bonded water in the second coordination sphere would be in a prime position to occupy the vacant site.

The loss of a proton to produce a hydroxo ligand on the pentacoordinated species made by the reaction of *cis-* or *trans*-aquoazido would facilitate π-bonding between cobalt and oxygen and possibly lead to a trigonal bipyramid intermediate and different product distribution than for the corresponding aquo pentacoordinated ions. However, for neither isomer does varying the hydrogen ion over the range 0.90–0.03 M significantly alter the over-all product distribution. In light of this behavior either the hydroxo path does not make a significant contribution or the hydroxo path leads to a product distribution similar to that for the aquo ligand path.

The present results are consistent with but do not prove formation of a five-coordinated intermediate. Further work is in progress attempting to produce, by other methods, the intermediate species postulated here.

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Acyclic Imides as Ligands. I. Diacetamide Complexes of Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Perchlorates

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Diacetamide is shown to form a series of new complexes having the general formula $[M(C_4H_7O_2N)_3](ClO_4)_2$, where M = Mn(II), Fe(II), Co(II), Ni(II), or Zn(II). The compound $[Cu(C_4H_7O_2N)_2](ClO_4)_2$ is also reported. Infrared studies demonstrate that diacetamide assumes the *trans-trans* configuration upon complexation to the metal ions with coordination occurring through oxygen. Magnetic and visible–near-infrared spectral data are as expected for octahedral complexes with weak field ligands. Conductivity data indicate that each of the complexes is a 1:2 electrolyte in dilute acetone solution.

Introduction

Considerable study has been made of the complexing ability of the amide linkage over the past few years. Recent publications by Bull,[1] Drago,[2] and Rollinson[3] and their various co-workers have illustrated the great range of amide-to-metal ion complexes which may be prepared. Lindquist[4] has included a list of amide-containing complexes in his recent summary of compounds involving oxygen-donating ligands. A perusal of these references reveals that nearly all of the amide complexes which have been reported are complexes of simple organic amides, whereas very few references are made to the complexing abilities of acyclic imides. Of outstanding interest in this regard have been the recent crystallographic examinations of some biuret ($NH_2CONHCONH_2$) complexes of cadmium(II), mercury(II), copper(II), and zinc(II). Whereas bis(biuret)cadmium chloride and bis(biuret)mercury(II) chloride have been shown to exist as infinite chains in the crystalline state[5] with the biuret molecules serving as monodentate ligands, the corresponding zinc(II) and copper(II) compounds are true molecular adducts with the biuret molecules serving as neutral chelating ligands with bond formation occurring exclusively through oxygen.[6] To our knowledge, the only reported complexes derived from acyclic imides are a 1:1 adduct between tin(II) chloride and N-phenyldiacetamide (N,N-diacetylaniline)[7] and bis(dibenzamido)copper(II).[8] We wish to report here some of our investigations on the complexing capability of diacetamide ($CH_3CONHCOCH_3$) with a series of dipositive transition metal ions.

Experimental

Reagents.—Diacetamide was prepared and purified according to the method of Polya and Tardrew.[9] Hydrated metal perchlorates were used as obtained from the G. Frederick Smith Co. Ethyl acetate (Baker Analyzed reagent), nitromethane (Matheson Coleman and Bell, Spectrograde), and absolute ethanol were used as received. Acetone (Baker Analyzed) was stored over Drierite and distilled as needed.

Preparation of Complexes.—The following general procedure was used for the preparation of the diacetamide complexes. Separate solutions of 0.010 mole of the metal perchlorate hydrate in 25 ml. of ethyl acetate and 4.04 g. (0.040 mole) of diacetamide in 25 ml. of ethyl acetate were filtered into a common receiver. Precipitation of the solid complexes usually began immediately.

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[1] W. E. Bull, S. K. Madan, and J. E. Willis, *Inorg. Chem.*, **2**, 303 (1963).

[2] J. H. Bright, R. S. Drago, D. M. Hart, and S. K. Madan, *ibid.*, **4**, 18 (1965), and references cited therein.

[3] C. L. Rollinson and R. C. White, *ibid.*, **1**, 281 (1962).

[4] I. Lindquist, "Inorganic Adduct Molecules of Oxo-compounds," Academic Press, New York, N. Y., 1963.

[5] L. Cavalca, M. Nardelli, and G. Fava, *Acta Cryst.*, **13**, 594 (1960).

[6] M. Nardelli, G. Fava, and G. Giraldi, *ibid.*, **16**, 343 (1963).

[7] J. F. J. Dippy and V. Moss, *J. Chem. Soc.*, 2205 (1952).

[8] H. Ley and F. Werner, *Ber.*, **46**, 4040 (1913).

[9] J. B. Polya and P. L. Tardrew, *J. Chem. Soc.*, 1081 (1948).

TABLE I

ANALYSES[a] AND YIELDS OF DIACETAMIDE COMPLEXES

Complex	C, %		H, %		N, %		Metal, %		Yield,	Color
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	%	
$[Mn(C_4H_7O_2N)_3](ClO_4)_2$	25.8	26.1	3.77	3.88	7.54	7.49	9.85	9.93	78	White
$[Fe(C_4H_7O_2N)_3](ClO_4)_2$	25.8	25.6	3.76	4.19	7.52	7.55	10.01	10.22	85	Yellow-green
$[Co(C_4H_7O_2N)_3](ClO_4)_2$	25.7	25.8	3.74	4.44	7.48	7.54	10.52	10.40	77	Pink
$[Ni(C_4H_7O_2N)_3](ClO_4)_2$	25.7	26.2	3.75	3.92	7.50	7.55	10.46	10.33	100	Pale blue
$[Cu(C_4H_7O_2N)_2](ClO_4)_2$	20.7	20.8	3.02	4.05	6.04	6.00	13.60	13.54	82	Blue
$[Zn(C_4H_7O_2N)_3](ClO_4)_2$	25.4	25.6	3.71	4.23	7.42	7.57	11.53	11.40	79	White

[a] Performed by Professor V. B. Fish, Lehigh University.

After approximately 10 min., the solid complex was collected by filtration and washed with five 10-ml. portions of anhydrous ether to remove ethyl acetate and residual diacetamide. Residual solvent and water were removed by placing the samples under vacuum at less than 0.01 mm. at room temperature for at least 24 hr. All samples were stored in a desiccator over Drierite as they are slightly hygroscopic. The yields, colors, and analyses of the samples are given in Table I. The presence of water in the complexes in quantities too small to affect carbon, nitrogen, and metal analyses will be considered in the discussion of the infrared spectra. The high hydrogen analyses may represent water absorption during weighing and prior to analysis.

Spectrophotometric Measurements.—Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer in the region 2–15 μ. The complexes were examined as mulls in Nujol oil and hexachlorobutadiene and as potassium bromide disks. The copper(II) complex underwent a color transformation from blue to red-brown upon grinding with potassium bromide; mulls of this compound appeared normal. We report here only frequencies determined on mulled samples since these should be more representative of the complexes than would frequencies obtained in the potassium bromide disks which have led to difficulties in numerous instances. Nujol oil was dried by percolation through anhydrous activated alumina and hexachlorobutadiene was dried by distillation from calcium hydride.

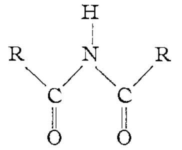
Electronic spectra in the visible and near-infrared regions were obtained with a Beckman DK-2A quartz prism ratio recording spectrophotometer. Spectra were obtained of acetone solutions in 1-cm. quartz cells. Certain other solvents could not be employed. The complexes were destroyed immediately by acetonitrile and water, rapidly by nitromethane, and over varying periods up to a few hours by ethanol. Solutions in acetone appeared to be stable indefinitely as there was neither a visible change upon dissolution nor a change in the electronic spectrum as a function of time.

Conductance Measurements.—Although acetone has a relatively low dielectric constant, it was necessary that conductance measurements be carried out in this solvent for the reasons outlined above. A normal bridge circuit consisting of a Freas conductance cell, Leeds and Northrup potentiometer, and oscilloscope was used for the conductance measurements.

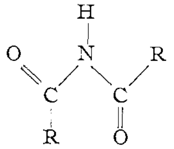
Susceptibility Measurements.—Magnetic measurements were made with a permanent magnet (4200 gauss) on solid samples in Pyrex tubes which had been calibrated[10] with mercury(II) tetrathiocyanatocobaltate(II) and Mohr's salt.

Results and Discussion

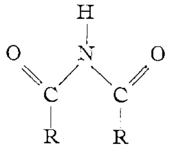
LaPlanche and Rogers[11] have conclusively demonstrated that the favored configuration of the peptide bond in N-monosubstituted amides is the *trans* form, in which the hydrogens on the amide nitrogen and the carbonyl oxygen are *trans* to each other about a carbon–nitrogen bond with a bond order presumably greater than one. Furthermore, they have shown that at room temperature formamide derivatives may exist in the *cis* form at concentrations up to 18%, whereas with acetamide derivatives or more complicated species the *trans* form is found exclusively. Uno and Machida[12] had previously shown in their infrared studies that the peptide bonds in certain acyclic imides (diamides) also exist in the *trans* form. Thus, N-acetylpropionamide, dipropionamide, N-propionyl-*n*-butyramide, and di-*n*-butyramide, appear to exist exclusively in the *trans-trans* planar configuration (I).



trans-trans
I



cis-trans
II



cis-cis
III

The *cis-cis* configuration (III) is found only in cyclic imides such as succinimide and phthalimide. In contrast, the preferred configuration of diacetamide (R = CH_3) is the *cis-trans* form (II), as shown by infrared[13] and an X-ray study.[14] A second modification was isolated and it apparently is the *trans-trans* isomer. This second form reverts to the *cis-trans* isomer slowly on standing in the solid state and immediately upon dissolution in organic solvents. When the *cis-trans* form is mulled in the presence of small quantities of alkali halides, slightly different *trans-trans* modifications are formed, which are dependent upon the particular alkali halide used.[15] Compression of *trans-trans*-diacetamide in a potassium bromide disk leads to formation of *cis-trans*-diacetamide.[15] This facile interconversion was interpreted in terms of ion–dipole interactions which must be more exothermic than the hydrogen bonds found for the pure compound in the solid state. It is not unreasonable to expect that transition metal ions should likewise stabilize the *trans-trans* modification of diacetamide. In fact, we have been able to synthesize a series of complexes of diacetamide with the general formula $[M(C_4H_7O_2N)_3](ClO_4)_2$ (M = Mn(II), Fe(II), Co(II), Ni(II), or Zn(II)) and the complex $[Cu(C_4H_7O_2N)_2](ClO_4)_2$ in which *trans-trans*-diacetamide is to be found.

Conductance and Magnetic Measurements.—In Table II are listed molar conductance values of 146 to

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(10) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 415.

(11) L. A. LaPlanche and M. L. Rogers, *J. Am. Chem. Soc.*, **86**, 337 (1964).

(12) T. Uno and K. Machida, *Bull. Chem. Soc. Japan*, **34**, 551 (1961).

(13) T. Uno and K. Machida, *ibid.*, **34**, 545 (1961).

(14) Unpublished results of T. Watanabe and Kasaki presented in ref. 13.

(15) T. Uno, K. Machida, and J. Hamanaka, *Bull. Chem. Soc. Japan*, **34**, 1448 (1961).

167 cm.^{2} ohm^{-1} for these complexes in acetone. Ion association obviously occurs, as evidenced by decreasing conductivities at the higher concentrations. In the light of the elemental analyses and other results to be discussed subsequently, we take these data to indicate that each of these complexes is a 1:2 electrolyte. Holt and Carlin[16] report that 1:1 electrolytes in acetone exhibit molar conductances of approximately 120 cm.^{2} ohm.$^{-1}$.

TABLE II

CONDUCTANCE PROPERTIES OF DIACETAMIDE COMPLEXES IN ACETONE

Compound	Concn., $M \times 10^3$	Molar conductance, cm.^{2} ohm^{-1}
$[Mn(C_4H_7O_2N)_3](ClO_4)_2$	1.0	152
	9.6	105
$[Fe(C_4H_7O_2N)_3](ClO_4)_2$	1.0	159
	2.4	149
$[Co(C_4H_7O_2N)_3](ClO_4)_2$	1.0	147
	8.4	105
$[Ni(C_4H_7O_2N)_3](ClO_4)_2$	1.0	146
	9.0	97
$[Cu(C_4H_7O_2N)_2](ClO_4)_2$	1.0	167
	3.0	144
$[Zn(C_4H_7O_2N)_3](ClO_4)_2$	1.0	157
	8.2	106

The magnetic properties of these complexes in the solid state near room temperature are given in Table III. The magnetic moments are believed accurate to ±0.10 B.M. There is no irregularity in the magnetic moments as the values for the Mn(II), Fe(II), Co(II), and Ni(II) complexes are within the ranges commonly observed for maximum spin octahedral complexes. The magnetic moment for the Cu(II) complex is also reasonable.

TABLE III

MAGNETIC PROPERTIES OF DIACETAMIDE COMPLEXES

Compound	Dia. cor. $\times 10^6$ c.g.s.u.[a]	χ_M cor. $\times 10^6$ c.g.s.u.	μ, B.M.[b]	T, °K.
$[Mn(C_4H_7O_2N)_3](ClO_4)_2$	193	15,369	6.06 ± 0.04	299
$[Fe(C_4H_7O_2N)_3](ClO_4)_2$	193	12,445	5.45 ± 0.03	298
$[Co(C_4H_7O_2N)_3](ClO_4)_2$	193	11,400	5.20 ± 0.06	296
$[Ni(C_4H_7O_2N)_3](ClO_4)_2$	193	4,151	3.14 ± 0.02	296
$[Cu(C_4H_7O_2N)_2](ClO_4)_2$	150	1,892	2.12 ± 0.03	296

[a] Approximated from values given in ref. 10. [b] $\mu_{eff} = 2.84\sqrt{\chi_M T}$ B.M.; average of two determinations.

Infrared Spectra.—Evidence of the mode of bonding of diacetamide to the various metal ions is provided by infrared spectroscopy. The infrared frequencies for these complexes are given in Table IV with the frequencies reported by Uno and Machida[13] for the *trans-trans* and *cis-trans* forms of diacetamide. An infrared spectrum of tris(diacetamide)nickel(II) perchlorate is shown in Figure 1. The first observation to be made of the data in Table IV is the remarkable correspondence between the spectra observed for the complexes and that reported for the *trans-trans* form of diacetamide. Noteworthy similarities are (1) a doublet in the N—H stretching region and (2) a single strong C=O stretching band near 1730 cm.$^{-1}$ with a weaker shoulder or side band near 1690 cm.$^{-1}$. By comparison, *cis-trans*-diacetamide exhibits a triplet in the N—H stretching region and a strong doublet in the 1730 cm.$^{-1}$ region. The *cis-trans* isomer also shows a very strong band at 1310 cm.$^{-1}$, a region in which *trans-trans*-diacetamide and the metal complexes exhibit nearly complete transmittance. We are certain that in the complexes reported here, diacetamide is to be found exclusively in the *trans-trans* form.

The most reasonable method of attachment of a *trans-trans*-diacetamide molecule to a transition metal ion is by chelation through the two amide oxygen atoms. The structural similarity of the ligand in this position to that found for the isoelectronic acetylacetonato ion is readily apparent. Of course, electron delocalization is expected to be considerably smaller in the diacetamide complexes than in the acetylacetonato complexes, since the mutual attraction between the metal ion and the amide oxygen atom is primarily electrostatic. The criterion for the existence of bonding through oxygen in amide complexes is the lowering of the carbonyl stretching mode. Under C_{2v} symmetry, *trans-trans*-diacetamide should exhibit symmetric and asymmetric stretching carbonyl modes. For *trans-trans*-diacetamide in Nujol and hexachlorobutadiene, the imide I_s band (symmetric stretch) and the imide I_a band (asymmetric stretch) appear at 1734 and near 1695 cm.$^{-1}$, respectively. The imide I_a band for the free ligand was difficult to locate accurately.[13] However, in the Co(II), Fe(II), and Ni(II) complexes studied here, the imide I_s band appears sharper when compared to the free ligand and the imide I_a band is sufficiently separated from the imide I_s band to be resolved. In each of the complexes studied, the imide I_s band of the ligand is shifted to a lower frequency by 8–15 cm.$^{-1}$, relative to *trans-trans*-diacetamide in the solid state, except in the case of Cu(II), where a shift of about 29 cm.$^{-1}$ is found. These frequency shifts are quite small relative to those normally observed for the carbonyl stretching mode in amide complexes.[17] Comparisons of these frequency shifts are difficult to make since coupling of vibrational modes for diacetamide is extensive in the *trans-trans* form and electron delocalization is less extensive in diacetamide than in amides. The latter point is substantiated by the observation

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(16) S. L. Holt, Jr., and R. L. Carlin, *J. Am. Chem. Soc.*, **86**, 3017 (1964).

(17) In ref. 1, frequency shifts of 32–72 cm.$^{-1}$ were reported for N,N-dimethylacetamide complexes of various amides.

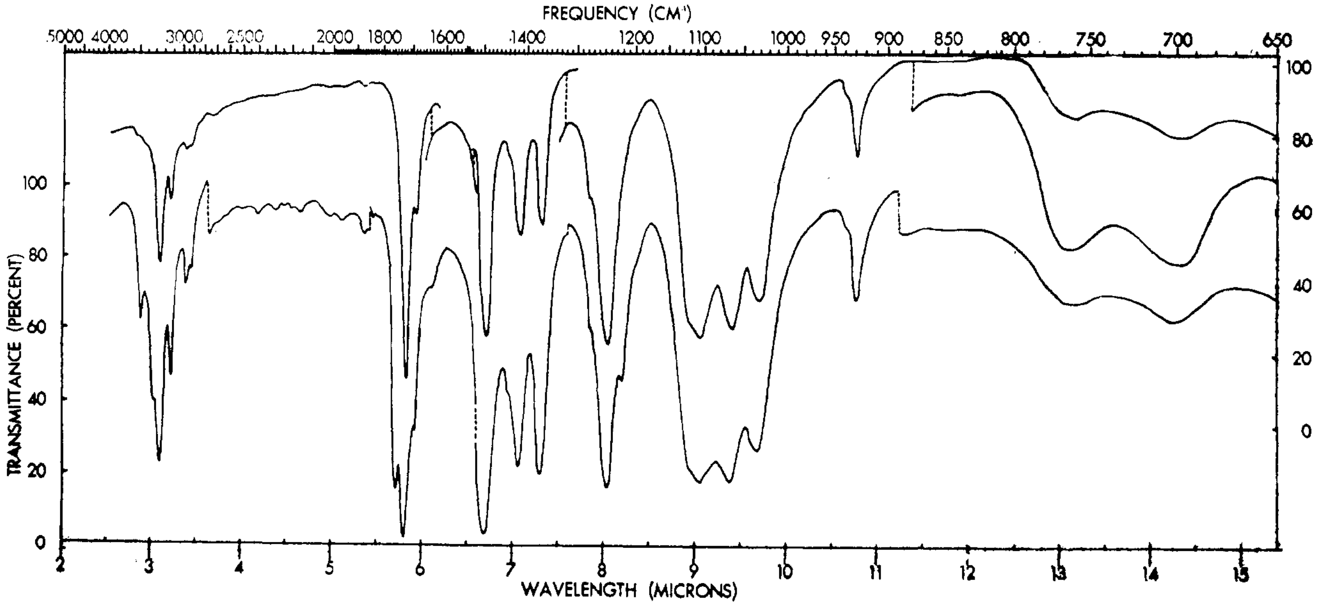

Figure 1.—The infrared spectrum of $[Ni(C_4H_7O_2N)_3](ClO_4)_2$. Lower curve: insufficiently dried sample which shows effect of water on the spectrum. Upper curve: same sample as lower curve after 24 hr. under vacuum at 0.010 mm. Hexachlorobutadiene mull: upper curve, 4000–1620 and 1530–1300 cm.$^{-1}$; lower curve, 4000–1850 and 1500–1300 cm.$^{-1}$. Nujol mull: upper curve, 1670–1520 and 1330–650 cm.$^{-1}$ with two concentrations from 880 to 650 cm.$^{-1}$; lower curve, 1850–1510 and 1320–650 cm.$^{-1}$.

Table IV

Infrared Spectra (cm.$^{-1}$) of Diacetamide Complexes[a]

						trans-trans-Diacetamide		*cis-trans*-Diacetamide	
Mn	Fe	Co	Ni	Cu	Zn	Frequencies[b]	Assignments[b]	Mull[b]	CCl_4 soln.
3268 m	3258 m	3278 m	3264 m	3196 m	3263 m	3280 s		3270 m	3300 m, sh
							NH str.	3245 m	3215 m
3118 m	3143 w	3160 w	3142 w	3073 m	3123w	3205 s		3190 m	3160 m
	2979 vw	3000 vw	2981 vw			2960 m	CH str.	2995 w	3000 w
2948 vw	2936 vw	2948 vw	2941 vw	2933 m	2940 vw	2920 m		2935 vw	
2740 vw		2755 vw		2741 w			Imide II + imide III	2725 vw	
1720 s	1723 s	1726 s	1725 s	1705 s	1719 s	1734 s	Imide I_s	1734 s	1745 s
								1700 s	1696 s
1692 m, sh	1689 m	1695 m	1693 m	1688 s, sh	1691 w, sh	(1695 w, sh)[c]	Imide I_a	1650 m, sh	1650 m, sh
1508 s	1496 s	1498 s	1497 s	1496 s	1500 s	1505 s	Imide II	1505 s	1497 s
1418 m	1417 m	1420 m	1417 m	1412 m	1416 m	1425 m	CH def.	1426 m	1418 m
1372 m	1372 m	1373 m	1372 m	1372 m	1371 m	1372 m	CH def.	1375 s	1376 s
	1279 w, sh	1277 w, sh	1278 w, sh	1289 w, sh		1295 w, sh	CNC sym. str.	1310 s	1297 s
1258 s	1251 s	1250 s	1250 s	1264 s	1265 s	1236 s	Imide III	1223 s	1214 s
1122 s, sh	1123 s, sh	1121 s, sh	1122 s, sh	1138 s, sh	1135 s, sh	1105	ClO_4^-[d]	1036 s	1029 s
1106 s	1109 s	1110 s	1109 s	1113 s	1105 s	1101	ClO_4^-	1013 m	1008 m, sh
1068 s	1067 s	1067 s	1069 s	1047 s, sh	1067 s	1075	ClO_4^-	836 m	840 w
1026 s	1036 s	1036 s	1038 s	1022 s	1026 s	1035 m	CH_3 wag	816 m	
						936	ClO_4^{-d}[e]		
930 m	932 m	932 m	933 w	928 m	933 m	920	CH_3 wag		
747 m, br	765 w, br	767 m, br	763 w, br	819 w, br	752 w, br	739 m	Imide V		
683 vw	705 m, br	704 m, br	702 w, br	702 vw	688 vw				

[a] $[M(C_4H_7O_2N)_n](ClO_4)_2$ where n is 3 except for copper where n is 2. Reproducibility of frequencies is ±10 cm.$^{-1}$ in the 4000–2500 cm.$^{-1}$ region; ±3 cm.$^{-1}$ in the 1700–650 cm.$^{-1}$ range. Notations: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad. Hexachlorobutadiene mulls: 4000–1650 and 1500–1200 cm.$^{-1}$; Nujol mulls: 2500–1490 and 1300–650 cm.$^{-1}$. [b] Reference 13. [c] Estimated from *trans-trans*-dibutyramide in ref. 12. [d] J. P. Mathieu and L. Mathieu, *Acta Cryst.*, **5**, 571 (1952). [e] Unresolved doublet in mulls; *ca.* 946 and 926 cm.$^{-1}$ in potassium bromide disk.

that secondary amides absorb at 1680–1630 cm.$^{-1}$ in the solid state[18] and diamides absorb at 1740–1700 cm.$^{-1}$.[12] However, in spite of these inherent difficulties, certain comparisons can be made between spectra of amides and diamides. In particular, those vibrations involving the amide hydrogen should be markedly affected by hydrogen-bonding effects in the solid state. The imide II and III bands, near 1500 and 1260 cm.$^{-1}$, respectively, are coupled vibrations involving the C–N–C asymmetric stretching mode and the N–H in-plane deformation. The imide II band arises primarily from the former mode and the imide III band involves mainly the latter mode. Miyazawa, Shimanouchi, and Mizushima[19] have shown that the cor-

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[18] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 205.

[19] T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956).

TABLE V

NEAR-INFRARED AND VISIBLE SPECTRA OF DIACETAMIDE COMPLEXES

Complex	Assignment	ν_{max}, cm.$^{-1}$	ϵ_{max}, l. mole^{-1} cm.$^{-1}$	Dq, cm.$^{-1}$
$[Fe(C_4H_7O_2N)_3](ClO_4)_2$	$^5T_{2g} \rightarrow {}^5E_g$	10,500	7.4	1050
$[Co(C_4H_7O_2N)_3](ClO_4)_2$	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	8,100	4.4	1010
	$\rightarrow {}^4A_{2g}(F)$	19,400	19.5	
	$\rightarrow {}^4T_{1g}(P)$	21,600	12.0	
$[Ni(C_4H_7O_2N)_3](ClO_4)_2$	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	9,000	5.8	900
	$\rightarrow {}^3T_{1g}(F)$	{13,600	4.6	
		14,900	5.8	
	$\rightarrow {}^3T_{1g}(P)$	25,800	11.0	
$[Cu(C_4H_7O_2N)_2](ClO_4)_2$	$^2T_{2g} \rightarrow {}^2E_g$	12,200	21.6	1210

responding amide II and amide III bands of amides are raised in frequency upon hydrogen bonding. Our observations on the diacetamide complexes show the imide II band near 1500 cm.$^{-1}$ to be shifted only very slightly by approximately 0–10 cm.$^{-1}$ to lower frequency and the imide III band is shifted to higher frequency by 14–29 cm.$^{-1}$ compared to the solid state. Both of these frequency shifts would probably be nearer to 0–10 and 25–40 cm.$^{-1}$ to higher frequency if a comparison were possible with spectra of *trans-trans*-diacetamide in dilute solution. The greater shift for the imide III band is to be expected. The out-of-plane N–H bonding mode (imide V) is also observed at higher frequency by 13–28 cm.$^{-1}$ for most of the complexes, whereas for the Cu(II) complex there is a larger shift of 80 cm.$^{-1}$.

The N–H stretching mode is split by Fermi resonance[20] into two bands of equal intensity found at 3280 and 3205 cm.$^{-1}$. In all of the complexes, both bands shift to lower frequency as a result of hydrogen bonding. In addition, the intensity of the lower frequency band is diminished considerably relative to the intensity of the higher frequency band.

We have reproduced in Figure 1 two infrared spectra of tris(diacetamide)nickel(II) perchlorate. The bands at 3500, 3342, 1755, 1630, and 1224 cm.$^{-1}$ observed for the incompletely dry sample may be associated with the presence of water. Lattice water is reported to absorb in the regions 3550–3200 and 1630–1600 cm.$^{-1}$.[21] Coordinated water exhibits absorption in the range 800–1000 cm.$^{-1}$.[21] No absorption was observed for the nickel, iron, and cobalt complexes in the 800–1000 cm.$^{-1}$ region even at very high mull concentration. The manganese and zinc complexes did exhibit extremely weak, broad absorption in this region, which may possibly be due to traces of coordinated water. The bands at 1755 and 1224 cm.$^{-1}$ observed for the nickel complex may indicate the presence of a minor modification of the *trans-trans*-diacetamide ligand in the presence of water. Although the counterpart of the 1224 cm.$^{-1}$ band was not observed for the other metal complexes, a band near 1755 cm.$^{-1}$ was observed for each of the complexes which diappeared after the complexes had been pumped on at 0.010 mm. at room temperature for about 1 day. This band for the zinc complex was diminished considerably, but it did not completely disappear.

Electronic Spectra.—Assigned near-infrared and visible electronic transitions for the diacetamide complexes in acetone solution are given in Table V. Although the complex cations probably have D_3 symmetry, their electronic spectra are extremely similar to those obtained for species with O_h symmetry, and so the assignments have been made on this basis. The Dq values for the Fe(II), Co(II), Ni(II), and Cu(II) complexes have been calculated on the basis of octahedral symmetry. The Dq value for the Cu(II) complex may represent an average field involving two bound diacetamide molecules and acetone molecules.

Although many amide complexes have been reported, the electronic spectral data are most prevalent for Ni(II) complexes. A comparison of the Dq values of various amides demonstrates that *trans-trans*-diacetamide has a larger crystal-field splitting ability than any other amide studied thus far. As shown by Drago and his co-workers,[22] the Dq values for various amides with Ni(II) do not necessarily follow the inductive order for groups bonded to carbon or the amide nitrogen. In fact, steric hindrance appears to be the predominant factor in determining the Dq value of amide ligands and inductive effects are only secondary.

A partial series of amide ligands and their Dq values in cm.$^{-1}$ as determined for amide complexes derived from nickel perchlorate is diacetamide (900) > N,N-dimethylformamide (850)[22] > diethylformamide (840)[22] > valerolactam (833)[2] > acetamide (824)[22] > N,N-dimethylacetamide (769)[22] > N-methyl-δ-valerolactam (759).[2] Thus far, all of the amides studied, with the exception of diacetamide,[23] exhibit Dq values equal to or less than that of water (Dq = 850 cm.$^{-1}$).

The larger value of Dq for diacetamide compared to other amides is excellent evidence for the importance of steric considerations in determining the d-orbital splitting capabilities of ligands. In fact, this steric factor appears to be as important as the sum of inductive and resonance factors. Both inductive and

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[23] Other diamides under study in our laboratories also have equally high Dq values.

resonance factors, which are said to cause buildup of charge on the amide oxygen atoms, are obviously smaller for diacetamide than for the sum of these effects for two amide molecules. Further studies on the importance of inductive and resonance effects in these systems are now being made.

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Bidentate Nitrato Amine Metal Complexes

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Two series of amine metal nitrates have been synthesized. These are $A_2M(NO_3)_2$, where A = isoquinoline, quinoline, and 2-picoline and M = Co(II), Ni(II), Cu(II), and Zn(II), and (isoquinoline)$_4$M(NO_3)$_2$, where M = Co(II) and Ni(II). Electronic spectra, infrared spectra, magnetism, conductivity, and molecular weight studies have been carried out. X-Ray powder photographs indicate that all the quinoline complexes are isomorphous. All the bis-amine complexes are assigned a six-coordinate structure involving bidentate nitrate groups. The tetrakis-isoquinoline derivatives have monodentate nitrate groups. The magnetism and spectra are discussed in terms of the proposed structures.

Introduction

There has been considerable interest during the past few years in the chemistry of the nitrate group because of its versatility as a ligand. It can in principle be ionic, covalent monodentate, covalent bidentate, or act as a bridging ligand in a polymer or in a polynuclear molecule. Examples of all these types of behavior are known to occur in simple nitrates.[1]

Complex transition metal nitrates which include some other ligand in addition to a covalent nitrate group have not been so well characterized. Complexes with triphenylphosphine[2] and its oxide,[3,4] triphenylarsine oxide,[3] hexamethylphosphoramide,[5] benzimidazole,[6] thiourea,[7] trimethylphosphine oxide,[3,8] pyridine N-oxide,[9] and some dimethylpyridines[10,11] have been reported recently, but in few cases are the structures known with certainty. An X-ray structural analysis[8] of dinitratobis(trimethylphosphine oxide)cobalt(II) shows the presence of two bidentate nitrate groups in a *cis* six-coordinate structure. Bidentate nitrate groups have been suggested to occur for various nickel derivatives,[2,5,9,10] but this has not been proven. As can be seen there are few data relating to amine metal nitrates. Of the complexes to be described here, dinitratobis(2-picoline)copper(II)[12] and hydrated dinitratobis(quinoline)copper(II)[13] have been reported briefly before.

Experimental

Preparation.—The bis-amine complexes were prepared by the interaction of the hydrated metal nitrate (1 equivalent) in 2,2-dimethoxypropane with the appropriate amine (2 equivalents). The nitrates were refluxed in the solvent for 0.5 hr. prior to the addition of the amine to ensure the dehydration of the nitrate. The cobalt, nickel, and zinc complexes were recrystallized from acetone or ethanol–2,2′-dimethoxypropane mixtures containing a small amount of the amine. The copper complexes were purified by Soxhlet extraction with dichloromethane. The tetrakis-isoquinoline derivatives were obtained by recrystallization in the presence of a large excess of isoquinoline.

Analyses.—These are listed in Table I. The carbon, hydrogen, and nitrogen analyses were carried out in the microanalytical laboratory of this college under the direction of Mr. Manohin.

Spectrophotometric Measurements.—Near-infrared and visible spectra were obtained with an Optika CF4 double-beam grating spectrometer. Infrared spectra were recorded with a Perkin-Elmer Model 21 instrument using liquid paraffin and hexachlorobutadiene mulls on sodium chloride plates.

Conductivity Measurements.—A Cambridge conductivity bridge was employed. Solutions, measured at room temperature, were not thermostated.

Molecular Weight Determinations.—A Gallenkamp Mod l 7665K semimicro ebulliometer was used. The instrument was calibrated with Analar benzoic acid. A series of five or six measurements was made over a concentration range of 0.025–0.125 *M*, and the molecular weight was determined from the slope of the graph resistance of the thermocouple, proportional to temperature, *vs.* concentration. A good straight line was generally obtained.

Magnetic Measurements.—A Newport Instruments magnetic (Gouy) balance (1.5-in. pole pieces) was employed. The magnetic tubes were calibrated with mercury tetrathiocyanato-

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