of 3.4×10^3) than with the other aminocarboxylate complexes. This too is understandable because NTA^{3-} as a leaving group has only weakly basic carboxylate sites free before cleavage of the copper–nitrogen bond in $CuNTA^-$.

In the three instances (Table V) where it was possible to measure the relative reactivity of tetren and Htetren$^+$ the latter was found to be about twice as reactive. The electrostatic attraction between CuL^{2-z} and Htetren$^+$ will assist the reaction, and if the proton remains on the tetren, it will be sufficiently distant from the tetren nitrogens coordinated to copper (see structure I) to prevent its disruption of this coordination. Also, transfer of the proton to the nitrogen of the aminocarboxylate may kinetically assist the cleavage of the aminocarboxylate copper bonding.

Only two systems were studied at high pH. For $CuDTPA^{3-}$ the same resolved rate constants were obtained regardless of the data employed. However with $CuHEEDTA^-$ it was not possible to fit the maximum point to the curve shown in Figure 1 unless the points above pH 11 were disregarded. There is no apparent reason for the large decrease above pH 11 since unprotonated tetren is the major reactant species in solution throughout this pH range. Similar unexplained results have been obtained for the reactions of diethylenetriamine with the copper(II)–cyclohexylenediaminetetraacetate complex.[3]

Comparison of Cu_{aquo}^{2+} and $CuNTA^-$.—It can be shown from the stability constant of $CuNTA^-$ and its kinetic behavior[16] that the dissociation rate of $CuNTA^-$ is slow at pH 5–6 ($k_d \approx 10^{-5}$ sec^{-1}), yet $CuNTA^-$ reacts faster with tetren in this pH range than does Cu_{aquo}^{2+}. The reaction of H_2tetren^{2+} is a factor of 5 larger for the NTA complex. Electrostatic factors become quite important in comparing the reaction of 2+ and 2+ ions to that of 1− and 2+ ions. The electrostatic advantage with $CuNTA^-$ must overcome the disadvantage that its rate-determining step with H_2tetren^{2+} is not the first bond formation as it is with Cu_{aquo}^{2+}. The difference in the position of the rate-determining step explains the crossover in the relative rate constants at pH 5. Additional protonation has a more adverse effect on the $CuNTA^-$ reaction because more of the tetren nitrogens need to coordinate to copper before the limiting step is reached in NTA^{3-} displacement and there are fewer basic sites on the leaving ligand to accept these protons. The experiments with methyl red show that NTA^{3-} is released in the rate-determining step and that the reaction is not a fast addition of tetren followed by a slow release of NTA^{3-}.

In general when a polyamine displaces an aminocarboxylate from a metal complex the rate is inversely proportional to the stability of the aminocarboxylate–metal complex. This rate is altered by the number of basic sites available for protons transferred from the polyamine to the leaving ligand. However there is no evidence that this transfer step limits the rate of the reaction with copper. Unlike the formation of the metal–polyamine complex from the hydrated metal ion, where the rate-determining step is the formation of the first metal–nitrogen bond, the transition state in the ligand-exchange mechanism involves at least three polyamine nitrogens bonded to the metal leaving only a single metal–nitrogen bond for the aminocarboxylate. Electrostatic effects are also important when comparing ligand-exchange reactions with formation reactions. When one reactant is a highly protonated polyamine, a ligand-exchange reaction may become more rapid than the rate of formation of the same polyamine–metal complex since the metal–aminocarboxylate complex has a reduced positive charge compared with the hydrated metal ion.

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The Zinc(II)-Catalyzed Reaction of Malononitrile with Ethyl Alcohol

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Malononitrile reacts with ethyl alcohol in the presence of zinc(II) halides to form a substituted pyridine (2,4-diamino-5-cyano-6-ethoxypyridine = L), which coordinates to the metal ion, forming the complex ZnL_2X_2 (X = Cl, Br, I). The complex and the free pyridine (isolated by hydrolysis of the complex) were characterized by chemical analysis and infrared, nuclear magnetic, visible–uv, conductance, and mass spectral measurements. A possible mechanism of formation is presented involving the condensation of two molecules of malononitrile and a molecule of ethyl alcohol followed by cyclization in the presence of the zinc(II) salt. When cadmium(II) chloride or bromide was employed, a mixture of CdL_2X_2 and a trimer of malononitrile was produced. With cadmium(II) iodide, only the trimer was obtained. No reaction took place in the presence of the mercury(II) halides.

Introduction

Metal complexes of alkyl and aryl nitriles, wherein bonding to the metal atom occurs *via* the nitrogen atom, are quite common and have been known for some time.[2] Recently, complexes of alkyl dinitriles[3,4] and

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[1] To whom correspondence should be addressed.

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diethylaminoacetonitrile[5,6] have been reported in which these molecules function as bidentate ligands by coordination *via* their CN triple bonds. This type of bonding results[3–6] in a lowering of the nitrile CN stretching frequency, relative to that of the free ligand, in contrast to terminal N bonding, which generally results[2] in an increased CN stretching frequency. A few exceptions in the latter case, involving cobalt(I)[7] and ruthenium(II)[8] complexes, have recently come to light. However, it should be noted that these substrates are particularly good π donors, in that they bind molecular nitrogen, and, in this context, the small decreases in the CN stretching frequencies of the N-coordinated nitriles observed are not too surprising.

In this context, we were quite surprised to isolate[9] a bright yellow crystalline compound from the reaction between zinc(II) chloride and malononitrile ($\mathrm{NCCH_2CN}$) in ethanol, which gave a chemical analysis corresponding to $\mathrm{ZnCl_2 \cdot 4NCCH_2CN \cdot 2CH_3CH_2OH}$ and exhibited a CN stretching frequency decrease of 65 cm^{-1}. Taken at face value, this implies an eight-coordinate zinc chelate complex. We now report the results of our efforts to determine the structure of the complex and a possible mechanism for its formation, as well as the course of the corresponding reactions with the cadmium(II) and mercury(II) halides.

Experimental Section

Reaction of Malononitrile with Zinc(II) Chloride in Ethanol.—To a solution of 0.05 mol of zinc(II) chloride (reagent grade) in 200 ml of 95% ethyl alcohol was added 0.10 mol of malononitrile, which had been recrystallized from ethyl alcohol prior to use. The solution was allowed to reflux for 2.5 hr. A bright yellow color appeared shortly after reflux began. Reducing the volume of the solution by reduced pressure produced a crystalline yellow solid which was isolated by filtration, washed with ethyl alcohol, and dried *in vacuo* over calcium sulfate; yield 40%; mp >300°. *Anal.* Calcd for $\mathrm{C_{16}Cl_2H_{20}N_8O_2Zn}$: C, 39.00; H, 4.09; N, 22.74; Cl, 14.39. Found: C, 38.78; H, 4.22; N, 22.55; Cl, 14.16.

Infrared Spectra.—These were recorded on a Perkin-Elmer Model 337 grating spectrophotometer. The samples were examined as Nujol mulls. A Perkin-Elmer Model 421 spectrophotometer was also used for high-resolution measurements. Absorption maxima were found at 3415 (s), 3385 (s), 3360 (sh), 3330 (s), 3235 (m), 3212 (m) (N—H stretching vibration region), and 2210 cm^{-1} ($\nu_{\mathrm{C\equiv N}}$). There were also various N—H, C—C, C=C, C=N, C—O, and C—H bands in the region 1600–600 cm^{-1}: 1632 (s), 1608 (s), 1565 (s), 1475 (sh), 1465 (s), 1442 (s), 1380 (m, sp), 1365 (m, sp), 1320 (w, sp), 1238 (s), 1202 (s), 1030 (s), 1010 (sh), 895 (m, sp), 795 (sh), 785 (s), 675 (w), 655 (w). The $\nu_{\mathrm{C\equiv N}}$ band of uncomplexed malononitrile is found at 2275 cm^{-1}.

Nmr.—Proton nuclear magnetic resonance spectra were recorded on a Varian A-60-A spectrometer, using tetramethylsilane as an internal standard. The compound was soluble in DMSO-d_6 (99.5% D) and a special 99.5% deuterated mixed solvent, Polysol-D [obtained from Stohler Isotope Chemicals, Rutherford, N. J.; composed (percentages unspecified) of DMSO-d_6, tetramethylsilane, and a deuterated chlorinated hydrocarbon], which is similar to DMSO in solubility characteristics but is less hygroscopic. Markedly different spectra were obtained, and these differences will be discussed shortly. The chemical shift in parts per million (δ) is followed by the splitting pattern (s = singlet, d = doublet, t = triplet, q = quartet), the number of protons, the coupling constant (J, Hz), and the assignment of the resonance signal. In DMSO: 1.25 (t, 3), 14, $-\mathrm{CH_2}\mathit{CH_3}$; 3.5 (s, 1.5), $\mathit{H{-}O{-}H}$; 4.18 (q, 2), 14, $-\mathit{CH_2}\mathrm{CH_3}$; 5.35 (s, 1), vinyl H; and 6.2 (s, 4), $-\mathrm{N}{-}\mathit{H}$. In Polysol: 1.27 (t, 3), 14, $-\mathrm{CH_2}\mathit{CH_3}$; 2.08 (s, 1.25), $-\mathrm{N}{-}\mathit{H}$; 3.49 (s, 2.75), $\mathit{H{-}O{-}H}$; 4.18 (q, 2), 14, $-\mathit{CH_2}\mathrm{CH_3}$; 5.37 (s, 1), vinyl H; and 5.91 (d, 2.75), 10, $-\mathrm{N}{-}\mathit{H}$.

Conductance.—The molar conductance at 25° of a 10^{-3} *M* solution of the complex in *N,N*-dimethylformamide was measured with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge and a cell with platinized electrodes. The complex was found to function as a nonelectrolyte, giving a value of 14.5 ohm^{-1} cm^2 mol^{-1}.

Visible–Ultraviolet Spectra.—The visible–uv spectrum of a 5.0×10^{-5} *M* acetonitrile solution of the complex was recorded on a Cary 14 spectrophotometer using matched 1-cm quartz cells. Bands were found at 34.2 kK (ϵ 18,700) and 38.9 kK (ϵ 17,400).

Mass Spectra.—The mass spectrum of the complex was measured on a CEC 21-110B double-focusing mass spectrometer by Mr. W. N. Einolf. Excitation conditions were 180° and 10^{-6} Torr. The parent ion peak was found at m/e 178 (molecular weight of $\mathrm{C_8H_{10}N_4O}$, hereafter referred to as L). Major peaks were also found at m/e 163, 150, 134, and 122, all of which may be accounted for in the proposed structure.

Reactions of Malononitrile with Zinc(II) Bromide and Iodide in Ethanol.—Analogous results were obtained when $\mathrm{ZnBr_2}$ and $\mathrm{ZnI_2}$ were employed in place of $\mathrm{ZnCl_2}$ in the above reaction. Satisfactory chemical analyses, conductance measurements, and infrared, nmr, and mass spectra were obtained which showed $\mathrm{ZnL_2Br_2}$ and $\mathrm{ZnL_2I_2}$ to be the products of the reaction.

Chemical Isolation of L.—One millimole of $\mathrm{ZnL_2Cl_2}$ (0.49 g) was placed in 10 ml of 6 *M* hydrochloric acid. To the bright yellow solution was slowly added a solution of 2 mmol (0.91 g) of $\mathrm{(C_6H_5)_4AsCl \cdot HCl}$ in a minimum amount of distilled water. An immediate precipitate formed. The solution was stirred magnetically for 1 hr to ensure complete reaction. A very pale yellow solid was isolated by filtration, washed with water, and dried *in vacuo* over $\mathrm{P_2O_5}$. *Anal.* Calcd for $\mathrm{[(C_6H_5)_4As]_2[ZnCl_4]}$: C, 59.20; H, 4.14. Found: C, 59.24; H, 3.89.

To the yellow filtrate containing $\mathrm{LH^+Cl^-}$ was slowly added dropwise, with stirring, a 6 *M* sodium hydroxide solution. As the pH of the solution approached 7, a yellow compound began to precipitate. Making the solution very slightly basic ensured complete precipitation of the yellow solid. The product was isolated by filtration, washed with water, and dried several hours *in vacuo* over $\mathrm{P_2O_5}$.

The impure product was then slowly added to a solution of 2 m g-atoms of sodium in 10 ml of ethyl alcohol. The solution was stirred magnetically for 90 min; then the ethanol was removed under a gentle stream of nitrogen. Ten milliliters of distilled water was added and the solution was stirred for 0.5 hr. The yellow compound was isolated by filtration, washed with distilled water and a little cold ethanol, and dried *in vacuo* over $\mathrm{P_2O_5}$ for several hours; yield 80%; mp 166–167°. *Anal.* Calcd for $\mathrm{C_8H_{10}N_4O}$: C, 53.92; H, 5.66; N, 31.44. Found: C, 53.92; H, 5.59; N, 31.62.

Infrared Spectra.—Peaks were found at 3468 (s), 3448 (sh), 3418 (s), 3360 (s), 3325 (s), 3235 (s) (N—H stretches), and 2205 cm^{-1} ($\nu_{\mathrm{C\equiv N}}$), along with numerous other N—H, C—C, C=C, C=N, C—O, and C—H peaks: 1628 (s), 1580 (s), 1448 (m, sp), 1430 (s, sp), 1382 (m, sp), 1360 (m, sp), 1318 (w, sp), 1220 (m, sp), 1192 (s), 1135 (m), 1105 (w), 1025 (m, sp), 980 (w), 895 (w), 775 (m, sp), 715 (m), 665 cm^{-1} (m).

Nmr.—In DMSO: 1.25 (t, 3), 15, $-\mathrm{CH_2}\mathit{CH_3}$; 3.32 (s, 0.6), $\mathit{{-}H{-}O{-}H}$; 4.18 (q, 2), 14, $-\mathit{CH_2}\mathrm{CH_3}$; 5.35 (s, 1), vinyl H; 6.2 (s, 4), $\mathit{{-}N{-}H}$. In Polysol: 1.25 (t, 3), 13, $-\mathrm{CH_2}\mathit{CH_3}$; 3.25 (s, 1.95), $\mathit{{-}N{-}H}$ and $\mathit{H{-}O{-}H}$; 4.18 (q, 2), 15, $-\mathit{CH_2}\mathrm{CH_3}$; 5.35 (s, 1), vinyl H; 5.9 (d, 3.2), 10, $\mathit{{-}N{-}H}$.

Conductance.—The compound is nonelectrolytic in DMF.

Visible–Ultraviolet Spectrum.—Absorption maxima (9.5×10^{-5} *M* acetonitrile solution) were found at 34.2 kK (ϵ 8450) and 37.6 kK (ϵ 8050).

Mass Spectrum.—The mass spectrum was identical with that for $\mathrm{ZnL_2Cl_2}$.

Reaction of L with Zinc(II) Chloride in Ethanol.—To a suspension of 1 mmol of L in 25 ml of warm ethanol was added slowly 0.5 mmol of $\mathrm{ZnCl_2}$. The addition of the $\mathrm{ZnCl_2}$ caused the L to go into solution. The solution was refluxed for 2.5 hr, after which the volume was reduced until solid product formed. The yellow solid, mp >300°, was isolated by filtration, washed with ethyl alcohol, and dried over $\mathrm{P_2O_5}$ *in vacuo*. *Anal.* Calcd

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for $C_{16}Cl_2H_{20}N_8O_2Zn$: C, 39.00; H, 4.09. Found: C, 38.85; H, 4.08.

Physical Measurements.—All measurements taken gave results *identical* with those obtained from the original complex formed.

Reaction of Malononitrile with Cadmium(II) Chloride and Bromide in Ethanol.—Carrying out the same reaction utilizing $CdCl_2$ and $CdBr_2$ instead of a zinc halide gave what appears to be a mixture of both CdL_2X_2 and $C_9H_6N_6$—a trimer of malononitrile (see below).

Reaction of Malononitrile with Cadmium(II) Iodide in Ethanol.—When CdI_2 was employed, the sole product was the yellow malononitrile trimer; mp >200° dec (lit.[10] mp 220–224°). *Anal.* Calcd for $C_9H_6N_6$: C, 54.55; H, 3.05; N, 42.40. Found: C, 53.98; H, 2.72; N, 42.33.

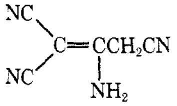
Physical Measurements.—Data from infrared, nuclear magnetic, and mass spectral measurements were in agreement with the formulation of the compound. There has been a fair amount of controversy in the literature[10–12] surrounding the structure of the malononitrile trimer. It appears that the trimer may assume any one of four different structures depending upon the reaction conditions employed. Our data lead us to believe that we have produced a mixture of two, and possibly three, of the isomers that are discussed by Junek and Sterk.[11]

Reaction of Malononitrile with Mercury(II) Halides in Ethanol.—When $HgCl_2$, $HgBr_2$, or HgI_2 was employed, no evidence of yellow color formation was observed. Reducing the volume to dryness yielded only starting materials.

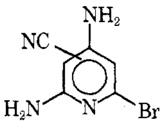
Analyses.—Microanalyses were performed by MHW Laboratories, Garden City, Mich., and the Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, Germany.

Discussion

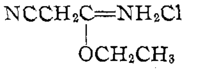
Possible Mechanism of Formation.—Carboni, *et al.*,[13] have described the preparation of substituted pyridines from derivatives of malononitrile, in particular, 2-amino-1,1,3-tricyanopropene



or more commonly, malononitrile dimer. The reaction of the dimer with hydrogen bromide in tetrahydrofuran produced



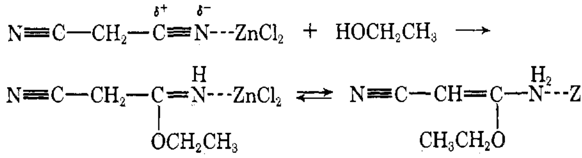
The same compound was obtained when $NCCH_2CN$ was used in place of the dimer. (The exact position of the cyano group could not be determined; it was presumed to be in the 3 or the 5 position.) McElvain and Schroeder[14] treated $NCCH_2CN$ with ethanol in the presence of hydrogen chloride and formed an imino ester hydrochloride



$$NCCH_2\underset{OCH_2CH_3}{C}{=}NH_2Cl$$

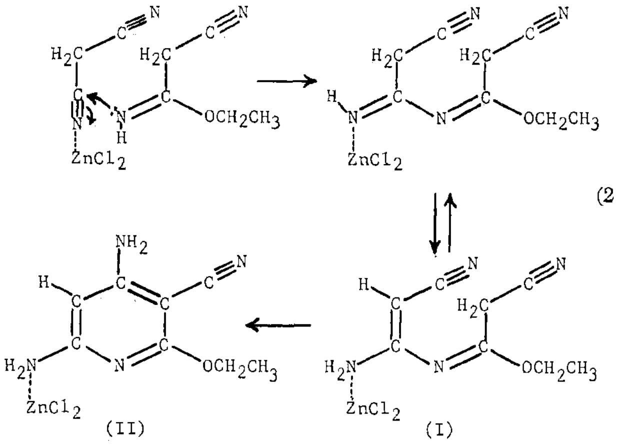
The apparent tendency of malononitrile to undergo a number of reactions with various acid catalysts has been described in the literature.[15]

In view of the foregoing, our approach to the elucidation of the structure of the reaction product was predicated on the assumption that malononitrile and ethyl alcohol were reacting, in the presence of the Lewis acid $ZnCl_2$, to form a condensation product. This product could then undergo cyclization to form a substituted pyridine. The reaction scheme



$$N{\equiv}C{-}CH_2{-}\overset{\delta+}{C}{\equiv}\overset{\delta-}{N}{\cdots}ZnCl_2 + HOCH_2CH_3 \longrightarrow$$

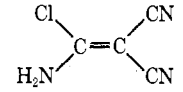
$$N{\equiv}C{-}CH_2{-}\underset{OCH_2CH_3}{C}{=}\overset{H}{N}{\cdots}ZnCl_2 \rightleftarrows N{\equiv}C{-}CH{=}\underset{CH_3CH_2O}{C}{-}\overset{H_2}{N}{\cdots}ZnCl_2 \qquad (1)$$



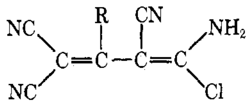
(2)

may be envisioned. The chemical analysis indicates that two new pyridine molecules are coordinated to every $ZnCl_2$ and it is possible that each zinc(II) ion could serve to activate two simultaneous addition reactions.

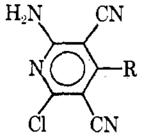
Little, *et al.*,[16] eliminated the possibility of forming a linear structure instead of the cyclization product in forming pyridines from tetracyanopropene salts. Their main consideration was that a molecule such as



which would be similar to



(their linear structural possibility) is quite acidic. Their cyclic structure



would not exhibit acidic properties, and this piece of evidence, coupled with other measurements, enabled them to decide in favor of the pyridine structure. We feel that, in the present case, the alternative linear structures, *e.g.*, structure I, would be subject to the same considerations, and, hence, the pyridine structure II would be expected to be formed.

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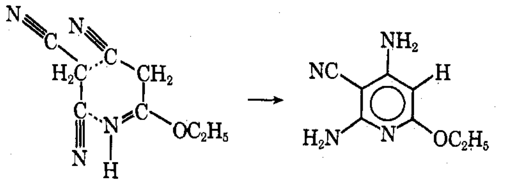
It can readily be seen that the –C≡N group may also be in the 3 position, depending on the orientation of the two fragments composing the ring, *i.e.*



We are unable to distinguish between the two possible structures on the basis of our measurements.

Verification of Structure.—The mass spectral measurements for both the complex and the ligand L were identical. Under the excitation conditions employed, the ligand is dissociated from the complex, leaving the nonvolatile zinc(II) chloride behind. The parent ion peak at *m/e* 178 corresponds to the molecular weight of the species $C_8H_{10}N_4O$. Precise mass measurements confirmed this to be the only possible empirical formula. Major peaks were found at *m/e* 163, 150, 134, and 122. These fragment peaks correspond to the loss of $-CH_3$, C_2H_4, C_2H_4O, and C_3H_4O, respectively. The loss of these stable fragments was also observed when a sample of 2-ethoxypyridine was placed in the mass spectrometer, thus lending further credence to the proposed aromatic structure. The $-CH_3$, $-CH_2-$, $-CH=$, and N—H resonances observed in the proton nmr spectrum of the free ligand are in good agreement with the proposed structure. The interpretation of the data with regard to the structure of the complex is, however, somewhat less straightforward. The fact that the $\nu_{C\equiv N}$ frequencies of the free and complexed ligand are virtually identical rules out the possibility of nitrile coordination. Steric hindrance would tend to prevent coordination *via* the pyridine nitrogen. Of the two amino groups, that in the 2 position is less sterically hindered and would be expected to be the favored coordination site.

A comparison of the infrared spectra of the ligand and the complex strongly supports coordination *via* an $-NH_2$ group, but it does not permit an unequivocal choice between the two groups. The significant differences which indicate the presence of both free and complexed $-NH_2$ groups in the complex include shifts of some, but not all, of the N–H stretching bands in the 3500–3200-cm^{-1} region and the appearance of an additional asymmetric $-NH_2$ deformation band (1608 cm^{-1}) and an additional $-NH_2$ rocking band (795 cm^{-1}) in the spectrum of the complex.

When the complex was dissolved in DMSO, only one proton nmr resonance signal for the –NH protons was observed. However, upon dissolution in Polysol, the singlet at δ 6.2, which had integrated for 4 protons, changed to a doublet at δ 5.91 accounting for 2.75 protons, and a new, sharp singlet appeared at δ 2.08 which accounted for 1.25 protons. Furthermore, the spectrum of the complex in DMSO was identical with that of the free ligand. These two observations lead to the following interpretation.

In DMSO, the ligand is completely replaced by solvent molecules to give a solution primarily composed of $Zn(DMSO)_xCl_2$ and free L. This gives rise to the lone signal at δ 6.2 which accounts for all of the $-NH_2$ protons. This conclusion is further supported by the fact that the result of an attempt to determine the molecular weight of the complex in DMF indicated that extensive dissociation takes place. Since the complex behaves as a nonelectrolyte in DMF, the L ligands must be the groups displaced by the DMF, and comparable behavior would be expected in DMSO.

In Polysol, however, dissociation is not complete, and two resonances are observed, that at δ 5.91 being due to the uncomplexed $-NH_2$ groups while that at δ 2.08 is attributed to the $-NH_2$ groups bonded to zinc(II). The shift to higher field strength in the latter case would be expected to result from diamagnetic shielding by the d^{10} metal ion. Why the resonances due to the uncomplexed 2- and 4-amino groups are differentiated in the nmr spectrum of the Polysol solution (the δ 5.91 resonance is a doublet) but not in the spectrum of the DMSO solution (only a singlet appears at δ 6.2) is not understood.

The striking difference in catalytic activity between the zinc(II) and mercury(II) halides is attributed to the fact that zinc(II), being a much harder metal ion,[17] would have a greater tendency to coordinate to the nitrile and thereby render it more susceptible to reaction. Intermediate behavior is observed for the cadmium(II) halides, cadmium(II) being intermediate in hardness. The reasons for the appearance of the trimer in this case are not understood, nor were they pursued. As mentioned earlier, the trimer has been previously prepared,[10–12] albeit not in this manner, and the reader is referred to the literature for the arguments concerning its structure.

Finally, it is of interest to note that adiponitrile reacts[18] with $ZnCl_2$ in ethanol to form only the colorless bis(dinitrile)-bridged complex $[Zn(NC(CH_2)_4CN)Cl_2]_2$. Likewise, succinonitrile forms[18] only $[Zn(NC(CH_2)_2CN)Cl_2]_2$ in 2-butanol. However, yellow colors develop[18] when $ZnCl_2$ is refluxed with either succinonitrile or glutaronitrile in methanol, indicating the possible occurrence of condensation reactions such as that described herein.

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