)_2(glyO)]^{2+}$ from Monodentate *trans*-$[Co(en)_2(H_2O/OH)(glyO/H)]^{3+/2+/+}$ Species

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Recently we have shown[1] that *cis*-$[Co(en)_2(OH_2)(gly\text{-}OH)]^{3+}$, *cis*-$[Co(en)_2(OH_2)(gly\text{-}O)]^{2+}$, and probably *cis*-$[Co(en)_2(OH)(gly\text{-}O)]^{+}$ react intramolecularly, with the ad-

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