of the stereoisomers but depends in part on other enthalpy changes which do not completely cancel when computing and comparing $\Delta\Delta H$ values. A further and detailed analysis of $\Delta\Delta H$ values for these and other pairs of Ni(II) and Co(II) complexes will be presented when additional data are obtained.

Although the relative stabilization of the planar and tetrahedral forms of Ni(II) and Co(II) with related ligands cannot yet be analyzed in detail, *the present work does provide the first clear demonstration that the tetrahedral stereoisomer is not exclusively populated in Co(II) complexes, which by virtue of their structural features, are not constrained to be either tetrahedral or planar.*[45]

Acknowledgment. Financial support by the National Science Foundation through Grants GP-2840 and GP-4899 is gratefully acknowledged.

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[45] The bis(salicylaldimino) complexes **1** with R = H and OH may be planar to an unknown extent in solution.[36] However, the spectra purported to demonstrate this structure are apparently mislabeled and do not convincingly resemble the spectrum of the planar model, N,N-bis-(salicylidene)ethylenediaminocobalt(II) (*cf.* Figure 3 in ref 36).

Rotational Conformers of Glutaronitrile in Complexes with Metal Ions

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Contribution from the Department of Chemistry, Harvey Mudd College, Claremont, California. *Received January 21, 1966*

Abstract: Infrared spectra have been utilized to characterize rotational conformations of glutaronitrile[2] in the compounds $Cu(gn)_2ClO_4$, $Ag(gn)_2ClO_4$, $Ag(gn)_2BF_4$, $3.75AgNO_3 \cdot (gn)$, $TiCl_4 \cdot (gn)$, and $SnCl_4 \cdot (gn)$. Glutaronitrile assumes the GG rotational conformation[3] in the complexes with silver(I) and copper(I) and the TT conformation in the complexes with tin(IV) and titanium(IV).

Among the four spectroscopically distinguishable rotational conformers, TT, GG, GG′, and TG of glutaronitrile,[3] the assignment of infrared frequencies of the TT conformer has eluded cogent verification. The TT conformer is absent in the solid state at low temperatures,[4] and its concentration in the liquid state is unknown. The population of the GG′ conformer can be assumed to be negligible because of steric reasons. The more stable of two solid modifications of gn has been identified as the GG conformer,[4] the conformation of the ligand in $Cu(gn)_2NO_3$.[5] The absence of certain key frequencies in the spectrum of the metastable modification of gn led to its assignment as the TG conformation.[4,6] While the existence of the metastable modification of gn was questioned in a recent adiabatic calorimetric study,[7] a differential scanning calorimetric study demonstrated the existence of the metastable modification and provided evidence in support of the assignment of the TG conformation to the metastable modification.[8] However, since the relative amounts of the metastable modification present depend on the rate of cooling of liquid gn, the rotational conformational purity of the metastable modification is still unknown. That mixtures of rotational conformers can exist in solid dinitriles is exemplified by mixtures of *trans* and *gauche* conformers in solid succinonitrile from 230 to 329°K.[9,10]

After subtracting absorption due to the solid TG and GG modifications from the spectrum of liquid gn, the remaining bands (all of very low intensities with the exception of a strong band at 737 cm^{-1}) were assigned to the TT conformer.[4,6] If the intense band at 737 cm^{-1} is indicative of a high concentration of the TT conformer in liquid gn,[11] it is noteworthy that almost all of the other frequencies presently assigned to the TT conformer are of exceedingly low intensity. Frequencies of the TT conformer coincident with those of the TG and GG conformers could not be detected by the subtractive method of Matsubara.[4,6]

It was of interest in this study to investigate whether the TT conformer of gn would be assumed in complexes with metal ions and to determine whether these results may be used in making spectral assignments for gn. Infrared spectral studies of complexes have been extremely valuable in establishing assignments of frequencies to the *trans* and *gauche* conformers of succinonitrile.[10,12,13]

Experimental Section

Materials. Eastman White Label glutaronitrile was refluxed over phosphorus pentoxide and fractionated *in vacuo*. Anhydrous

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[1] Petroleum Research Fund Undergraduate Research Scholar, 1965.

[2] The symbol gn is used for glutaronitrile.

[3] For nomenclature of rotational conformers, see S. Mizushima, "Structures of Molecules and Internal Rotation," Part I, Academic Press Inc., New York, N. Y., 1954, Chapter V.

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[7] H. L. Clever, C. A. Wulff, and E. F. Westrum, Jr., *J. Phys. Chem.*, **69**, 1983 (1965).

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[9] (a) W. E. Fitzgerald and G. J. Janz, *J. Mol. Spectry.*, **1**, 49 (1957); (b) T. Fujiyama, K. Tokumaru, and T. Shimanouchi, *Spectrochim. Acta*, 20, 415 (1964).

[10] I. Matsubara, *J. Chem. Soc. Japan*, 34, 1710 (1964).

[11] The mole fraction of the TT conformer of gn vapor at 298°K has been estimated to be 0.43. See ref 7.

[12] M. Kubota and S. R. Schulze, *Inorg. Chem.*, 3, 853 (1964).

[13] M. Kubota, D. L. Johnston, and I. Matsubara, *ibid.*, **5**, 386 (1966).

Table I. Infrared Spectra of Complexes of Glutaronitrile with Silver(I) and Copper(I) (ν, cm^{-1})[a]

gn[b]	Cu(gn)$_2$ClO$_4$	Ag(gn)$_2$ClO$_4$	Ag(gn)$_2$BF$_4$	3.75AgNO$_3$·(gn)	Assignment
	275 s	259 s	255 s	270 w	C–C–N bending
	388 s	380 vs	380 vs	380 w	C–C–N bending
		468 mb	468 mb	470 mb	
			518 s*		
537 ms	536 s	534 s	532 s	531 m	C–C–C bending
	623 vs*	622 vs*		712 w*, 720 m*	
				727 m*, 750 w*	
754 ms			756 wsh		
768 ms	767 s	772 s	765 s	767 w	CH$_2$ rock
837 ms	825 w			805 vs*, 810 vs*	
873 ms	875 m	872 s	874 s	869 w	CH$_2$ rock
		889 w	890 w		
903 ms	908 s	904 vs	908 s	902 w	C–CN stretch
		1005 wsh	1007 msh		
1010 m					
1026 m	1025 s	1028 msh	1019 s	1024 vs*, 1036 vs*	C–C stretch
1065 m	1067 ssh			1068w	
	1092 vs*	1080 vs*	1034 vs*		
1190 ms	1192 m	1198 w	1196 w	1198 sh	CH$_2$ twist
1279 w	1272 m	1269 s	1272 s	1267 s	CH$_2$ twist
1287 w			1290 msh	1278 sh, 1295 vs*	
1316 ms	1314 vs	1308 s	1310 vs		CH$_2$ wag
1350 ms	1350 s	1351 s	1354 s	1372 vs*	CH$_2$ wag
1433 s	1413 vs	1414 vs	1418 vs	1412 vs	CH$_2$ bend
				1445 vs*	
1460 ms	1461 vs	1456 m	1458 m	1458 vs	CH$_2$ bend
				1730 w*, 1747 m*	
2020 w	2020 w	2016 m	1805 w	1757 m*	
2247 s	2271 s	2274 vs	2276 vs	2270 vs	C–N stretch and C–N–M
2924 ssh	2930 vs	2932 s	2938 s	2925 s	C–H stretch
2950 s	2955 vs	2956 m	2960 m	2956 vs	
	2985 w	2986 w	2990 wsh	3015 w	

[a] Frequencies assigned to anions are marked with asterisks. [b] Spectrum of the stable modification at −40°, from ref 5.

silver tetrafluoroborate from Alpha Inorganics Inc. was used without further purification. Anhydrous silver perchlorate and hydrated cupric perchlorate from G. F. Smith Chemical Co. were dried *in vacuo* at 100°. Dichloromethane and 2-butanol were purged with nitrogen for the synthesis of the copper(I) compound. The purification of solvent and precautions used to prevent reaction of the tin(IV) and titanium(IV) compounds with moisture have been described.[12]

Syntheses of Complexes. Complexes of gn with chlorides of tin(IV) and titanium(IV) were prepared according to the method described.[12] *Anal.* Calcd for $SnCl_4 \cdot (CN)_2C_3H_6$: Sn, 33.5; Cl, 40.0; C, 16.9; H, 1.7; N, 7.9. Found: Sn, 33.0; Cl, 39.8; C, 16.9; H, 2.0; N, 8.0. Calcd for $TiCl_4 \cdot (CN)_2C_3H_6$: Cl, 50.0. Found: Cl, 49.8.

Dropwise addition of a solution of 0.50 g (5.3 mmoles) of gn in 15 ml of benzene to a solution of 0.50 g (2.4 mmoles) of anhydrous silver perchlorate in 25 ml of benzene gave a white precipitate, which was washed with benzene and dried *in vacuo* at 58°. *Anal.* Calcd for $Ag((CN)_2C_3H_6)_2ClO_4$: Ag, 27.3; C, 30.4; H, 3.1; N, 14.2. Found: Ag, 27.0; C, 30.6; H, 3.2; N, 14.0.

The analogous compound with silver tetrafluoroborate was prepared in the same manner as the compound with silver perchlorate. *Anal.* Calcd for $Ag((CN)_2C_3H_6)_2BF_4$: Ag, 27.5; C, 30.6; H, 3.1. Found: Ag, 27.9; C, 30.8; H, 3.3.

Dropwise addition of a solution of 1.66 g (18 mmoles) of gn in 10 ml of 2-butanol and 5 ml of dichloromethane to a solution of 1.8 mmoles of cuprous perchlorate[14] in 50 ml of 2-butanol gave a white precipitate which was washed with dichloromethane and dried *in vacuo*. *Anal.* Calcd for $Cu((CN)_2C_3H_6)_2ClO_4$: Cu, 18.1; ClO_4, 28.3; C, 34.2; H, 3.44; N, 15.9. Found: Cu, 18.3; ClO_4, 28.6; C, 33.9; H, 3.16; N, 15.6.

Silver nitrate (0.85 g, 5 mmoles) was dissolved after vigorous stirring in 1.8 g (19 mmoles) of gn. The addition of 20 ml of dichloromethane yielded a white precipitate, which was washed with several portions of dichloromethane and dried *in vacuo;* mp 101–102°. *Anal.* Calcd for $3.75AgNO_3 \cdot (CN)_2C_3H_6$: Ag, 55.4; C, 8.28; H, 0.83; N, 11.0. Found: Ag, 55.6; C, 8.31; H, 0.90; N, 10.6. A solution of 0.50 g (5.3 mmoles) of gn in 5 ml of acetone was added to a solution of 3.0 g (18 mmoles) of silver nitrate in 6 ml of water. Ethanol (30 ml, 95%) was added and the solution was cooled in ice until white crystals were formed. The product was washed with acetone and dried *in vacuo;* mp 100–101°. *Anal.* Found (in three separate syntheses): Ag, 55.5, 55.2, 55.3.

Spectra and Analyses. Silver was determined by the Volhard method, copper by titration with EDTA, and perchlorate was analyzed gravimetrically as the tetraphenylarsonium salt. Carbon, hydrogen, and nitrogen analyses were performed by Drs. Weiler and Strauss, Oxford, England, and the Galbraith Laboratories Inc., Knoxville, Tenn.

Infrared spectra were obtained with a Perkin-Elmer Model 621 spectrophotometer. Compounds were sampled in Nujol and hexachlorobutadiene mulls between silver chloride plates for the 4000–500-cm^{-1} region and between high density polyethylene for the 500–200-cm^{-1} region. The spectra of the tin(IV) and titanium(IV) compounds were recorded in at least ten independent trials for each compound in order to distinguish frequencies which result from decomposition of these compounds. For example, decomposition of $SnCl_4 \cdot$(gn) was noted by appearance of bands at 3200, 1615, 1210, 1035, and 835 cm^{-1}. Considerable decomposition was evident when the compounds were sampled in potassium bromide pellets.

Results

The spectra showing two patterns (*vide infra*) of absorption by the ligand gn are given in Figure 1. Correlations and frequencies are presented in Tables I and II.

Discussion

That glutaronitrile reacts with a bonding capacity equivalent to two acetonitrile molecules is evident from a comparison of the stoichiometries of Cu(gn)$_2$ClO$_4$, Ag(gn)$_2$BF$_4$, and $SnCl_4 \cdot$(gn) with those of Cu(CH$_3$-

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Table II. Infrared Spectra of Complexes of Glutaronitrile with Tin(IV) and Titanium(IV) (ν, cm^{-1})

$SnCl_4 \cdot (gn)$	$TiCl_4 \cdot (gn)$	*n*-Pentane[a]	Assignment
243 s			C–C–N bend
275 m			Sn–N stretch
	308 w		
332 s, 368 w			
380 sh, 396 msh	390 vs		
455 w, b			
502 vs	502 s		C–C–C bend
592 s	592 s		C–C–C bend
672 w	672 w		
733 vs	730 vs	728	CH_2 rock
786 mb	799 mb		
828 m	828 w		
912 vs	916 s		C–CN stretch
969 m	970 m		C–CN stretch
1015 w	1015 w		
1025 w	1025 w	1025	
1057 w, 1075 w	1055 m		C–C stretch
1172 m	1170 s	1176	CH_2 twist
1248 m	1245 m		
1268 s	1267 s	1265	CH_2 wag
1310 s	1308 s	1308	CH_2 wag
1315 s	1313sh		
1370 s	1370 s	1370	CH_2 wag
1415 sh, 1418 s	1412 s, 1418 wsh		CH_2 bend
1454 m	1452 m		CH_2 bend
2295 vs	2294 vs		C–N–M
2926 w, 2950 m	2929 w, 2948 m		C–H stretch
2980 m	2978 w		

[a] Methylene deformation frequencies in the spectrum of solid *n*-pentane; from ref 26.

$CN)_4ClO_4$,[15] $Ag(CH_3CN)_4BF_4$,[16] and $SnCl_4 \cdot 2CH_3CN$.[17] The shift in frequencies due to nitrile C–N stretching at 2249 cm^{-1} in pure gn to 2295 cm^{-1} in the complexes with tin(IV) and titanium(IV) and to 2274 cm^{-1} in the complexes with silver(I) and copper(I) is indicative of a linear C–C–N–M bond.[12,17,18] The lack of absorption at 2249 cm^{-1} which indicates that both nitrile moieties of gn are bonded to metal atoms, and the linearity of the C–C–N–M system, point to the bridging rather than the chelating mode of bonding for gn in these compounds. Bonding of both cyano groups of gn with silver(I) and copper(I) contrasts with the low reactivity of the cyano moiety in cyanopyridines.[14] The polymeric nature of the tin(IV) and titanium(IV) compounds has been previously considered.[12]

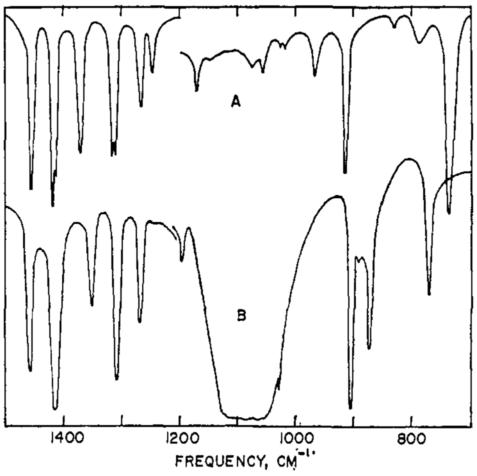

Figure 1. Infrared spectra of complexes of glutaronitrile: (A) $SnCl_4 \cdot (gn)$; (B) $Ag(gn)_2ClO_4$.

The unusual stoichiometry of the silver nitrate–glutaronitrile compound deserves comment. In six separate trials, the compound obtained from an excess of either component was observed to have a fairly sharp melting point and consistent analysis for the stoichiometry $3.75AgNO_3 \cdot (gn)$. While complexes of succinonitrile (hereafter referred to as sucn) with silver(I) are of stoichiometries $Ag(sucn)_2ClO_4$ and $Ag(sucn)_2BF_4$, the complexes obtained with the nitrate anion were $2AgNO_3 \cdot sucn$ and $AgNO_3 \cdot sucn$.[13] Infrared spectra of these compounds indicated nitrato–silver bonding, similar to nitrato–silver bonding shown by X-ray diffraction studies of the silver tris(acetylacetonato)-nickelate(II)–silver nitrate adduct, $AgNi(C_5H_7O_2)_3 \cdot 2AgNO_3$.[19] High silver nitrate content has also been observed in systems such as $4AgNO_3 \cdot sucn$,[20] $8AgNO_3 \cdot$ dioxane,[21] and $2AgNO_3 \cdot C_{10}H_{10}$ (*vs.* $AgBF_4 \cdot C_{10}H_{10}$).[22]

A careful comparison of the spectrum of $3.75AgNO_3 \cdot (gn)$ with the spectra of other complexes shown in Table I led to the assignment of frequencies of the nitrate anion. These include a broad band at 1372 cm^{-1} which is ν_3 of the nitrate ion of D_{3h} point group symmetry, and bands at 810 (ν_2) and 727 cm^{-1} (ν_4) are in support of this assignment. The broad intense bands at 1445 (ν_4)[23] and 1295 cm^{-1} (ν_1), however, also point to nitrato–silver bonding. Other nitrato frequencies include those at 1036, 1024 (ν_2); 805 (ν_6); 750 (ν_3); 712 (ν_5); and 1730, 1747, 1757 cm^{-1} ($\nu_2 + \nu_3$).

Compared to the spectrum of gn in the liquid phase,[6] considerable simplification is observed in the spectra of the complexes of gn with silver(I), copper(I), tin(IV), and titanium(IV). Where absorption bands at 1415 and 1460 cm^{-1} in liquid gn are broad and considerably more intense than other bands in the 1200–1500-cm^{-1} region, in the spectra of the complexes these bands are sharpened and their intensities significantly reduced. Glutaronitrile exists as a mixture of rotational conformers, TT, GG, and TG, in the liquid phase. Simplification in the spectra of gn in the complexes is due to the existence of only one of these conformations in each of the complexes. Bonding of each of the two nitrile moieties in gn coupled with packing requirements of the crystal lattice apparently restricts free rotation about the two internal rotation axes of gn.

Simplification of the spectrum of gn follows two patterns, of which an example of each is shown in Figure 1. Pattern A was observed in the spectra of $SnCl_4 \cdot (gn)$ and $TiCl_4 \cdot (gn)$, while pattern B was observed in the spectra of the complexes with copper(I) and silver(I). With the exception of frequencies due to anions, the frequencies tabulated in Table I deviate only slightly among those compounds with spectral pattern

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B. A comparison of the data in Table I with data for the ligand in $Cu(gn)_2NO_3$[6] and for gn in the low-temperature stable form[6] suggests that the ligand gn in the complexes with silver(I) and copper(I) exists in the GG conformation. The present data clarify anomalous features in the spectra of gn in the complex $Cu(gn)_2NO_3$ and in the low-temperature stable modification.[6] Absorption due to the nitrate anion and possible distortion of the nitrate anion[15b] lead to confusion of assignments. For example, a strong band at 1350 cm^{-1}, which is characteristic of the GG conformation of trimethylene dihalides[24] and which was observed in the spectrum of the stable low-temperature modification of gn,[4,6] was not observed in the spectrum of $Cu(gn)_2NO_3$.[6] This band, which is clearly present in the spectra of $Ag(gn)_2ClO_4$, $Ag(gn)_2BF_4$, and $Cu(gn)_2ClO_4$, is obscured by nitrate absorption in the spectrum of $3.75AgNO_3 \cdot (gn)$. A band at 1300 cm^{-1} in the spectrum of $Cu(gn)_2NO_3$ seemed to be shifted considerably compared to the bands at 1316 and 1314 cm^{-1}, respectively, in liquid gn and in the low-temperature GG modification.[4,6] Peaks at 1314, 1308, and 1310 cm^{-1} in the spectra of $Cu(gn)_2ClO_4$, $Ag(gn)_2ClO_4$, and $Ag(gn)_2BF_4$ show the shift to be very small.

Assignments based on the earlier work[6,24] for the intense bands of gn in the GG conformation in the complexes of silver(I) and copper(I) are given in Table I. Methylene deformation frequencies and C–C–C bending frequencies are shifted very slightly in the complexes as compared to pure gn. The C–C–N bending frequencies are shifted about 10 cm^{-1} to higher energy in the complexes. This trend, also apparent in the spectra in the complexes of succinonitrile,[13] may be ascribed to the weak perturbation of the methylene groups upon formation of weak donor–acceptor bonds at the remote nitrile nitrogen atoms. On the other hand, methylene deformation frequencies in complexes of ethylenediamine are difficult to characterize because of shifts due to bonding of metal ions and coupling with NH_2 vibrations.[25]

Conspicuously absent in the spectra of $TiCl_4 \cdot (gn)$ and $SnCl_4 \cdot (gn)$ with spectral pattern A is the strong 1350 cm^{-1} band characteristic of GG systems.[4,6,24] Also not observed in the spectral pattern A are strong bands at 860, 945, 1224, and 1328 cm^{-1}, which are predominant in the spectrum of the metastable modification of gn, which has been assigned the TG conformation.[6] The most substantive feature of spectral pattern A is the intense 733-cm^{-1} band which is due to the CH_2 rocking vibration of the methylene chain in the all-planar *trans* conformation.[6,26,27] Except for the absence of a rocking frequency expected at 861 cm^{-1}, methylene deformation frequencies of $SnCl_4 \cdot (gn)$ and $TiCl_4 \cdot (gn)$ are in surprising agreement with frequencies in the spectrum of crystalline *n*-pentane which exists in the TT conformation.[26] The spectra of gn in $SnCl_4 \cdot (gn)$ and $TiCl_4 \cdot (gn)$ are in accord with previously prescribed symmetry considerations for the TT conformer,[6,27] and assignments are proposed for the most intense bands in Table II.[28]

Except for the intense 732-cm^{-1} CH_2 rocking frequency and four frequencies coincident with those due to the TG and GG conformers, the present assignments to the TT conformation of gn disagree markedly with those designated by Matsubara.[4,6] His subtractive procedure gave TT assignments to at least eight exceedingly weak bands. If the intense 732-cm^{-1} absorption band is any indication of the relative abundance of the TT conformer in liquid gn, it is unlikely that most of the other fundamentals should be so weak. Since the frequencies assigned to the TT conformer of gn observed in the spectra of $SnCl_4 \cdot (gn)$ and $TiCl_4 \cdot (gn)$ correspond closely to regions of strong absorption in the spectrum of liquid gn, these TT frequencies would certainly have eluded detection by the subtractive technique.

Inasmuch as the frequencies of succinonitrile in the *trans* conformation in $SnCl_4 \cdot (sucn)$ and other complexes are only slightly shifted as compared to pure succinonitrile,[12,13] it is expected that the present frequencies assigned to gn in the TT conformation in the complexes should not differ appreciably from frequencies of pure gn in the TT conformation.

The frequencies in the 500–3000-cm^{-1} region are nearly identical for the titanium and tin complexes, with the exception of the broad bands at 786 and 799 cm^{-1}. That these two frequencies should not be assigned to the ligand gn, but rather should be assigned to a combination mode involving metal–chloride vibration, is suggested by the increased intensity of the 799-cm^{-1} band in the spectrum of $2TiCl_4 \cdot (gn)$.[29]

The *cis* orientation of ligands about the octahedrally coordinated tin atom in complexes of nitrile with tin(IV) chloride is generally favored over the *trans* orientation.[30] While the multiplicity of frequencies observed in the 300–400-cm^{-1} region in the spectrum of $SnCl_4 \cdot (gn)$ supports the *cis* configuration,[30] this assignment is tentative since gn absorbs at 341 and 376 cm^{-1} and a normal coordinate treatment predicts two frequencies in this region for the TT conformer of gn.[6] Assignment of the 275-cm^{-1} band to Sn–N stretching in $SnCl_4 \cdot (gn)$ compares favorably with a similar assignment of a band at 263 cm^{-1} for $SnCl_4 \cdot (sucn)$.[13] Frequencies in the 300–400-cm^{-1} region in the spectra of complexes of titanium(IV) chloride[31,32] have been assigned to Ti–Cl stretching modes.[32] The *cis* orientation of nitrile moieties about the titanium atom in $TiCl_4 \cdot (gn)$ is suggested by the similarity of absorption in the 300–400-cm^{-1} region in the spectrum of $TiCl_4 \cdot (gn)$ and the spectra of $TiCl_4 \cdot 2,2$-bipyridine[31,32] and $TiCl_4 \cdot$*o*-phenanthroline.[32]

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Amide Contact Shift Studies and the Assignment of the Methyl Peaks in N,N-Dimethylamides

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Abstract: The nmr contact shifts for a series of amides and lactams in six-coordinate nickel(II) complexes are reported. Mechanisms to account for the nonequivalence in the contact shifts of the two N-methyls of the N,N-dimethylamides are considered. Comparison of the contact shifts in the amides and lactams are employed to assign the spectral peaks to methyl groups which are *cis* and *trans* to the carbonyl oxygen.

While engaged in a study of nmr contact shifts in paramagnetic transition metal complexes of various amide and lactam ligands, we were faced with the problem of assigning the various ligand resonances to the appropriate protons of the ligands and then, by a continuous dilution method,[2] identifying these resonances with the corresponding signal in the contact shift spectra of their paramagnetic complexes. There have been literature assignments for the nmr spectra of such relatively simple amides as N,N-dimethylformamide (DMF),[3,4] N,N-dimethylacetamide (DMA),[3,4] and N,N-diethylformamide (DEF).[5,6] The N-alkyl groups in these amides are magnetically nonequivalent due to a high barrier to rotation about the carbonyl carbon–nitrogen bond[7] which causes the N-alkyl groups to preferentially occupy sites in the OCN plane which are either *cis* or *trans* with respect to the carbonyl bond. The separate resonances are assigned to the *cis* or *trans* positions on the basis of the relative magnitudes of their coupling constants ($J_{H_{A,B}-H_C}$) with the formyl proton in formamides or the acetyl methyl protons in acetamides.[3,5] Assignments of the N-methyl resonances of DMA and DMF by this method indicate that the *cis* methyl group is more shielded than the *trans* or more distant methyl group. Yet the magnetic nonequivalence of these two sites is generally arttibuted to the magnetic anisotropy of the carbonyl group.[5,8,9] Several studies both theoretical[9] and experimental[9-11] indicate that the magnetic anisotropy of the carbonyl group should provide a deshielding effect throughout the molecular plane. The theoretical and experimental assignments are clearly contradictory. The spectral assignments based on the coupling constant arguments are compelling, but not rigorous and another independent assignment is needed to confirm these results.

Recent studies in this laboratory have provided new information concerning the relative chemical shifts in amide molecules and the question of carbonyl anisotropy. This paper will deal with the results of a contact shift nmr study of Ni(II) amide complexes as a means of identifying *cis* and *trans* resonances in the free amide. This new evidence supports the previous assignments based on coupling constants. In a subsequent article a possible explanation for the observed difference in the chemical shifts of two N-methyl groups of DMA and DMF will be presented.

Experimental Section

Nmr Spectra. The nmr spectra were obtained with a Varian Model A-60 and a Varian Model DP-60 spectrometer. All spectra were obtained at approximately room temperature (27 ± 2°). *All* nmr spectra were measured relative to tetramethylsilane (TMS) as an internal standard.

Reagents and Solutions. Eastman White Label grade amides were distilled from barium oxide at reduced pressure and a center fraction accepted. Reagent grade nitromethane, nitrobenzene, chloroform, acetone, methylene chloride, and carbon tetrachloride were stored over Linde 3A molecular sieves for use as solvents. All solutions of hygroscopic materials were prepared in a drybox equipped with an automatic continuous air flow drying system. When accurate complex or ligand concentrations were necessary, materials were weighed in stoppered volumetric flasks. All solutions for nmr work which did not include a paramagnetic species were carefully degassed by repeated freezing with liquid N_2 and evacuation at low pressures.

Preparation of Complexes. The octahedral amide complexes of $Ni(ClO_4)_2$ were prepared by the reaction of anhydrous $NiCl_2$ with a solution of anhydrous $AgClO_4$ in the respective amide or in an amide–methylene chloride solution. AgCl was removed by centrifugation and filtration. The complexes were precipitated by addition of diethyl ether or carbon tetrachloride. Complexes were then recrystallized from a methylene chloride solution containing excess amide by slow addition of diethyl ether with stirring. Representative C, H, and N analyses are shown below. *Anal.* Calcd for $Ni(DMA)_6(ClO_4)_2$: C, 36.9; H, 6.9; N, 10.8. Found: C, 36.3; H, 7.0; N, 10.5. Calcd for $Ni(DMF)_6(ClO_4)_2$: C,

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[1] (a) Abstracted in part from the Ph.D. Thesis of B. B. Wayland, University of Illinois, 1964; National Science Foundation Graduate Fellow, 1963; (b) National Science Foundation Graduate Fellow, 1963.

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