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Complexes of Dinitriles with Tin(IV) and Titanium(IV) Chlorides[1]

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Complexes of succinonitrile, glutaronitrile, and adiponitrile with tetrachlorides of tin and titanium have been synthesized and characterized. Infrared spectral data and other structural considerations suggest that these compounds are polymeric and that the dinitriles are bridging rather than chelating ligands. Bonding of the nitrile moieties to two adjacent metal atoms restricts rotation in the succinonitrile ligand. Unlike the stable low temperature conformer of succinonitrile, which is *gauche*, the ligand assumes the *trans* rotomeric conformation in these complexes.

Introduction

Whereas the tendency of simple alkyl and aryl mononitriles to behave as Lewis bases in reactions with a wide variety of metal chlorides is fairly well established,[3] the reactions of polynitriles with metal acceptors have not as yet been elucidated Inasmuch as it is well known that polyamines are excellent chelating agents, it would be desirable to investigate possible chelating tendencies of the polynitriles.

The solubility of some metallic fluorides in succinonitrile has been cited as evidence that complexes are formed; however, no solid complexes were isolated or definite species characterized in solution.[4] Silver(I) forms high melting compounds with dinitriles, as exemplified by silver fluoroborate complexes of malononitrile, succinonitrile, and phthalonitrile.[5] Because the acetonitrile complex has the stoichiometry $Cu(CH_3CN)_4NO_3$, the compound $Cu(C_2H_4(CN)_2)_2NO_3$ was thought to be bonded with the succinonitrile as a chelate.[6] Recent infrared[7] and crystallographic studies[8] of the succinonitrile and glutaronitrile complexes of copper(I) nitrate indicate that the dinitriles are not chelating agents in these compounds.

Since there is considerable prior work[3] on the reactions of mononitriles with group IV metal halides, the reactions of dinitriles with these halides have been investigated as model systems. In reactions of mononitriles with group IV metal halides MX_4, compounds of stoichiometry $MX_4 \cdot 2RCN$ usually are formed.[3] In some instances, compounds of the type $MX_4 \cdot RCN$ are formed as solid adducts[3a] or as complexes in benzene solution.[9] The compound $MX_4 \cdot 2RCN$ usually is presumed to be octahedral, and if the ligand is bidentate such as 2,2′-dipyridyl or *o*-phenylenebis(dimethylarsine), chelation has been suggested as the mode of bonding for the complex $MX_4 \cdot B$.[10] It is of interest to study the chelating tendencies of the potentially bidentate dinitriles, recognizing, however, that if bonding with acceptor atom "A" by the nitrile moieties is accomplished by the lone pair electrons on the nitrogen atom of the nitrile, rather stringent steric restrictions may prevail. When the typical lone pair bond is formed, it is imperative to recognize that a colinear A–N–C–C system results, as has been demonstrated by X-ray crystallographic studies of $BF_3 \cdot CH_3CN$[11] and $PdCl_2 \cdot 2C_6H_5CN$.[12] It is obvious that if such a colinear arrangement of atoms must be maintained, chelation by two nitrile moieties in a "short-chained" dinitrile would not be favored. Further, if chelation is a driving force in the formation of the complex, it would appear that bonding through the nitrile π-system may be realized. Such π-bonding would be analogous to acetylenic π-bonding, which is fairly well known.

We have found that the dinitriles $NC(CH_2)_xCN$, where $x = 1$, 2, 3, or 4, readily form compounds with a variety of anhydrous metal halides. In this report, we discuss the insoluble compounds formed with tin and titanium.[12a]

Experimental

Reagents.—Matheson Coleman and Bell titanium tetrachloride (99.5%), succinonitrile, and adiponitrile, Eastman White Label glutaronitrile, and Baker and Adamson tin(IV) chloride (anhydrous) were used without further purification. Eastman practical malononitrile and phthalonitrile were sublimed. Reagent grade benzene was stored over sodium wire. Dichloromethane was fractionated from phosphorus pentoxide and pentane was distilled from sulfuric acid.

Syntheses of Complexes.—Because of the extremely reactive nature of the compounds, all operations in the synthesis and sampling of the compounds were conducted in a drybox, the anhydrous condition of which was maintained by circulating the air over several open dishes of phosphorus pentoxide. The

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[2] National Science Foundation Undergraduate Research Participant, 1961; California Foundation for Biochemical Research Scholar, 1962.

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[12a] NOTE ADDED IN PROOF.—Since submission of this report, it has come to our attention that S. C. Jain and R. Rivest, *Can. J. Chem.*, **41**, 2130 (1963), have prepared similar compounds.

TABLE I

ANALYTICAL DATA AND INFRARED NITRILE STRETCHING FREQUENCIES

	Calcd.		Found		Dec. temp., °C.	Frequencies, cm.$^{-1}$	
	Metal	Cl	Metal	Cl		Nitrile	Complex
$SnCl_4 \cdot (CN)_2(CH_2)_2$	34.9	41.7	34.9	41.4	155	2258	2306
$SnCl_4 \cdot (CN)_2(CH_2)_3$	33.5	40.0	33.2	39.7	143	2251	2300
$SnCl_4 \cdot (CN)_2(CH_2)_4$	32.2	38.4	31.8	38.0	120	2248	2292
$TiCl_4 \cdot (CN)_2(CH_2)$		55.5		54.8	130	2275	2305
$TiCl_4 \cdot (CN)_2(CH_2)_2$	17.8	52.6	18.5	52.2	190	2258	2300
$TiCl_4 \cdot (CN)_2(CH_2)_3$		50.0		48.3	165	2251	2284
$TiCl_4 \cdot (CN)_2(CH_2)_4$		47.6		47.1	175	2248	2283
$TiCl_4 \cdot (CN)_2C_6H_4$		44.6		43.5	145	2249	2276

compounds generally were prepared by dissolving the dinitriles in anhydrous benzene or dichloromethane and then adding the metal halide dropwise. The white tin and yellow titanium complexes, which are precipitated immediately, were filtered, washed thoroughly with benzene to remove excess nitrile or halide, and then washed with pentane and dried *in vacuo*. All the titanium compounds were purified by vacuum sublimation at approximately 120°. A gooch crucible placed below the sublimer cold finger was found to be particularly desirable not only to catch loosely held sublimed product, but also to serve as an additional nucleation site within the sublimer. Illustrative of the syntheses is the example described below. Analytical data are summarized in Table I.

Tin(IV) Chloride–Succinonitrile.—Succinonitrile (0.68 g., 8.5 mmoles) was dissolved in 20 ml. of dry benzene and 2.5 g. (9.6 mmoles) of tin(IV) chloride was added dropwise. The white precipitate which immediately formed was filtered and washed thoroughly with benzene and pentane. The product (2.77 g., 96% yield) dried *in vacuo* begins to decompose at 155° in a sealed capillary. The compound is insoluble in chloroform, dichloromethane, benzene, and nitrobenzene. The compound dissolves in acetonitrile. *Anal.* Calcd. for $SnCl_4C_4H_4N_2$: C, 14.10; H, 1.18; N, 8.23. Found: C, 13.64; H, 1.90; N, 8.49.

Interaction of Succinonitrile with Weaker Lewis Acids.—Infrared examination of benzene solutions of succinonitrile containing an excess of silicon tetrachloride and dimethyltin dichloride (from Metal and Thermit Corp.) indicated that the free succinonitrile absorption bands remain virtually unchanged.

Interaction of Tin(IV) Chloride with Malononitrile and Phthalonitrile.—Addition of titanium(IV) chloride to dilute solutions of malononitrile and phthalonitrile yields immediate precipitation of the yellow complexes described above. On the other hand, addition of up to a fourfold molar excess of tin(IV) chloride to benzene solutions (0.2 *M*) of phthalonitrile and malononitrile does not yield a product in the manner observed with the other dinitriles. Infrared analysis of these solutions indicates that in addition to an intense band at the "free" nitrile stretching frequency, an intense band at increased frequency appears, presumably due to a complex. These are for malononitrile alone in benzene, 2274 cm.$^{-1}$; for malononitrile with excess tin(IV) chloride, 2291 cm.$^{-1}$; and for phthalonitrile, 2249 and 2272 cm.$^{-1}$.

Analysis and Infrared Spectra.—All hydrolyses of samples were conducted in a stoppered pressure equalizing addition funnel to preclude loss of hydrogen chloride. Chloride was determined gravimetrically or mercurimetrically. Tin was determined gravimetrically, after hydrolysis and ignition as the oxide. The infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. The spectra in the potassium bromide region were obtained with a Perkin-Elmer Model 112 with potassium bromide optics. All samples were examined either in Nujol mulls or potassium bromide disks.

Results and Discussion

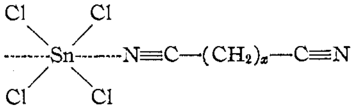
Silicon tetrachloride and dimethyltin dichloride form adducts with strong bases such as pyridine, but do not interact strongly with the mononitriles. The dinitriles appear to behave similarly, suggesting that the donor properties of the nitrile moieties are not strongly enhanced in the dinitriles.

The infrared spectra of the compounds served as an excellent means of monitoring the purity of the compounds. In particular, the appearance or disappearance of bands near 3400, 2290, and 1630 cm.$^{-1}$ was extremely sensitive to contamination of the compounds, either by exposure to water, thermal decomposition, or initially impure reagents. The stoichiometry suggests several interesting structural possibilities, all of theoretical and practical concern to systems where the nitrile moiety forms a donor–acceptor bond: (1) The dinitrile is monodentate and the acceptor atom is five-coordinate. (2) The acceptor atom exhibits the usual coordination number six and the dinitrile behaves as a chelating agent utilizing two nitrile lone electron pair donor centers. (3) The acceptor atom is six-coordinate; the dinitrile serves as a chelate utilizing the nitrile π-systems. (4) The dinitrile serves as a bridging ligand, with two nitrile π-systems forming two bridges between metal atoms. (5) The dinitrile is a bridging ligand, each nitrile moiety forming the typical lone electron pair bond to two adjacent metal atoms.

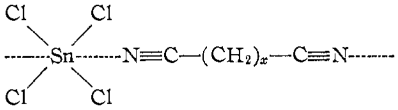
Whereas the alkyl and aryl mononitrile complexes of palladium(II), boron(III), tin(IV), and titanium(IV) chloride are soluble in benzene, nitrobenzene, and dichloromethane, the dinitrile complexes are but sparingly soluble. This would suggest either that the crystal lattice packing in these complexes leads to significantly stronger bonding between units or that the complexes are polymeric, hence tied together by nitrile groups. The infrared spectra of the complexes reveal only a single strong band near 2300 cm.$^{-1}$ in the region 1500–2800 cm.$^{-1}$. If the dinitrile is monodentate and thus possesses an unbonded nitrile group, it would be likely that in addition to the band characteristic of the complex, a band near the "free" nitrile frequency, 2250 cm.$^{-1}$, would be present. If the dinitrile forms a π-type bond involving the nitrile system, absorption bands would be expected in the region of reduced frequency, say 1500–2200 cm.$^{-1}$.

The single sharp intense band near 2300 cm.$^{-1}$ for the dinitrile complexes at frequencies approximately 30 to 60 cm.$^{-1}$ greater than the frequencies of the free dinitriles (see Table I) resembles the increases in frequencies and absorption intensities observed when the mononitriles form the donor–acceptor bond.[3b,9,13,14] In the compounds $BF_3 \cdot CH_3CN$[11] and $PdCl_2 \cdot 2C_6H_5CN$[12] where the colinear C–C–N–A linkage has been crystallographically established, characteristic increases in nitrile stretching frequencies as well as absorption intensities are observed, *viz.*, 2248–2359 cm.$^{-1}$ for the boron trifluoride compound[3b] and 2230–2292 cm.$^{-1}$ for the palladium chloride compound.[15]

It would be reasonable to suggest that the increases in nitrile frequency and absorption intensity upon donor–acceptor bond formation by the dinitrile ligands are diagnostic of the typical nitrile lone electron pair bond. Furthermore, the appearance of a single sharp absorption band suggests that each nitrile moiety in the dinitrile is forming such a bond. It is apparent that unless the two nitrile moieties are separated by a sufficient distance, chelation by dinitriles in the complexes with tin and titanium would be extremely unlikely due to stringent steric restrictions. It is proposed that the dinitriles must be bridging adjacent acceptor atoms as in



$$\cdots\mathrm{SnCl_4}\cdots N{\equiv}C{-}(CH_2)_x{-}C{\equiv}N$$



$$\cdots\mathrm{SnCl_4}\cdots N{\equiv}C{-}(CH_2)_x{-}C{\equiv}N\cdots$$

The dinitrile complexes possess properties generally associated with polymeric substances; they are intractable, insoluble, and nonmelting. This contrasts to the mononitrile complexes, which are not polymeric. The behavior of the dinitrile as a bridging ligand to form a polymer is not entirely novel, as recent reports indicate similar behavior by dibasic molecules such as pyrazine[16] and 4,4′-bipyridine,[17] which because of their geometry favor bridging rather than chelation. It is interesting to note that even ethylenediamine under certain environments will tend to be a bridging rather than a chelating ligand.[18]

The interaction of tin(IV) chloride with phthalonitrile and malononitrile deserves some comment. The presence of infrared absorption bands in the free nitrile stretching region, as well as bands due to a complex, suggests that free dinitrile may exist in equilibrium with complex as is observed with the mononitrile complexes.[3b,9] It is possible that only one nitrile moiety of the dinitrile is bonded to tin. The decreased basic strength of the nitrile groups due to inductive and resonance effects in malononitrile and phthalonitrile apparently contributes to the weaker interaction with the weaker Lewis acid, tin(IV) chloride. Not to be overlooked are the stereochemical requirements of the bonds formed by malononitrile and phthalonitrile with tin. Unlike the other aliphatic dinitriles, where rotational freedom between methylene groups allows projection of nearly parallel linear C–C–N–A linkages conducive to bridging, the direction of the linear C–C–N–A bonds in complexes of these two dinitriles are restricted to the tetrahedral angle in malononitrile and the sp^2 angle in phthalonitrile. This restriction coupled with the expected right angles in the octahedral tin coordination sphere may lead to considerable steric repulsions. Dimerization of malononitrile[19] and dehydrohalogenation due to the acidic malononitrile proton may also be complicating factors.

Rotational Isomers.—When each of the nitrile moieties of succinonitrile is bonded to two adjacent acceptor atoms "A," it is apparent that rotational conformers, *trans* or *gauche,* of the ligand may thereby be stabilized. (We assume the eclipsed conformers to be unimportant.) Infrared studies of the symmetrically disubstituted ethane, 1,2-dicyanoethane (succinonitrile), indicate that a mixture of two spectroscopically identifiable isomers exists in the liquid state, as well as in the solid above −43.7°.[20] Below this temperature, which is reproducible ascending or descending, a sharp, pronounced change in spectra occurs. Considerable spectral simplification in the form of disappearance or reduction of intensities of bands at 1270, 917, 760, and 530 cm.$^{-1}$, which occur below −43.7°, has led to the interpretation that a mixture of rotational conformers, *trans* and *gauche*, exists above the transition point and that the low temperature form is of the *gauche* conformation.[7,20] X-Ray and infrared studies of the low temperature form and of the succinonitrile–copper(I) nitrate complex support the contention that the low-temperature isomer is *gauche*.[7,8] That a change in structure occurs at the above mentioned transition temperature is also supported by measurement of the static dielectric constant of solid succinonitrile as a function of temperature.[21]

The data tabulated in Table II reveal striking differences in the spectra of free succinonitrile and the succinonitrile–metal halide complexes. It is evident that considerable spectral simplification occurs upon formation of the complex. Absorption bands near 530, 762, 917, and 1270 cm.$^{-1}$ which disappear when liquid succinonitrile is cooled below −43.7° to yield the *gauche* conformer alone previously have been assigned to the *trans* conformer.[7,20] In the complexes, we find that these are near frequencies where predominant bands appear, diagnostic of the *trans* conformer of succinonitrile. Further, it is observed that spectral simplification has occurred in each case where there is a C_2, but not a C_{2h}, assignment, that is at 480,

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Table II

Infrared Spectra of Succinonitrile and Succinonitrile Complexes

Assignment		Succinonitrile		$SnCl_4 \cdot (CN)_2C_2H_4$		$TiCl_4 \cdot (CN)_2C_2H_4$	
C_2 *gauche*	C_{2h} *trans*	Liquid (60°) (ref. 23)	Solid (−50°) (ref. 7)	(Nujol)	(KBr)	(Nujol)	(KBr)
A C–C–C bend		478 vs	483 ms				
	B_u C–C–C bend	530 w		536 m		538 s	536 s
B C–C–C bend		601 vs	603 ms				
	A_u CH_2 rock	762 s		756 ms	752 m	754 s	754 s
					762 m		
A C–CN stretch			810 ms		808 w		
B CH_2 rock		818 s	820 s		824 w		
	B_u C–CN stretch	917 s		932 s	922 m	938 s	937 s
A CH_2 rock		962 vs	963 vs		963 m		964 msh
B C–CN stretch		1002 vs	999 vs		997 m		1000 w
A C–C stretch		1025 w	1032 m				
A CH_2 twist	A_u CH_2 twist	1197 m	1189 m	1197 s	1197 s	1198 s	1197 s
A CH_2 wag		1230 s	1225 s		1233 w		
	B_u CH_2 wag	1270 m		1267 s	1273 w	1267 s	1267 s
B CH_2 wag		1338 s	1332 s		1336 w		1334 w
B CH_2 bend	B_u CH_2 bend	1425 vs	1414 vs	1417 s	1418 vs	1417 m	1418 s
A CH_2 bend			1431 vssh				
					1635 mb		1612 sb
C–N stretch		2255 vs	2257 s		2258 s		
						2276 sh	2280 s
C–N–M				2306 s		2293 s	
C–H stretch		2965	2959 wsh		2960		2950
		2985 vs	2994 m		3000		2980
					3480 sb		3380 sb

602, 812, 819, 962, 1000, 1030, 1228, and 1335 cm.$^{-1}$. The bands at 1197 and 1417 cm.$^{-1}$ are characteristic of both *trans* and *gauche*. The assignments by Matsubara,[7] who utilized a Urey–Bradley potential function, have been exceedingly accurately verified. Unlike that which is observed in the complexes of ethylenediamine,[18] it is noteworthy that in the dinitrile complexes, the methylene deformation frequencies are not greatly affected by formation of the donor–acceptor bond. Slight deviations which occur, notably for the B_u C–CN stretch and the B_u C–C–C bend, undoubtedly are due to effects of coordination of the nitrile with metal.

We have attempted the displacement of the ligand in the complexes by bromide in a solid potassium bromide matrix, hence allowing a study of succinonitrile alone in the *trans* configuration. The spectra of the complexes in potassium bromide disks with varying degrees of pressure revealed that displacement occurs rapidly, especially with the tin complexes where decomposition is nearly complete. The titanium complex is only slightly dissociated in potassium bromide. The product is a mixture primarily of the *trans* conformer, the *gauche* conformer, as well as a yet unidentified product with absorption bands near 3480 and 1635 cm.$^{-1}$. The spectra of the succinonitrile complexes of tin(IV), titanium(IV), and zirconium(IV) chlorides indicate that the succinonitrile absorption bands do not appear to be highly dependent on the metal atom. Investigations to characterize rotational conformers in glutaronitrile complexes are being conducted.

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