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Acrylamide and N,N-Dimethylacrylamide Complexes. I. N-Coordination to Tin(IV) Halides[1]

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The complexes $SnX_4 . 2AA$ (X = Cl, Br; AA = acrylamide), $SnCl_4 . 2AA{-}d_2$, ($AA{-}d_2 = CH_2CHCOND_2$) and $SnX_4 . 2DAA$ (DAA = N,N-dimethylacrylamide) have been prepared and characterized. Whereas the DAA complexes exhibit the «normal» O-coordination, the AA complexes appear to be the first examples of N-coordinated amides. The primary evidence for the different modes of bonding comes from mass spectral studies, with photoelectron, infrared, and nmr spectroscopy providing supporting evidence. Fragmentation patterns for $SnCl_4 . 2DAA$ and $SnCl_4 . 2AA$ show SnO^+ and SnN^+, $SnNH^+$ and $SnNH_2^+$ peaks, respectively. Apparently anomalous data from infrared and nmr studies are explained in terms of new resonance forms which contribute to the electronic structure through N-coordination. On the basis of low-frequency infrared studies, the AA complexes are assigned the cis, *and the DAA complexes the* trans, *configurations. An evaluation of the utilization of the shifts upon coordination of the infrared bands $\nu(NH_2)$, $\nu(CO)$, $\delta(NH_2)$ and $\nu(CN)$, as a means of determination of the mode of bonding of amides, is presented.*

Introduction

To our knowledge, with the exception of some urea complexes, the mode of attachment of all amides and N,N-disubstituted amides to metals reported to date occurs through oxygen rather than nitrogen (see, *e.g.*, references 3-14 and references contained therein). By far, the most utilized. physical method to determine the mode of bonding of an amide to a metal has been infrared spectroscopy. In particular, the shift in the CO stretching frequency has served as the essentially unequivocal means by which the nature of the attachment has been determined; examination of the resonance forms of an amide predicts a marked decrease in ν(CO) upon coordination through oxygen, whereas an increase in the carbonyl frequency is expected if complexation occurs through nitrogen. Unfortunately, since no N-bonded amide complexes have been reported, a comparison of the shifts of various amide bands upon coordination could not be made, although N-coordinated ureas have shown an increase in the CO stretching frequency of 10-60 cm^{-1} upon complexation.[15,16]

We wish now to report the first examples of N-bonded amides, which allow us not only to elucidate some factors responsible for N-coordination rather than the « normal » O-complexation, but also to evaluate the role of relative shifts in the amide bands in the infrared upon coordination as evidence for the nature of attachment of amides to metals.

Experimental Section

All preparations were carried out in a dry, nitrogen atmosphere, box.

Preparation of the complexes. The compounds $SnCl_4 . 2AA$, $SnBr_4 . 2AA$ (AA = acrylamide), $SnCl_4 . 2DAA$, $SnBr_4 . 2DAA$ (DAA = N,N-dimethylacrylamide) were prepared by adding $SnCl_4$ or $SnBr_4$ dissolved in $CHCl_3$ dropwise into a $CHCl_3$ solution containing an excess of the ligand. The DAA complexes precipitated immediately from solution whereas the AA complexes were obtained as oils, which crystallized slowly when stored under nitrogen in the cold.

Anal.[17] Calcd. for $SnCl_4 . 2CH_2CHCONH_2$: C, 17.88; H, 2.48; N, 6.95; Cl, 35.2; mol. wt 402.5. Found: C, 17.70; H, 2.60; N, 6.81; Cl, 35.20; mol. wt. (cryoscopic in nitrobenzene), 425. Calcd. for $SnCl_4 . 2CH_2CHCON(CH_3)_2$: C, 26.2; H, 3.93;

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(3) W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 2144 (1960).
(4) S. C. Jain and R. Rivest, *Can, J. Chem.*, *45*, 139 (1967).
(5) S. C. Jain and R. Rivest, *J. Inorg. Nucl. Chem.*, *29*, 2787 (1967).
(6) J. Archambault and R. Rivest, *Can. J. Chem.*, *38*, 1331 (1960).
(7) R. C. Paul, B. R. Sreenahan, and S. L. Chadha, *J. Inorg. Nucl. Chem.*, *28*, 1225 (1966).
(8) R. C. Aggarwal and P. P. Singh, *J. Inorg. Nucl. Chem.*, *28*, 1651 (1966).
(9) R. C. Aggarwal and P. P. Singh, *ibid*, *28*, 1655 (1966).
(10) R. C. Aggarwal and P. P. Singh, *Z. Anorg. Allgem. Chem.*, *332*, 103 (1964).
(11) C. L. Rollinson and R .C. White, *Inorg. Chem.*, *1*, 281 (1962).
(12) S. K. Madan and J. A. Sturr, *J. Inorg. Nucl. Chem.*, *29*, 1669 (1967).
(13) S. K. Madan, *Inorg. Chem.*, *6*, 421 (1967).
(14) W.-E. Bull, S. K. Madan, and J. E. Willis, *ibid*, *2*, 303 (1962).
(15) N. N. Greenwood and B. H. Robinson, *J. Chem. Soc.*, *511* (1967).
(16) R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, *79*, 1575 (1957).
(17) Elemental Analyses performed by Galbraith Laboratories, Knoxville, Tennessee.
(18) N. Jonathan, *J. Mol. Spect.*, *6*, 205 (1961).

N, 6.11. Found: C, 26.03; H, 3.90; N, 6.07. Calcd. for $SnBr_4 . 2CH_2CHCONH_2$: C, 12.8; H, 1.78; N, 5.0. Found: C, 12.54; H, 1.82; N, 5.02 . Calcd. for $SnBr_2 . 2CH_2CHCON(CH_3)_2$: C, 19.5; H, 2.92; N, 4.55. Found: C,19.8; H, 2.93; N, 4.56.

Deuterated acrylamide, $CH_2CHCOND_2$ (AA–d_2), was prepared by the method of Jonathan.[18] The complex $SnCl_4 . 2AA–d_2$ was prepared as described above for $SnCl_4 . 2AA$. The complex $SnCl_4 . 2$ Am (Am = acetamide) was prepared as described elsewhere.[10] Attempts to synthesize $SnI_4 . 2AA$ were unsuccessful.

Infrared Spectra. Infrared spectra of the complexes were recorded as Nujol mulls, halocarbon mulls, and CH_2Cl_2 and methyl acetate solutions in the 4,000-265 cm^{-1} region on a Perkin-Elmer Model 521 grating infrared spectrophotometer. The spectra in the 650-265 cm^{-1} region were recorded as Nujol mulls between CsBr discs on a Perkin-Elmer Model 221 spectrophotometer equipped with a CsBr interchange. The instruments were calibrated with indene and band positions reported are expected to be precise to ± 3 cm^{-1}.

Nuclear Magnetic Resonance Spectra. The nmr spectra of AA, Am, $SnCl_4 . 2AA$ and $SnCl_4 . 2$ Am were obtained in methyl acetate solution at 25.5± 0.5°C on a Varian DP–60 spectrophotometer. The spectra of DAA and $SnBr_4 . 2DAA$ were obtained in CH_3NO_2 solutions. Spectra of $SnCl_4 . 2AA$ were also recorded both at 50°C and at –20°C in CH_3NO_2 solution. Tetramethylsilane served as the internal standard for all measurements.

Differential Thermal Analysis. DTA measurements were carried out on a DuPont Model 900 Thermal Analyzer on the complexes $SnCl_4 . 2AA$ and $SnCl_4 . 2DAA$. Both compounds decompose rather than melt; the decomposition points for $SnCl_4 . 2AA$ and $SnCl_4 . 2DAA$ were 310 and 170°C, respectively.

Mass Spectra. Mass spectra were obtained on the complexes $SnCl_4 . 2AA$ and $SnCl_4 . 2DAA$ at 125 and 100°C, respectively, on a Varian M66 Mass Spectrometer using an ionizing voltage of 70 ev. Background spectra were recorded at 10^{-7} Torr.

Photoelectron spectroscopy. Photoelectron spectra were obtained on AA and $SnCl_4 . 2AA$ with a Varian IEE spectrometer. Spectra were calibrated relative to the position of the carbon peak. The spectra were recorded by a voltage screen, and in the vicinity of spectral lines the voltage scans were stepped in increments of 0.2 volt. Scan times were sufficiently long (50-650 sec.) so that count variations (intensities) for spectral lines were significantly above background. Spectral line locations were found to be reproduceable to ± 0.3 v.; shifts were considered significant if they were 1 volt or larger.

Results

The mass spectral data for $SnCl_4 . 2AA$ and $SnCl_4 . 2DAA$ showing pertinent data as to the mode of bonding in these molecules are presented in Table I.

Table I. Mass Spectrometric Data for $SnCl_4 . 2AA$ and $SnCl_4 . 2DAA$ [a]

Complex	m/e	Species
$SnCl_4 . 2DAA$	132	$^{116}SnO^+$
	134	$^{118}SnO^+$
	136	$^{120}SnO^+$
$SnCl_4 . 2AA$	130	$^{116}SnN^+$
	131	$^{116}SnNH^+$
	132	$^{116}SnNH_2^+$, $^{118}SnN^+$
	133	$^{118}SnNH^+$
	134	$^{120}SnNH_2^+$, $^{120}SnN^+$
	135	$^{120}SnNH^+$
	136	$^{120}SnNH_2^+$

[a] Fragmentation patterns obtained from ionizing voltage of 70 ev.

Table II. Main Bands in the Infrared Spectra (3800-1000 cm^{-1}) of $SnX_4 . 2$ amide

Compound	State	ν(NH_2)	ν(CO)	ν(C=C)	δ(NH_2)	ν(CN)	r(NH_2)
AA	A	3350 s, 3175 s	1672 s	1650 ms	1612 s	1280 m	1137 m
	B	3350 s, 3175 s	1670 s	1652 ms	1611 s	—	—
	C	3460 s, 3375 s, 3205 m	1687 s	1644 m	1612 ms	—	—
	D	3505 s, 3392 s, 3200 m			—	—	—
$SnCl_4 . 2AA$	A	3400 s, 3320 s, 3290 s, 3250 s, 3220 s	1655 s	1618 s	1540 s 1530 m	1285 m	1100 m
	B	3405 s, 3325 s, 3298 s, 3255 s, 3230 s	1655 s	1620 s	1540 s 1530 s	—	—
	C	3395 s, 3350 s, 3310 sh, 3265 sh, 3240 s	1659 s	1623 m	1558 ms 1551 ms	—	—
	D	3430 s, 3345 s, 3310 sh, 3265 m, 3242 sh	—	—	—	—	—
$SnBr_4 . 2AA$	A	3378 s, 3300 s, 3280 s, 3240 s, 3210 s	1645 s	1610 s	1530 s	1285 m	1095 ms
	B	3405 s, 3320 s, 3295 s, 3255 s, 3225 s	1655 s	1620 s	1545 s	—	—
AA–d_2	A	2520 s, 2360 s	1655 s	1615 s	—	—	—
$SnCl_4 . 2AA–d_2$	E	2560 s, 2480 s, 2415 s	1648 s	1620 s	—	—	—
DAA	F	——	1648 s	1610	—		—
$SnCl_4 . 2DAA$	A	——	1575 s	1632 s	—		—
	B	——	1580 s	1639 s	—		—
	C	——	1565 s	1625 s	—		—
$SnBr_4 . 2DAA$	A	——	1570 s	1630 s	—		—
	B	——	1578 s	1634 s	—		—

A, Nujol mull; B, halocarbon mull; C, methyl acetate solution, 0.1 mm matched cells; D, Nitromethane solution, 0.1 mm cell; E, oil smear; F, neat liquid; s, strong; m, medium, sh, shoulder.

The infrared bands in the 3800-1000 cm^{-1} region which have a bearing on the determination of the mode of bonding and/or the discussion which follows, are listed in Table II and illustrated in Figures 1 and 2. It should be added that only those bands which could be assigned with confidence are presented. The assignments of the bands were greatly facilitated by comparing the spectra of the complexed AA and deuterated AA to those of free AA and AA–d_2 in a study by Jonathan.[18] The low-frequency region (650-265 cm^{-1}) of the spectra of the compounds studied is presented in Table III, and a representative spectrum is shown in Figure 3.

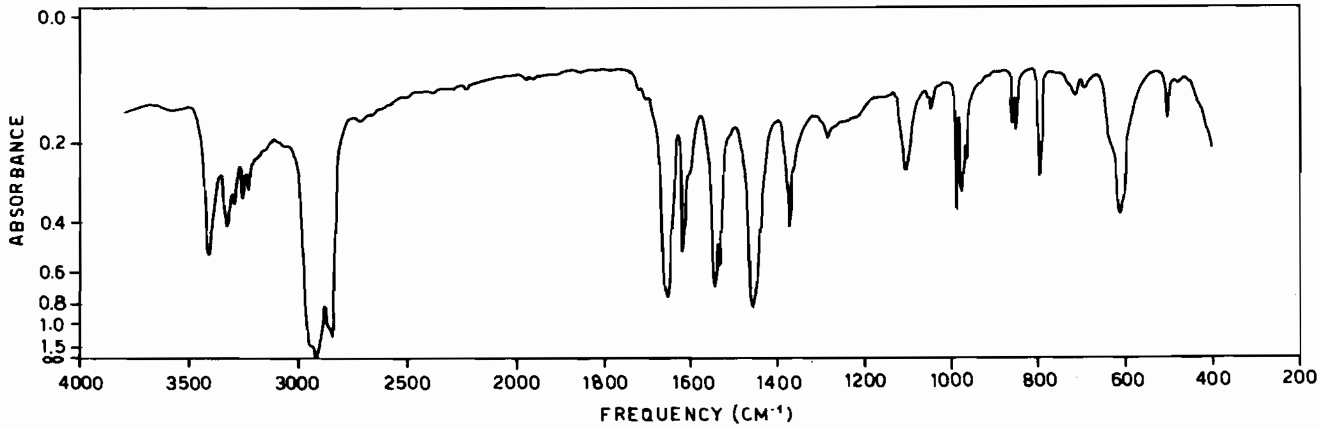

Figure 1. Infrared Spectrum (Nujol Mull) of $SnCl_4.2AA$.

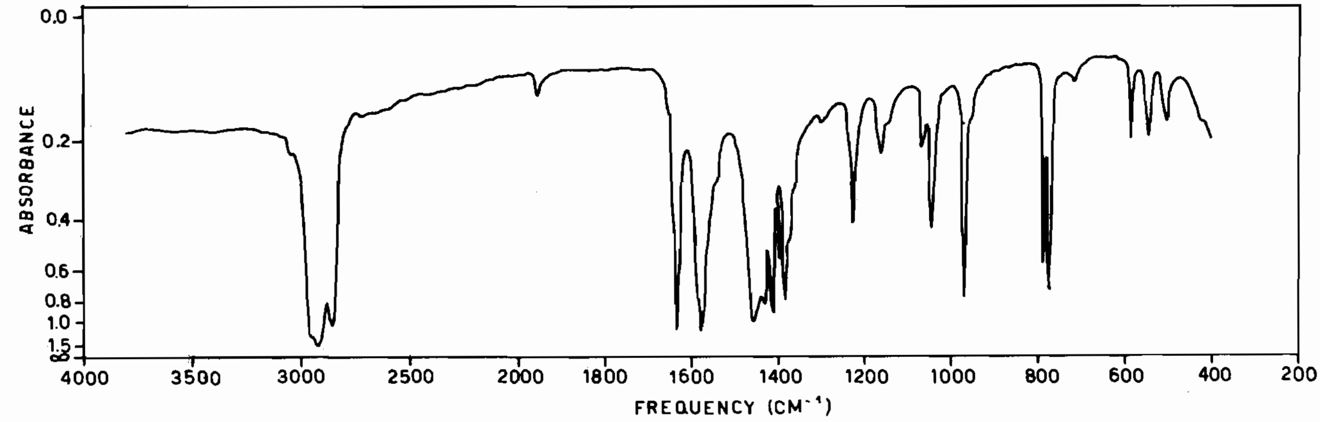

Figure 2. Infrared Spectrum (Nujol Mull) of $SnCl_4.2DAA$.

The amine, N-methyl and vinyl proton signals of free and complexed AA and DAA are shown in Table IV. The chemical shifts and coupling constants for the vinyl protons as shown in Table IV. were calculated with IBM 360/44 and CDC 3600 computers using the LAOCOON(III) program (A. A. Bothner-By and S. M. Castellano). The vinyl proton line positions of the calculated and observed agreed to within 0.4 Hz, which is well within experimental error.

The photoelectron spectroscopy data for free and complexed AA are shown in Table VI. All line locations were referenced to the carbon 1S line in each compound so that shifts in voltage due to different equilibrium charging effects are removed. Due to relatively rapid sublimation of the samples, the oxygen peak was dominated in both cases by the « Scotch Tape » substrate and consequently could not be used in the analysis. Therefore, the oxygen data should be constant within experimental error and this is indeed what is observed. Thus, these data provide a built-in check on the performance of the spectrometer. Some data were taken on $SnCl_4$. 2DAA complex but are not given in Table VI since we were unable to obtain data on the free ligand; however, they are not inconsistent with the data on the AA system.

The data in Table IV on the vinyl protons are the calculated values of the chemical shifts and coupling constants, based on the following representation of AA or DAA.

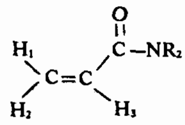

Table V gives the differences in the chemical shifts and coupling constants for the protons in free and complexed AA and DAA.

Table III. Low-Frequency Infrared Spectra (650-265 cm^{-1}) of SnX$_4$.2 amide[a]

Compound	Ligand	ν(SnO)	ν(SnN)	ν(SnX)
AA	620 s, 509 s, 313 s, 305 sh	—	—	
AA—d$_2$	610 s, 520 sh, 490 m, 458 s	—	—	
SnCl$_4$.2AA	643 sh, 610 s, 500 m, 385 s, b	—	476 w	341 s, 313 s, b 305 sh
SnCl$_4$.2AA—d$_2$	643 m, 617 s, 543 m 500 m, 472 s	—	468 sh 422 m	370 s, 336 s,
SnBr$_4$.2AA	637 sh, 599 s, 503 m 376 s, b	—	466 m	—
2186	640 sh, 607 m, 557 w, 545 sh, 498 m, 414 m, 385 sh, 361 ms	—	—	—
SnCl$_4$.2DAA	589 m, 504 m, 429 w, 545 m 366 sh, b, 305 m, b	545 m	—	328 s, b
SnBr$_4$.2DAA	589 m, 500 m, 429 w, 547 m 365 m, b, 336 m, b, 305 m, b	547 m	—	—

[a] All solid compounds recorded as Nujol mulls; DAA was recorded as neat liquid film between CsBr discs. Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; b, broad.

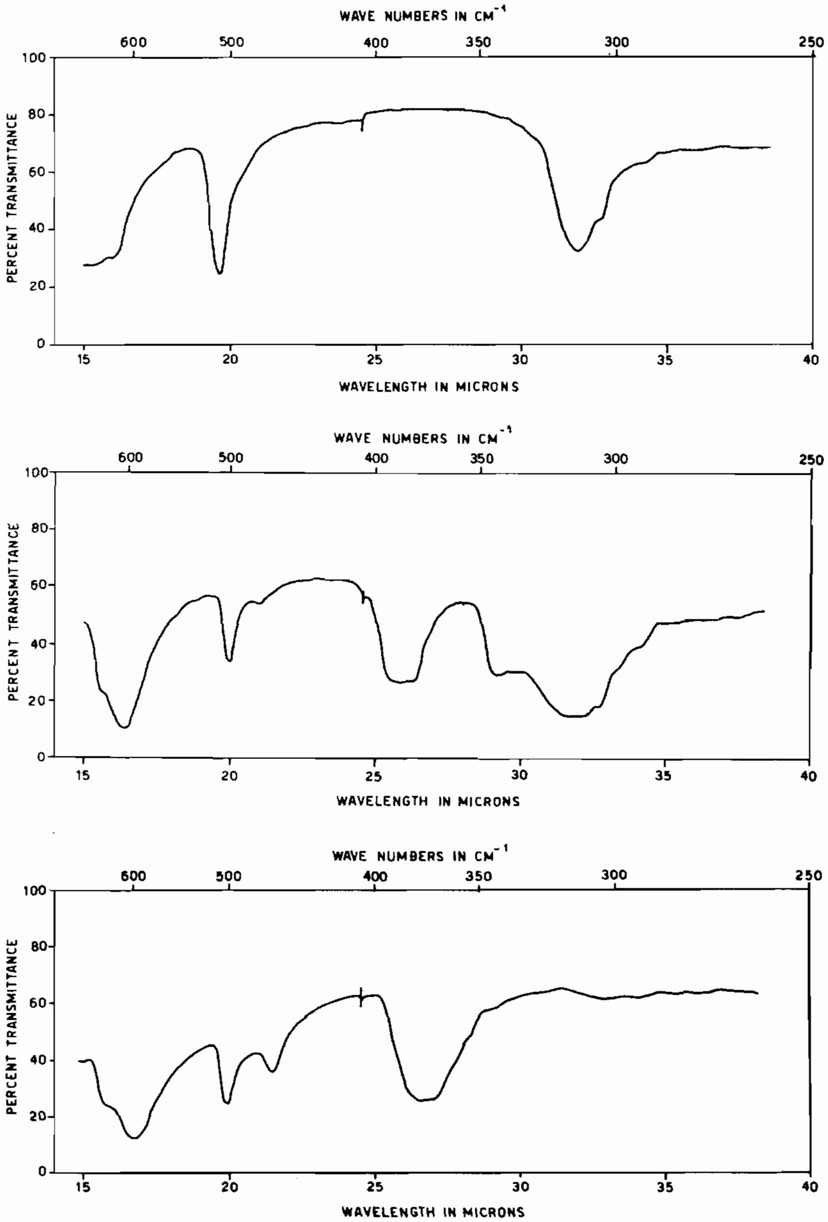

Figure 3. Low-frequency Infrared Spectrum (Nujol Mull) of, Top: AA, Middle: SnCl$_4$.2AA, Bottom: SnBr$_4$.2AA.

Table IV. Chemicals Shifts and Coupling Constants in Proto n NMR Spectra of $SnCl_4 . 2$ amide

Compound	Solvent			δ NCH or NH[a]
DAA	CH_3NO_2	$\delta_1 = 6.12$	$J_{1,2} = 2.57$	δ NCH_3 = 3.00
		$\delta_2 = 5.63$	$J_{1,3} = 16.32$	2.93
		$\delta_3 = 6.68$	$J_{2,3} = 10.76$	
$SnCl_4 . 2DAA$	CH_3NO_2	$\delta_1 = 6.43$	$J_{1,2} = 0.94$	δ NCH_3 = 3.33
		$\delta_2 = 6.03$	$J_{1,3} = 16.90$	3.28
		$\delta_3 = 6.74$	$J_{2,3} = 11.56$	
AA	$CH_3CO_2CH_3$	$\delta_1 = 6.24$	$J_{1,2} = 1.56$	δ NH = 6.98
		$\delta_2 = 5.62$	$J_{1,2} = 17.11$	
		$\delta_3 = 6.29$	$J_{2,3} = 10.78$	
$SnCl_4 . 2AA$	$CH_3CO_2CH_3$	$\delta = 6.60$	$J_{1,2} = 0.12$	δ NH = 8.16
		$\delta = 6.11$	$J_{1,3} = 16.94$	
		$\delta = 6.53$	$J_{2,3} = 10.99$	
Am	CH_3NO_2	—	—	δ NH = 6.6
$SnCl_4 . 2Am$	CH_3NO_2	—	—	δ NH = 7.4

[a] δ in ppm downfield from TMS. J. values in Hz.

Table V. Changes in Chemical Shifts and Coupling Constants upon Complexation of AA and DAA

	Vinyl protons[a, b]		Other protons	
Amide			$\Delta\delta$ NCH_3	$\Delta\delta$ NH
	$\delta_1 = 0.31$	$J_{1,2} = -1.63$	0.3	
DAA	$\delta_2 = 0.40$	$J_{1,3} = +0.58$		
	$\delta_3 = 0.06$	$J_{2,3} = +0.80$		
	$\delta_1 = 0.36$	$J_{1,2} = -1.44$		1.08
AA	$\delta_2 = 0.49$	$J_{1,3} = -0.17$		
	$\delta_3 = 0.24$	$J_{2,3} = +0.21$		

[a] $\Delta\delta = \delta_i$ (complex) $- \delta_i$ (amide) in ppm. [b] $\Delta J = {}_{i,j}$ (complex) $- J_{i,j}$ (amide) in Hz.

Table VI. Photoelectron Spectroscopy Data for AA and $SnCl_4 . 2AA$

Line	AA	$\Delta(C_{1s}{}^{AA})$[a]	$SnCl_4 . 2AA$	$\Delta(C_{1s}{}^{2AA})$[a]	$\Delta(AA)-\Delta(2AA)$[b]
C_{1s}	1094.8	—	1094.1	—	—
O_{1s}	846.8	248.0	845.7	248.4	−0.4
N_{1s}	978.6	116.2	976.7	117.4	−1.2
Sn(3d 5/2)			881.7	212.4	
Cl_{2p}			890.4	203.7	
			1178.8	−84.7	

[a] Referencing the data to the carbon 1S line of AA and $SnCl_4 . 2AA$ respectively. [b] $\Delta(AA)-\Delta(2AA)$ notation for $\Delta(C_{1s}{}^{AA})-\Delta(C_{1s}{}^{SnCl4 . 2AA})$. The minus sign indicates that the line for the given electron in the complex appears at a lower voltage than the corresponding line in the free ligand. Thus, the minus sign indicates an increase in binding energy between the electron and its nucleus.

Discussion

The two frequencies most often examined in the infrared spectra of complexed amides in order to determine the mode of bonding (N or O) are the amide I (CO stretching) and amide II (NH_2 bending) bands. When an amide is coordinated through oxygen, the ν(CO) band normally decreases by 30-80 cm^{-1}. The amide II band has been found to increase by 5-25 cm^{-1} for some complexes,[3,10] but decreases by as much as 50 cm^{-1} for others.[3,9] For N,N-disubstituted amides, the amide II band, of course, is not observed, and one relies primarily on the shift of the amide I band to determine the mode of bonding.

The complexes $SnX_4 . 2DAA$ (X = Cl, Br) show CO stretching frequencies 68-63 cm^{-1} lower than that of free DAA (Table II). In addition, a band not traceable to the free ligand appears in the spectra of $SnCl_4 . 2DAA$ and $SnBr_4 . 2DAA$ at 545 and 578 cm^{-1}, respectively, and these bands are tentatively assigned as the Sn–O stretching frequencies. Bands in this region have been assigned as such by other workers.[8,19]

Furthermore, the fact that two proton signals are observed for the methyl groups in the DAA complex is indicative of O-coordination. This is due to restricted rotation about the CN bond, and has been observed else-where in the coordination of DMF to a variety of Lewis acids.[20]

There is little doubt, therefore, that the DAA complexes, like those of every N,N-disubstituted amide reported to date, contain the metal-oxygen attachment.

The nature of the linkage of DAA to tin was confirmed by mass spectral studies. Weak peaks corresponding to SnO^+ fragments for the three major isotopes were observed at m/e 132, 134 and 136. The chance that these weak peaks arose from doubly charged species of mass 264, 268, and 272 was ruled

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(19) M. P. Brown, R. Okawara, and E. G. Rochow, *Spectrochim. Acta*, *16*, 595 (1960).

(20) A. Fratiello, D. P. Miller, and R. Schuster, *Mol. Phys.*, *12*, 111 (1967).

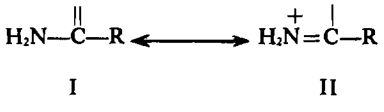
out by examination of the spectra for singly-charged species in the 264-272 mass region. Since no peaks in the higher region were found, the assignment shown in Table I is regarded as correct.

The assignment of the mode of bonding for the AA complexes is not at all straightforward in light of infrared and nmr spectral studies on these complexes. In themselves, infrared and nmr studies do not provide unequivocal means of determining the mode of attachment in AA complexes; indeed, support for either N or O linkages can be rationalized from the data (*vide infra*).

However, prime evidence as to the mode of bonding is provided by investigation of the mass spectra of $SnCl_4 . 2AA$. It is shown in Table I that all isotopic fragments of SnN^+, $SnNH^+$, and $SnNH_2^+$ appear in the mass spectrum of this compound. Tin-oxygen bonds are eliminated by the presence of the m/e 131 and 133 peaks. Although the bands in the m/e 130-136 region are all very weak, they are totally reproducible; furthermore, examination of the 260-272 m/e region reveals a complete absence of bands, and therefore, the bands at m/e 130-136 do not represent doubly charged species. It must be concluded, therefore, that the assignments made for the fragmentation pattern for $SnCl_4 . 2AA$, as shown in Table I, are correct, and that AA is coordinated to tin *via* nitrogen.

Additional strong support for this mode of bonding (Sn–N) is obtained from the photoelectron spectroscopy data (see Table VI). A significant change in the nitrogen binding energy is observed indicating that it is involved in the bonding with the tin. Furthermore, the direction of this change indicates a greater binding energy of the N for its electron exists in the complex over that of the free ligand, which is expected.

If one compares the amide I and II bands of coordinate AA with those of coordinated DAA and O-bonded unsubstituted amides, then it is found that these bands shift in the same direction, but are not of comparable magnitude (Table II). For example, the normal decrease in the $\delta(NH_2)$ band upon coordination is less than 50 cm^{-1}, but the amide II band of coordinated AA is found 60-82 cm^{-1} lower than that of free AA. Whereas the normal decrease in the amide I band is usually greater than 30 cm^{-1} upon O-coordination, this band decreases by only 15-27 cm^{-1} in the case of complexed AA. If coordination of an amide to a metal takes place *via* nitrogen, then an increase in the CO stretching frequency would be expected from examination of the following resonance forms:

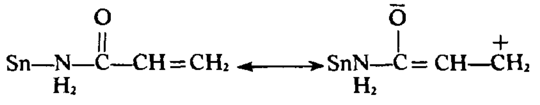


$$H_2N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R \longleftrightarrow H_2\overset{+}{N}{=}\overset{\overset{\displaystyle \bar{O}}{|}}{C}{-}R$$

I II

Coordination through oxygen should lead to a predominance of II, whereas form I should be prevalent if the attachment is through nitrogen. While examination of the shifts in the infrared spectra for the $SnX_4 . 2AA$ complexes would at first appear to support coordination of AA through oxygen, these results can be rationalized in terms of an N-bonded structure.

If, indeed, coordination of AA takes place through the nitrogen atom, then new resonance forms may be written.



$$Sn{-}\underset{H_2}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH{=}CH_2 \longleftrightarrow Sn\underset{H_2}{N}{-}\overset{\overset{\displaystyle \bar{O}}{|}}{C}{=}CH{-}\overset{+}{C}H_2$$

III IV

If these resonance forms are important, then at least two consequences become apparent. First of all, the $C=C$ stretching frequency should be significantly lower for complexed than for free AA, whereas that of DAA should not be affected very much upon coordination. Examination of the spectra in the $C=C$ stretching frequency region reveals that $\nu(C=C)$ decreases by 25-40 cm^{-1} for complexed AA compared to that of free AA, whereas the $C=C$ stretching frequencies of $SnX_4 . 2DAA$ actually increase slightly (15-30 cm^{-1}) compared to that of free DAA. Since these shifts are in the apposite direction, these data constitute strong evidence for different modes of attachments in the AA and DAA complexes. In addition, the fact that the CO stretching frequency does not increase in the case of coordinated AA may now be explained in light of resonance forms III and IV. Since these forms appear, indeed, to be important, it now becomes difficult to predict, *a priori*, in which direction the $\nu(CO)$ frequency will shift upon coordination.

The second indication of forms III and IV is that the chemical shift of the vinyl protons of coordinated AA should be further downfield than that of coordinated DAA. Data in Tables IV and V bear this prediction out; δ_1, δ_2 and δ_3 show a greater downfield shift for coordinated AA than for coordinated DAA when compared to their respective uncoordinated forms. That there should be a downfield shift of the vinyl protons upon coordination through either oxygen or nitrogen is expected from inductive effects; N or O should show stronger σ-inductive power when coordinated since it assumes a positive charge upon coordination. The downfield shift would be further enhanced if coordination takes place through nitrogen, since resonance form IV has been shown to contribute significantly to the overall electronic structure.

If one compares the shift of the amino protons of AA upon coordination with those of an unsubstituted O-bonded amide, then it would be expected that a larger downfield shift should occur for the amino protons of an N-bonded amide rather than an O-bonded one. This is so, since upon coordination through N, form III is the prevailing species, and the nitrogen atom assumes a positive charge. Upon O-coordination, resonance form II is favored over I, but here N would assume only a partial positive charge. The NH bond is weakened in either case, but a larger positive charge would be felt from N, rather than O, coordination.

If a comparison of the shift of the amino proton signals is made for complexed and free AA with that of complexed and free acetamide, which is known to bond through oxygen, then these signals are found about δ 1.3 downfield for complexed AA *vs.* free AA, but only about δ 0.8 downfield for the O-bonded acetamide than for uncoordinated acetamide.

The fact that in the highly conjugated acrylamide molecule more resonance forms contribute to the overall structure in the N- rather than O-bonded moiety results in the metal-nitrogen linkage as the lower in energy of the two possible modes of attachment. It might be expected that the same should be true for DAA, unless steric factors and/or initial charge densities on O and N (see following paper) are important. The importance of steric effects receives support from examination of the low-frequency infrared spectra of the complexes, which allows speculation on the stereochemistry of the molecules.

In the spectra of $SnX_4 . 2DAA$ in the 650-265 cm^{-1} region (Table III), only one SnO stretching frequency is observed, and for $SnCl_4 . 2DAA$, only one major SnCl stretching frequency can be assigned. The other bands in 300-400 cm^{-1} can all be attributed to ligand vibrations, since they are also present in the spectrum of $SnBr_4 . 2DAA$, and ν(SnBr) bands in octahedral complexes are normally found below 265 cm^{-1}.[21,22] The spectra show that the $SnX_4 . 2DAA$ complexes are of approximately D_{4h} symmetry, and as such only one Sn—X stretching frequency (E_u) is infrared active. The two DAA ligands, therefore, appear to be coordinated in positions trans to each other.

The molecules $SnX_4 . 2AA$ appear to be of approximate C_{2v} symmetry, since at least three bands arising from Sn—Cl stretching frequencies can be assigned. Unlike the DAA complexes, there is no band in the 500-600 cm^{-1} region which can be assigned as a tin-ligand stretching vibration, lending further evidence that the AA complexes are not O-bonded. A new band appears at 476 and 466 cm^{-1} in the spectra of $SnCl_4 . 2AA$ and $SnBr_4 . 2AA$, respectively; this band is not traceable to the free ligand and is tentatively assigned ν(Sn—N).

Since the acrylamide complexes appear to belong to the point group C_{2v}, two SnN (A_1+B_1) and four SnCl ($2A_1+B_1+B_2$) bands are expected to be infrared active. Although only three SnCl stretching bands can be assigned for $SnCl_4 . 2AA$, the 313 cm^{-1} band is very broad and possibly is made up of two unresolvable bands. The assignment of the SnN band is more difficult; since so many ligand vibrations occur in this region, any assignments of the SnN stretching frequencies for these molecules must not be regarded as unequivocal.

The fact that the O-bonded DAA complexes appear to assume the *trans* whereas the N-bonded AA complexes assume the *cis* configurations, shows that steric effects are important in the determination of the stereochemistry of these complexes.

In order to test for the possibility of an equilibrium in solution between the N- and O-bonded forms, the infrared spectra of $SnX_4 . 2AA$ (X = Cl, Br) were recorded in solution kept at 50°C for 2 hours. There was no change in band intensities or positions from those recorded at room temperature. Nmr spectra were recorded on solutions of these complexes at 50°C and at –20°C; again, there appeared to be no changes in the spectra compared to those obtained at room temperature. These studies minimize the possibilities of either intra- or intermolecular conversion occurring to produce linkage isomers in solution.

Evaluation of the Utilization of Shifts of Various Amide Bands to Determine the Nature of the Attachment. The NH stretching frequencies. Whereas the shifts in ν(NH) upon coordination are not normally used as a criterion to determine the mode of bonding of an amide to a metal, some authors[10] have pointed out that an increase in the NH stretching frequencies is observed upon O-coordination, and have speculated that a corresponding decrease in ν(NH) should be observed upon N-complexation.

As can be seen by the resonance forms above and in the paper by Gerrard, *et al.*,[3] the nitrogen atom assumes a positive charge upon coordination of an amide regardless of the mode of bonding. Hence, there is no mechanism by which the NH bond is strengthened on complexation, and, therefore, a decrease in the NH stretching frequency should occur for either mode of attachment.

In studies where an increase in the NH stretching frequencies were observed upon coordination, the authors invariable have compared the NH stretching frequencies of the coordinated amide with those of the free amide whose infrared spectrum was obtained in the solid state. Spectra obtained in this manner show NH stretching frequencies lowered by some 100 cm^{-1} through hydrogen bonding; a meaningful comparison can be made only if dilute solution spectra of the free amide are available. The solution studies in this work and by Gerrard *et al.*,[3] illustrate this clearly, and the point to be made here is that shifts observed in the NH stretching frequencies upon coordination of an amide are of little value in the determination of the mode of bonding.

The CO stretching frequency. Whereas a shift to lower frequencies of this band has generally been regarded as a critical test for O-coordination, our studies indicate that the position of the amide I band, does not, *per se*, provide unequivocal evidence for the nature of the attachment. Shifts in the carbonyl absorption must be interpreted with caution, and then only after the relative importance of all factors contributing to the structure of the complexes has been assessed.

The NH_2 bending frequency. Since the NH bond is lengthened upon coordination of an amide through either oxygen or nitrogen, it would be expected that the amide II band should decrease regardless of the nature of the attachment. This is not always observed, however (*vide supra*), and the observed shift in

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(21) M. F. Farona and J. G. Grasselli, *Inorg. Chem.*, 6, 1675 (1967).
(22) R. J. H. Clark, *Spectrochim. Acta*, 21, 955 (1965).

frequency of this band constitutes only very tenuous evidence on which to base an assignment.

The CN stretching frequency. Not only is this band often difficult to assign in the spectra of coordinated amides, but it has already been shown to be unreliable for the purpose of determining the mode of bonding,[23] and will not be discussed further.

The NH_2 rocking frequency. Shifts in this band are not normally reported in the studies of amide complexes; thus, the paucity of information prevents us from making comparisons with the N-bonded acrylamide complexes. However, since the NH bond is lengthened upon coordination through either nitrogen or oxygen, a decrease in this band is expected regardless of the nature of the attachment.

Conclusions

It is apparent that infrared evidence alone does not provide an adequate means by which the nature of the attachment of an amide to a metal can be determined. This type of study requires the use of several physical methods in addition to infrared studies; only then may one make assignments with confidence.

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(23) E. W. Randall, C. M. S. Yoder, and J. J. Zuckerman, *Inorg. Chem.*, *5*, 2240 (1966.