Metal(II) Chloride Complexes of *N*-Methylformamide

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The preparation and properties of some *N*-methylformamide complexes of MCl_2 (M = Mg, Mn, Co, Ni, Cu, Zn, and Cd) are described.

IN THE course of studies on reactions of coordinated formamides (*1*), a series of metal chloride complexes of *N*-methylformamide (NMF) was prepared and characterized. The compounds and analytical data are given in Table I. A number of physical properties are given in Table II. The shift of the carbonyl stretching bands to lower frequency relative to NMF shows that coordination occurs via oxygen (*1*). The structures of the Co, Ni, and Cu complexes are based on electronic spectra (Table III). The complexes are hydrolyzed by water, and are at least somewhat soluble in polar organic solvents—e.g., ethanol, nitromethane, and butanol—except that the manganese compound is generally insoluble.

Table I. Analyses

	Found					Calculated				
Compound	C	H	N	Cl	M	C	H	N	Cl	M
$MgCl_2(NMF)_4(H_2O)_2$	26.6	6.7	14.9	19.8	6.2	26.2	6.5	15.2	19.3	6.6
$MnCl_2(NMF)_2$	19.4	4.9	11.7	29.2	13.4	19.7	4.1	11.5	29.1	13.1
$CoCl_2(NMF)_3$	24.0	5.2	13.5	23.9	18.9	23.4	4.9	13.7	23.2	19.2
$NiCl_2(NMF)_4$	26.1	5.8	15.2	19.7	16.5	26.2	5.5	15.3	19.4	16.1
$CuCl_2(NMF)_2$	18.9	4.0	11.5	28.3	25.2	19.0	4.0	11.1	28.1	25.1
$ZnCl_2(NMF)_2$	19.3	3.9	10.5	28.2	25.7	18.9	3.9	11.0	27.9	25.7
$ZnI_2(NMF)_2$	11.0	2.3	6.0	57.9[a]	14.7	11.0	2.3	6.4	58.1[a]	14.9
$CdCl_2(NMF)_2$	15.7	3.4	9.2	23.9	37.4	15.9	3.3	9.3	23.6	37.3

[a] Iodine.

Table II. Physical Properties

Compound	Probable Structure	$\nu_{c=0}$[a]	$\Delta\nu_{c=0}$[b]	M.P., ° C.	Color	Hygroscopic
$[Mg(NMF)_4Cl_2]\cdot 2H_2O$	Octahedral	1666	−6	130–34[c]	White	No
$MnCl_2(NMF)_2$	Octahedral-polymeric	1654	−18	129[d]	Light pink	Yes
$Co(NMF)_3Cl_2$	$[Co(NMF)_6][CoCl_4]$ (oct) (tet)	1650	−22	130–32	Blue	No
$[Ni(NMF)_4Cl_2]$	Octahedral	1646	−26	127[b]	Yellow	Yes
$[Cu(NMF)_2Cl_2]$	Square planar or tetragonal	1642	−30	112[b]	Green	Slightly
$[Zn(NMF)_2Cl_2]$	Tetrahedral	1650	−22	88–90	White	No
$[Zn(NMF)_2I_2]$	Tetrahedral	1645	−27	76–80[c]	White	No
$[Cd(NMF)_2Cl_2]$	Tetrahedral	1653	−19	>250	White	No

[a] $Cm.^{-1}$. Errors on frequencies ca. ±4 $cm.^{-1}$. Spectra run as Nujol mulls between KRS-5 windows on Perkin-Elmer 257 spectrophotometer. [b] $\Delta\nu = \nu_{NMF} - \nu$ complex. $\nu_{NMF} = 1672$ $cm.^{-1}$. [c] Softens over wide range. [d] Decomposes without melting.

Table III. Electronic Spectra[a]

$CoCl_2(NMF)_3$			$NiCl_2(NMF)_4$		$CuCl_2(NMF)_2$
(mw)	1612		(mw)	1257	810 (broad)
	1558	(sh-b)			
			(m)	710	
				790	
(s)	698		(ms)	421	
	670				
	650				
	630				
	616	(sh)			
(w)	533				
	516	(sh)			
	459	(sh)			

[a] Solids as Nujol mulls on Cary 14 spectrophotometer: w = weak, m = medium, s = strong, sh = shoulder, b = broad. Range 300 to 1700 mμ.

The electronic spectra were obtained as Nujol mulls of the solids, since there is evidence that changes in species occur in solution. For example, in the case of $CoCl_2(NMF)_3$, the electronic spectrum of the solid, compared with the spectra of $[Co(NMF)_6]^{2+}$ and $(CoCl_4)^{2-}$, indicates that the solid has the structure $[Co(NMF)_6][CoCl_4]$. If the compound is dissolved in NMF, the $(CoCl_4)^{2-}$ species is attacked by the formamide. In dilute solution, only $Co(NMF)_6^{2+}$ and free chloride ion are present. In nitromethane, only a tetrahedral species is present, which is not $(CoCl_4)^{2-}$. In addition, the solution is nonconducting. This may be explained by the disproportionation:

$$[Co(NMF)_6][CoCl_4] \xrightarrow{CH_3NO_2} 2\,[Co(NMF)_2Cl_2] + 2\,NMF$$

Since these complexes are subject to possible solvolysis and rearrangement, depending on the solvent, mull spectra were used for characterization purposes.

Table IV. Synthetic Procedure

Metal Salt[a]	Step					Recovery of Product[b]
	1	2	3	4	5	
$MgCl_2$	20 ml. NMF, stir until dissolved	10 ml. EOF, stir 1 hr.	Triturate 3-4 times with 50-ml. portions of ether	Add 5 ml. abs. alc., stir 10 min.	Add 10 ml. ether, stir until obtain fine power	1
$MnCl_2$	6 ml. NMF, dissolve	5 ml. EOF, stir 1 hr.	50 ml. ether, stir 1 hr., decant off, repeat	Add 5 ml. abs. alc., stir ½ hr., add 10 ml. ether, stir	Scrape solid off walls, crush, and stir until obtain fine powder	1
$CoCl_2$	5 ml. NMF, dissolve	5 ml. EOF, stir 1 hr.	Add 50 ml. ether, stir ½ hr., decant off ether	Add 5 ml. abs. alc., stir 10-15 min.	Add 25 ml. ether, stir overnight	2
$NiCl_2$	20 ml. EOF, heat, stir 1 hr.	Slowly add 20 ml. NMF, stir vigorously	Initially obtain green gelatinous solid, stir	After 1-2 hr., obtain fine yellow powder	Stir until no trace of green solid remains	2
$CuCl_2$	10 ml. NMF, dissolve	5 ml. EOF, stir 1 hr.	Add 25 ml. ether, stir	Obtain green powder continue stirring 1-2 hr.		2
$ZnCl_2$	5 ml. NMF, dissolve	5 ml. EOF, stir 1 hr.	Add 15 ml. ether, stir overnight	Filter, wash solid with ether, dry in vac.	Recrystallize from benzene	3
$CdCl_2$	7 ml. NMF, 1 ml. H_2O, stir ½ hr.	Obtain thick paste, strong stirring needed	10 ml. EOF, stir 1½ hr.	Add 10 ml. abs. alc. stir overnight		4
ZnI_2	1 ml. NMF and 29 ml. ether	Stir overnight				2

[a] Use 0.01 mole of appropriate hydrated metal salt. [b] Filter, wash, and dry in vacuum. 1. Wash with mixture of 5 ml. alc. + 10 ml. ether, then with ether. 2. Wash with ether. 3. Wash with benzene, then with ether. 4. Wash with alcohol, then with ether.

The synthesis of these complexes generally consisted of dissolution of the hydrated metal chloride in NMF and dehydration with ethyl orthoformate (EOF), followed by the recovery of the complex, usually by addition of ether. The procedures and quantities of reagents used are summarized in Table IV.

LITERATURE CITED

(1) Mackay, R. A., Poziomek, E. J., *Inorg. Chem.* 7, 1454 (1968).

RECEIVED for review July 29, 1968. Accepted December 23, 1968. Elemental analyses performed by the Analytical Research Department, Chemical Research Laboratory, Edgewood Arsenal, Md. 21010.

Synthesis of Hydrazonium Salts

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The trimethylhydrazonium iodide, chloride, hexachlorostannate, tosylate, and fluoborate salts of benzaldehyde, 4′-nitrobenzaldehyde, anisaldehyde, and 2′,4′-dichlorobenzaldehyde (I) have been prepared and characterized. Similarly, the iodide, chloride, hexachlorostannate, hexafluorophosphate, tetrafluoborate, perchlorate, nitrate, and tosylate bistrimethylhydrazonium salts of glutaraldehyde (II) and trimethylhydrazonium salts of 4-cyano-2,2-dimethylbutyraldehyde (III) have been prepared and characterized. In addition, the bromide and hexafluoroarsenate salts of II are reported. Infrared and NMR data on these compounds are included.

RECENT interest in the chemistry of hydrazonium salts (*5, 6, 7*) prompts this report. As a part of another study, various trimethylhydrazonium salts of benzaldehyde, 4′-nitrobenzaldehyde, anisaldehyde, 2′,4′-dichlorobenzaldehyde (I), glutaraldehyde (II), and 4-cyano-2,2-dimethylbutyraldehyde (III) have been prepared by alkylation of the corresponding dimethylhydrazones (Figure 1). All of these are new compounds except Ia and Ic, *p*-toluenesulfonates (tosylates), and Ib, iodide (*7*).

The structures of these compounds were assigned on the basis of their accurate elemental analyses and infrared and nuclear magnetic resonance spectra (Table I). The chloride salts did not all analyze correctly because of their hygroscopic nature. Their structures are assigned on the basis of spectroscopic evidence (Table I) and the fact that they were readily converted to the corresponding hexachlorostannates. In the infrared, the $>C{=}N-$ absorption was independent of the anion, but in the aromatic salts it varied with the electronegativity of the ring substituent (Table I), the more electronegative groups shifting the