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Acrilamide and N,N-Dimethylacrylamide Complexes. II. N-Protonation and N-Bonding to Some Transition Metal Perchlorates and Tetrafluoroborates [1]

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Simple molecular orbital calculations were carried out on acrylamide (AA) and N,N-dimethylacrylamide (DAA), the results indicating that molecules of lower energy are formed upon coordination through N rather than O. Protonation studies in FSO_3H by nmr show that both AA and DAA are N-protonated, in agreement with the m.o. calculations. Complexes of some first row transition metal perchlorates and tetrafluoroborates exhibit attachment through nitrogen for the AA but O-coordination for the DAA molecules. Steric factors are invoked to explain the different modes of bonding.

Introduction

In the preceding paper[3] it was shown, primarily by mass spectrometric evidence, that acrylamide (AA) bonds to the Sn(IV) halides *via* nitrogen, whereas N,N-dimethylacrylamide (DAA) prefers the oxygen attachment to the same metal.

This paper reports the results of some molecular orbital calculations which were carried out on the AA and DAA molecules in order to provide some theoretical basis for N-bonding in acrylamide complexes.

It was of interest to carry out further coordination studies on AA and DAA to determine if N-bonding is maintained for a variety of Lewis acids. To this end, protonation studies were carried out in FSO_3H, and also several new complexes of transition metal perchlorates and tetrafluoroborates were prepared and characterized.

Experimental Section

The program developed by Peter Gund, University of Massachusetts (QCPE 110) was used to carry out simple Hückel molecular orbital calculations using the omega self consistent charge density technique.[4] The Hückel parameters used were those recommended by Streitwieser.[5]

Nuclear magnetic resonance studies were carried out on solutions of AA and DAA in FSO_3H on a Varian A60-A spectrometer with a variable temperature probe for the purpose of determining the site of protonation on AA and DAA.

Solutions for spectra were prepared by dissolving AA or DAA in FSO_3H at –80°C. Spectra were first taken at –50°C and then at ambient probe temperature. The spectra showed no change when solutions were allowed to stand for 48 hours at room temperature. Chemical shifts are referenced to external tetramethyl silane.

Conductivity measurements were carried out in nitromethane solutions on a Beckman model RC-18A conductivity bridge at room temperature. Resistance readings on approximately 10^{-3} *M* solution of the complexes were made.

Mass spectral data were obtained on a Bendix Time-of Flight Mass Spectrometer and also on an MS-12 magnetic deflection spectrometer . On the MS-12, the sample was introduced by a direct insertion probe into the electron beam using an ionization voltage of 70 ev.

Infrared spectra in the 4,000-250 cm^{-1} region were recorded as Nujol mulls or oil smears on KRS-5 discs on a Perkin-Elmer model 521 Grating Infrared Spectrophotometer.

Optical spectra were obtained for the nickel complexes in the near infrared and visible regions on a Beckman DU-2 spectrophotometer, using 1.0 cm matched quartz cells. Solutions of the complexes studied were made up in CH_3NO_2 and contained excess of the appropriate amide.

Solvents used in this study were reagent grade and were generally employed without further purification with the following exception. Anhydrous ether was distilled over $LiAlH_4$ immediately before use. Nitromethane for conductivity studies was purified by repeated treatment with $NaHCO_3$ and H_2SO_4 solutions, dried, distilled and stored over anhydrous $CaCl_2$. The FSO_3H was freshly distilled before use.

Acrylamide was purchased from Eastman Organics

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[3] M. F. Farona, J. G. Grasselli, H. Grossman and W. M. Ritchey, *Inorg. Chim. Acta*, 3, 495 (1969).

[4] A. Streitwieser, *J. Am. Chem. Soc.*, *82*, 4123 (1960).

[5] A. Streitwieser, Molecular Orbital Theory for Organic Chemists, John Wiley and Sons, 1961, chepters 4 and 5.

Table I. Colors, Melting Points and Analyses of AA and D AA Complexes

Compound	Color	M.P ^{a} (°C)	Analysis, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
$[Cu(AA)_6](ClO_4)_2$	1 bl	105-108	31.38	4.39	12.20	30.75	4.32	11.83
$[Cu(AA)_6](BF_4)_2$	1 bl	104-108	32.58	4.56	12.66	32.33	4.52	12.53
$[Ni(AA)_6](ClO_4)_2$	1 gr	190-195	31.60	4.42	12.28	31.47	4.30	12.27
$[Ni(AA)_6](BF_4)_2$	1 gr	185-190	32.82	4.59	12.76	32.89	4.62	12.67
$[Fe(AA)_6](ClO_4)_2$	y	122-124	31.75	4.44	12.34	31.43	4.32	12.13
$[Cd(AA)_6](ClO_4)_2$	wh	97 d	29.30	4.10	11.39	28.52	4.19	11.11
$[Zn(AA)_5(H_2O)](ClO_4)_2$	wh	>250	28.25	4.27	10.98	28.42	4.27	10.80
$[Cu(DAA)_4(H_2O)_2](ClO_4)_2$	bl	44-48	34.56	5.80	8.06	33.01	5.87	7.62
$[Cu(DAA)_4(H_2O)_2](BF_4)_2$	bl	62-65	35.87	6.02	8.37	36.08	5.87	8.37
$[Cu(Am)_6](ClO_4)_2$	1 bl	89-93	23.37	4.90	13.52	22.16	4.82	12.84

^{a} uncorrected. Abbreviations: 1 = light, wh = white, bl = blue, gr = green, y = yellow.

Chemicals, and N,N-dimethylacrylamide was obtained from City Chemical Corp. and K and K Laboratories. Both were used as obtained.

The metal perchlorate and tetrafluoroborate hydrates were purchased from Alfa Inorganics, Inc., and used as obtained.

Preparation of the Complexes. Given below is the preparation of one of the complexes, $[Ni(AA)_6](BF_4)_2$. It is typical and all complexes were prepared analogously.

To 3.5 g of 2,2-dimethoxypropane was added 1.0 g (2.9 mmol) of $Ni(BF_4)_2 \cdot 6H_2O$ and the mixture was stirred for two hours at room temperature to remove the coordinated water. After this time, 2.2 g (31 mmol) of AA was added and the reaction mixture was stirred for 5 minutes. On addition of 10 ml of $CHCl_3$, a green powder precipitated. This was washed with a 10:3 (v/v) chloroform: ether mixture, dried at room temperature under high vacuum, and stored in a desiccator.

These compounds are all hygroscopic; therefore, they were stored in a vacuum desiccator over P_4O_{10}.

The analytical data, which were determined by Galbraith & Co., Knoxville, Tenn., along with colors and melting points of the complexes prepared in this study, are presented in Table I.

It should be pointed out that analytical data are lacking on $Ni(DAA)_6(ClO_4)$ and $Ni(DAA)_6(BF_4)_2$, since we were unable to obtain anything but oily products for these complexes. However, the optical spectra and ligand field calculations (see Tables V and VI) are consistent with octahedral coordination.

Results and Discussion

Since π electrons offer better energy matching with metal d orbitals and are more polarizable than nonbonded electrons, one might expect the π electrons in amides to be kinetically more basic than the oxygen lone pair. For this reason, simple Hückel molecular orbital calculations were carried out in order to predict whether an electrophile (Lewis acid) would attack oxygen or nitrogen. Three parameters are commonly used with varying degrees of success and their relative merits have been discussed.[5]

First of all, one may assume that it is the highest filled π molecular orbital that is most important in the transition state forming the bond between electrophile and nucleophile. This leads to the prediction of electrophilic attack at the atom having the highest electron density, $F_{r'}$ in the highest filled molecular orbital.[6] As may be seen in Table II, frontier molecular orbital densities predict attack at O rather than N for both formamide and acrylamide.

Table II. Frontier, Total π Electron Densities and Localization Energies of Formamide and Acrylamide

	Fr F_N	Fr F_O	π_r π_N	π_r π_O	L_O—L_N
$HCONH_2$	0.25	0.56	1.9	1.3	0.3 β
$CH_2CHCONH_2$	0.09	0.49	1.9	1.3	1.3 β

Alternatively, one might simply predict that electrophilic attack would occur at the site of highest electron density.[7] As can be seen in Table II, the total π electron densities, $\pi_{r'}$ predict in each case attack on nitrogen.

The most successful parameter however, has been the localization energy, which represents the energy required to remove two electrons from the π system in question and localize them on a given atom.

The site of smallest localization energy is presumed to be the place of attack by the electrophile. Table II shows the tabulation of the oxygen localization energy (L_O) minus that of nitrogen (L_N). In each case less π energy is lost by localizing the nitrogen electrons rather than those on oxygen. However, for a simple amide such as formamide, the L_O—L_N difference is only 0.3 β units, which can presumably be overcome by other factors. For the conjugated acrylamide, removal of the electrons on oxygen, rather than nitrogen, from the π system requires a substantially larger 1.3 β (β ≃ 23 Kcal/mole), and apparently prohibitive, cost of energy.

In valence bond terminology, as shown in the preceding paper,[3] coordination through oxygen favors resonance form II, whereas I and III are important in

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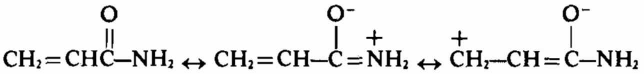
(6) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, *20*, 722 (1952).

(7) G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, *57*, 2086 (1935).

N-coordination:



$$CH_2{=}CH\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2 \leftrightarrow CH_2{=}CH{-}\overset{\overset{\displaystyle O^-}{|}}{C}\overset{+}{=}NH_2 \leftrightarrow \overset{+}{C}H_2{-}CH{=}\overset{\overset{\displaystyle O^-}{|}}{C}{-}NH_2$$

I II III

It is apparent, therefore, that resonance form III is favored over II for bonding in acrylamide, and N-coordination is predicted for the acrylamide molecule to Lewis acids.

These calculations suggest a theoretical basis for the mode of coordination found for the Sn^{IV} halides with acrylamide,[3] but the prediction of N-bonding should also hold true for N,N-dimethylacrylamide as well, which was found[3] to coordinate through oxygen. Steric arguments were invoked to account for the differences in the modes of attachment of AA and DAA to the Sn^{IV} halides.

In order to provide experimental verification of the above prediction that AA and DAA prefer to coordinate through nitrogen except when steric factors are important, protonation studies of AA and DAA in the acid FSO_3H were carried out by nmr spectroscopy to determine the site of protonation. Figures 1-3 show the vinyl proton signals for free and protonated AA and DAA at ambient probe temperature. The spectra are similar but less well resolved at –50°.

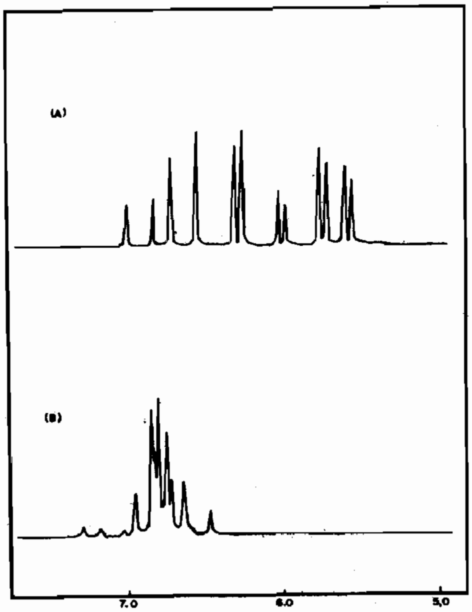
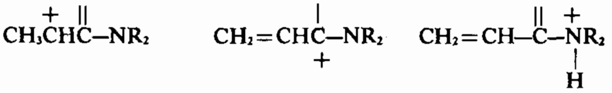


Figure 1. Vinyl proton nmr spectral region of N,N-dimethylacrylamide. A. in CH_3NO_2. B. in FSO_3H.

Acrylamide offers three possible sites of protonation leading to ions I, II, and III shown below.



$$CH_3\overset{+}{C}H\overset{\overset{\displaystyle O}{\|}}{C}{-}NR_2 \qquad CH_2{=}CH\underset{+}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}NR_2 \qquad CH_2{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle H}{|}}{\overset{+}{N}}R_2$$

I II III

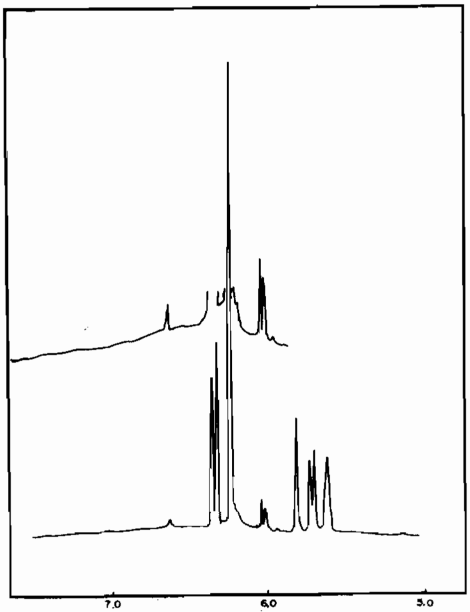


Figure 2. Vinyl proton nmr spectral region of acrylamide in CH_3NO_2 solution.

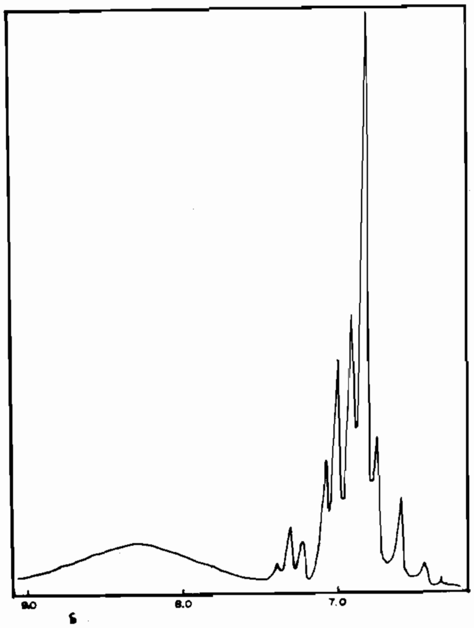
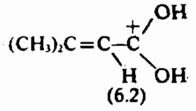
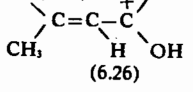


Figure 3. Vinyl proton nmr spectral region of acrylamide in FSO_3H.

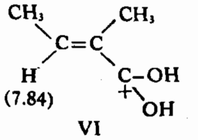
The absence of a doublet CH_3 proton peak in the region δ4.0-5.0 immediately rules out ion I. The nmr spectra of ions IV, V and VI reported by Deno and coworkers[8] provide models for II.



IV



V



VI

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[8] N. C. Deno, C. U. Pittman, and M. J. Wisotsky, *J. Am. Chem. Soc.*, *86*, 4370 (1964).

Table III. Infrared Spectra (cm^{-1}) of AA and DAA Complexes

Compound	$\nu(NH_2)$ [a]	ν(CO)	ν)C=C)	$\delta(NH_2)$	ν(CN)	Remarks
AA	3505 s, 3392 s, 3200 m	1672 s	1650 ms	1612 s	1280 m	[b]
$[CuAA_6](ClO_4)_2$	3410, 3350, 3325, 3250, 3230	1660 s	1621 s	1567 s, 1545 s	1285 m	[c]
$[CuAA_6](BF_4)_2$	3445, 3365, 3318, 3270, 3222	1663 s	1625 s	1580 s, 1557 s	1287 m	[c]
$[NiAA_6](ClO_4)_2$	3415, 3340, 3306, 3270, 3236	1664 s	1625 s	1574 s	1283 m	[c]
$[NiAA_6](BF_4)_2$	3425, 3338, 3308, 3268, 3240	1665 s	1623 s	1577 s	1281 s	[c]
$[Zn(AA)_5(H_2O)](ClO_4)_2$	3408, 3380, 3330, 3294, 3250	1665 s	1614 s	1573 s	1282 s	[c]
$[CdAA_6](ClO_4)_2$	3428, 3338, 3305, 3268, 3223	1657 s	1618 s	1570 s	1284 s	[c]
$[FeAA_6](ClO_4]_2$	3438, 3338, 3298 3262, 3225	1650 s	1611 s	1558 s	1282 s	[c]
DAA	——	1648 s	1610 s	—	—	[d]
$[Cu(DAA)_4(H_2O)_2](ClO_4)_2$	——	1584 s	1640 s	—	—	[e]
$[Cu(DAA)_4(H_2O)_2](BF_4)_2$	——	1585 s	1640 s	—	—	[e]
$[NiDAA_6](ClO_4)_2$	——	1594 s	1645 s	—	—	[f]
$[NiDAA_6](BF_4)_2$	——	1596 s	1647 s	—	—	[f]
CH_3CONH_2, AM	——	1672 s	—	1610 s	—	[g]
$[Cu(Am)_6](ClO_4)_2$	——	1580 s	—	1654 s	—	[g]

[a] All $\nu(NH_2)$ are of medium intensity unless indicated otherwise. [b] $\nu(NH_2)$ in CH_3NO_2 solution, other frequencies from Nujol mull. [c] Nujol mull between KRS-5 discs. [d] Neat liquid. [e] Nujol smear between KRS-5 discs. [f] Oil smear between NaCl discs. [g] Nujol mull between NaCl disc. Abbreviations: s, strong, m, medium, AM = acetamide.

The measured chemical shifts, relative to internal tetramethyl ammonium ion at 3.1 ppm, are indicated adjacent to the protons of interest. A correction factor of 0.3 ppm must be subtracted from chemical shifts in FSO_3H referenced to external tetramethylsilane.

The vinyl proton resonances at carbon 2 of IV and VI are shifted downfield from their positions in their corresponding free acids by 0.4 and 0.6 ppm, respectively. The vinyl proton at carbon 3 of V is similarly downfield shifted from its position in the spectrum of the free acid by 0.4 ppm.

If ions IV, V and VI provide models for the ion II, since protons on carbon 2 are at lower fields than those on carbon 3 in acrylamides, we would expect to find in the spectrum of II in FSO_3H, a preservation of the general appearance of the nmr spectrum of the free amide with an overall downfield shift of, perhaps, 0.5 ppm. Comparison of the spectra of the free acrylamide and N,N-dimethylacrylamide with their corresponding protonated species shown in Figures 1-3, demonstrate that this is not the case. The resolved vinyl proton resonance of AA in FSO_3H occur at δ 6.40, 6.60, 6.73, 6.84, 6.90, 7.00, 7.05, 7.25 and 7.30 and the amino protons at δ 8.38. The spectrum of DAA is very similar in appearance with vinyl proton resonances at δ 6.45, 6.61, 6.70, 6.73, 6.80, 6.83 and 6.94 and methyl on nitrogen at δ 3.60.

It seems generally agreed that simple aliphatic amides are oxygen protonated in strong acid.[9,10] Furthermore, Fraenkel and Franconi[10] have found that in 100% sulfuric acid at 29°C, the methyl groups of O-protonated N,N-dimethylformamide, propionamide and other aliphatic amides exhibit chemical shift differences of .06 to 0.18 ppm. However, even at −50°C we have been unable to resolve the methyl resonances of N,N-dimethylacrylamide which occur as a sharp singlet in FSO_3H and, therefore, conclude that it is not oxygen protonated to give II.

In addition, the chemical shift of the tetramethyl ammonium ion in FSO_3H is 3.40 ppm relative to external tetramethyl silane, in satisfactory agreement with the observed 3.60 ppm methyl shift of DAA for N-protonation in FSO_3H. Because of the similarity between the spectra of AA and DAA in FSO_3H, we conclude that both are N-protonated to give ion III.

These results are in exact agreement with those predicted by simple molecular orbital calculations, and lend further support to the speculation that steric factors are important in coordination of DAA, but not AA, to Lewis acids.

Transition Metal Complexes. In light of the results of Sn^{IV} complexes of AA and DAA[3] and the outcome of the molecular orbital calculations and protonation studies above, it would be predicted that complexes of transition metals with AA should be N-bonded, whereas complexed DAA, because of steric hindrance of the N,N-dimethyl groups, should show the O-attachment.

A variety of AA and DAA complexes of first-row transition metal perchlorates and tetrafluoroborates were prepared and investigated with the purpose of determining the mode of attachment of the amide.

Whereas the prime evidence for the mode of bonding in the Sn^{IV} complexes[3] came from investigation of the fragmentation patterns, mass spectroscopy proved to be of little value in the study of the transition metal complexes. Apparently, the weakest bond is bet-

(9) J. J. Edward and I. C. Wang, *Can. J. Chem.*, *40*, 966 (1962).
(10) G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, *82*, 4478 (1960).

ween the metal and ligand; hence, only the fragmenmentation pattern of the ligands could be detected. No metal-containing fragment was observed.

However, infrared spectra of the transition metal complexes are essentially identical to those of the Sn^{IV} complexes of AA and DAA.[3] These are summarized in Table III. Table IV shows the shifts of the ν(CO), ν(C=C) and $\delta(NH_2)$ upon coordination.

Table IV. Shifts in Certain Amide Bands Upon Coordination (cm^{-1})

Compound	$\Delta\nu$(CO)	$\Delta\nu$(C=C)	$\Delta\delta(NH_2)$
$[CuAA_6](ClO_4)_2$	−12	−29	−45
$[CuAA_6](BF_4)_2$	−9	−25	−32
$[NiAA_6](ClO_4)_2$	−8	−25	−38
$[NiAA_6](BF_4)_2$	−7	−27	−35
$[Zn(AA)_5(H_2O)](ClO_4)_2$	−17	−36	−39
$[CdAA_6](ClO_4)_2$	−15	−32	−43
$[FeAA_6](ClO_4)_2$	−22	−39	−54
$[Cu(DAA)_4(H_2O)_2](ClO_4)_2$	−64	+30	—
$[Cu(DAA)_4(H_2O)_2](BF_4)_2$	−63	+30	—
$[Ni(DAA_6](ClO_4)_2$	−54	+35	—
$[Ni(DAA_6](BF_4)_2$	−52	+37	—
$[Cu(Am)_6](ClO_4)_2$	−92		

The infrared spectra of the AA and DAA complexes of the transition metals show a very close resemblance to those of the Sn^{IV} halide complexes. Although ν(CO) shows a shift to slightly lower frequencies upon coordination of AA (7-22 cm^{-1}) they are considerably less than the corresponding shifts for DAA upon cordination (52-64 cm^{-1}). These shifts are of comparable magnitude with those found for the tin complexes. More important are the shifts of the ν(C=C) bands upon coordination. They are observed to shift in opposite directions, like those of the Sn^{IV} complexes, and identical arguments to those invoked in the preceding paper apply to the transition metal complexes, as well. It is clear, therefore, that the modes of attachment of AA and DAA to tin and the transition metals are analogous; it is concluded, therefore, that the AA molecule coordinates to metals through nitrogen, whereas in corresponding complexes, DAA prefers the oxygen attachment. These results are in exact agreement with predictions made from the results of the Sn^{IV} complexes, molecular orbital calculations, and protonation studies.

A comparison of the optical spectra of the Ni^{II} complexes of AA and DAA can be made with those reported by Drago *et al.*[11] for acetamide (Am) and N,N-dimethylacetamide (DMA). These spectra are given in Table V.

As shown in Table V, the three expected bands are observed, and calculations of Dq, β, and the position of the second band were made according to the example reported by Drago.[12] The good agreement of the calculated and experimental positions of ν_2 is taken as evidence for octahedral coordination. These are shown in Table VI.

Table V. Spectra Bands (CH_3NO_2) for $Ni(ClO_4)_2$ Complexes of the Amides

Compound	$\nu_{max}(cm^{-1})$	ε [a, b]	Assignment
$Ni(AA)_6^{2+}$	8,660	6.2	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$
	13,700)	5.0	$\rightarrow {}^3T_{1g}(F)$
	14,490 sh)	5.4	
	25,000	16.3	$\rightarrow {}^3T_{1g}(P)$
$Ni(DAA)_6^{2+}$	9,300	4.5	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$
	15,380	7.0	$\rightarrow {}^3T_{1g}(F)$
	26,320	35.2	$\rightarrow {}^3T_{1g}(P)$
$Ni(Am)_6^{2+}$ [c]	8,240		$^3A_{2g} \rightarrow {}^3T_{2g}(F)$
	13,370)		$\rightarrow {}^3T_{1g}(F)$
	14,700 sh)		
	24,510		$\rightarrow {}^3T_{1g}(P)$
$Ni(DMA)_6^{2+}$ [c]	7,690		$^3A_{2g} \rightarrow {}^3T_{2g}(F)$
	12,900)		$\rightarrow {}^3T_{1g}(F)$
	14,920 sh)		
	23,920		$\rightarrow {}^3T_{1g}(P)$

[a] Values of ε are given in liter $mole^{-1}$ cm^{-1}. [b] ε values for $Ni(DAA)_6^{2+}$ are approximate. [c] Data taken from Drago, *et. al.*, reference 11.

Table VI. Dq, β and the Position of the Second Band for Ni^{II} Complexes of AA and DAA. Position of $\nu_2[^3T_{1g}(F)]$ (cm^{-1}).

Compound	Dq(cm^{-1})	β(%)	Calcd.	Observed [a]
$[Ni(AA)_6](ClO_4)_2$	866	15.8	14,210	14,100 [b]
$[Ni(DAA)_6](ClO_4)_2$	930	13.4	15,300	15,380

[a] Spectra recorded in CH_3NO_2 solutions. [b] Average value of the observed doublet.

The spectra of the AA and DAA complexes of Ni^{II}, when compared with those of Am and DMA complexes, are very similar. A minor difference is observed, and that is that the Dq value for the N-bonded AA complex is slightly lower than that of the O-bonded DAA complex, whereas the Dq values for the O-bonded Am and DMA complexes show the unsubstituted amide to possess the higher value. This is a minor point and probably cannot be regarded as a helpful measurement in determining the mode of bonding of amide to metals.

Attempts to obtain nitrogen hyperfine splittings by electron spin resonance studies on the copper complexes were unsuccessful for solid samples contained in a diamagnetic host.

Acknowledgment. We are grateful to Mr. Freeman Bentley, of the Wright-Patterson Air Force Materials Laboratory, for partial support of this work. We are indebted to Dr. H. A. Kuska, The University of Akron, for helpful discussions.

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(11) R. S. Drago, D. W. Meek, M. D. Joesten, and L. La Roche, *Inorg. Chem.*, 2, 124 (1963).

(12) R. S. Drago, Physical Methods in Inorganic Chemistry Reinhold Publishing Corp., New York, 1965, Appendix D.