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Alkyl Dinitrile Complexes of Cobalt(II), Nickel(II) and Zinc(II)

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A series of alkyl dinitrile complexes of the type $[M(NC(CH_2)_nCN)Cl_2]_2$ *[n = 2-4; M = Co^{II}, Ni^{II}, Zn^{II}] has been prepared by the reaction of the appropriate metal chlorides and dinitriles in 2- or t-butanol [ethanol/chloroform, for n = 2 and M = Co^{II}; ethanol, for n = 4 and M = Zn^{II}]. The observation of only blue-shifted (relative to the uncomplexed dinitriles)* $\nu_{C\equiv N}$ *bands in the infrared spectra of the complexes supports their formulation as dinuclear species containing two N-bonded bridging dinitrile groups. The Co^{II} and Ni^{II} complexes undergo reversible hydration to form octahedral dinuclear complexes. The nature of the solvent, coupled with the chain length of the dinitrile and the nature of the metal, can markedly affect the course of the reaction. $Zinc^{II}$, but not Hg^{II}, catalyzes a reaction between malononitrile and ethanol which results in the formation of a pyridine derivative. No such reaction takes place if the malononitrile is replaced by adiponitrile. The effects of the charge on the metal, the energy level of the d orbitals of the metal, and the geometry of the ligand on the coordination behavior (CN triple bond coordination versus N-coordination) of* $NC(CH_2)_nCN$ *and* $NC(CH_2)_nNR_2$ *molecules are also discussed.*

Introduction

Striking differences in the coordination behavior of alkyl dinitriles of the type $NC(CH_2)_nCN$ have been observed, depending upon the nature of the metal coordination center. In the complexes $Cu(NC(CH_2)_nCN)_2NO_3$ [1-3] (n = 2-4), $M(NC(CH_2)_nCN)_2ClO_4$ [4,5] (M = Cu^I, Ag^I; n = 1, 2) and $M(NC(CH_2)_nCN)Cl_4$ [5-7] (M = Ti^{IV}, Sn^{IV}; n = 1-4), the dinitrile molecules function as bridging ligands between metal atoms, coordinating *via* the lone pairs on the nitrogen atoms. However, in the complexes $M(CO)_3(NC(CH_2)_nCN)X$ [8,9] (M = Mn^I, Re^I; n = 1-3; X = Cl, Br) the dinitriles coordinate as bidentate ligands *via* the CN triple bonds. An exception is found[9] in the complex $Mn_2(CO)_6(NC(CH_2)_3CN)Cl_2$, which contains both bridging Cl and dinitrile (N-coordinated) groups. In view of this disparate behavior, it was of considerable interest to investigate[10] the coordination chemistry of alkyl dinitriles with typical transition metals in their normal oxidation states, *e.g.*, Co^{II}, Ni^{II}, and Zn^{II}, with regard to the effects of such factors as the nature of the metal atom and the number of carbon atoms in the dinitrile skeleton (n = 1-4). We now report the results of this study.

(1) Y. Kinoshita, I. Matsubara, and Y. Saito, *Bull. Chem. Soc. Japan*, *32*, 741, 1216 (1959).
(2) Y. Kinoshita, I. Matsubara, T. Higuchi, and Y. Saito, *Bull. Chem. Soc. Japan*, *32*, 1221 (1959).
(3) I. Matsubara, *Bull. Chem. Soc. Japan*, *34*, 1710, 1719 (1961); *35*, 27 (1962).
(4) M. Kubota, D. L. Johnston, and I. Matsubara, *Inorg. Chem.*, *5*, 386 (1966).
(5) M. Kubota and D. L. Johnston, *J. Amer. Chem. Soc.*, *88*, 2451 (1966).
(6) M. Kubota and S. R. Schulze, *Inorg. Chem.*, *3*, 853 (1964).
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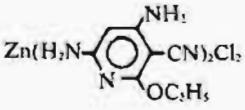
Experimental Section

Reactions with Malononitrile. The reaction between $ZnCl_2$ and malononitrile (n = 1) in boiling ethanol has been shown[11] to result in the formation of the bright yellow complex



wherein the ligand is coordinated *via* one of its amino groups. The postulated mechanism[11] of the reaction involves the zinc(II)-catalysed addition of ethanol to a CN triple bond of the malononitrile, followed by condensation with another malononitrile molecule [also probably catalysed by zinc(II)] and eventual cyclization. The corresponding reaction between $CoCl_2 \cdot 6H_2O$ and malononitrile in ethanol yields an impure, extensively hydrated green complex which is probably an analog of the zinc(II) complex (the $\nu_{C\equiv N}$ bands of both are found at 2210 cm^{-1}). Heating $Ni(NO_3)_2 \cdot 6H_2O$ and malononitrile in 2-butanol at 60-80° yields a dark red solid, also extensively hydrated, which exhibits a $\nu_{C\equiv N}$ band at 2237 cm^{-1}. Unfortunately, repeated preparations of this complex did not yield reproducible analyses. The $\nu_{C\equiv N}$ frequency lowerings exhibited by these complexes (relative to the $\nu_{C\equiv N}$ frequency of uncomplexed malononitrile at 2275 cm^{-1}) were initially incorrectly interpreted[10] as being evidence for coordination of the CN triple bonds in all three cases, although this may still be true for the nickel(II) complex since 2-butanol generally does not add to the CN triple bond in these reactions, *vide infra*.

(10) M. Y. Al-Janabi, Ph. D. Dissertation, University of Delaware, June, 1968.
(11) J. L. Silver, M. Y. Al-Janabi, R. M. Johnson, and J. L. Burmeister, *Inorg. Chem.*, *10*, 000 (1971).

Reactions with Succinonitrile. Preparation of $[Co(NC(CH_2)_2CN)Cl_2]_2 . 6H_2O$. The solvent employed was a mixture of 45% (by volume) chloroform, 10% water, and 45% ethanol. The reaction was carried out in a nitrogen atmosphere. Fifty mmoles of succinonitrile was added to a solution of 16.6 mmole of $CoCl_2 . 6H_2O$ in 60 ml of the solvent. The solution was refluxed for 3 hr, filtered, and the precipitate obtained was washed throughly with chloroform and ethyl ether, and dried *in vacuo* over calcium chloride. It was then dissolved in 50/50 (v/v) acetone-chloroform. The solution was filtered, and the filtrate reduced to one-half of its original volume, filtered again, and the filtrate was allowed to stand in a refrigerator for several months, during which time pink crystals appeared. They were collected by filtration, washed with ethyl ether and dried *in vacuo* over calcium chloride. The completely dry solid is blue in color but, upon exposure to moisture, rapidly reverts to the hydrated pink form.

Anal. Calcd. for $C_8Cl_4Co_2H_{20}N_4O_6$: C, 18.20; H, 3.78; N, 10.61; Cl, 26.89. Found: C, 17.84; H, 4.87; N, 10.65; Cl, 26.82.

Preparation of $[Ni(NC(CH_2)_2CN)Cl_2]_2 . 8H_2O$. One hundred mmoles of $NiCl_2 . 6H_2O$ was suspended in 25 ml of 2-butanol, and heated to 66° with stirring. Four hundred mmoles of succinonitrile was added, whereupon the solution became light blue in color. Refluxing the solution for 30 min did not result in any further change. The blue solid was isolated by filtration, washed thoroughly with 2-butanol and ethyl ether, and dried *in vacuo* over calcium sulfate. If the blue solid is heated for two hr at 80°, its color changes to yellow. The blue color reappears upon exposure to moist air.

Anal. Calcd. for $C_8Cl_4H_{24}N_4Ni_2O_8$: C, 17.02; H, 4.25; N, 9.93; Cl, 25.12. Found: C, 17.17; H, 4.57; N, 9.94; Cl, 25.45.

Preparation of $[Zn(NC(CH_2)_2CN)Cl_2]_2$. Twenty mmoles of succinonitrile was dissolved in 15 ml of 2-butanol and then added to a solution of 5 mmol of $ZnCl_2$ in 50 ml of 2-butanol. The solution was refluxed for 4.5 hr, then 50 ml of the solvent was removed *in vacuo*. The remaining solution was allowed to stand overnight at room temperature, then filtered. After the filtrate was evaporated almost to dryness, the solid which formed was removed by filtration and recrystallized from 2-butanol. The colorless crystals were washed with ethyl ether and dried *in vacuo* over calcium chloride.

Anal. Calcd. for $C_8Cl_4H_8N_4Zn_2$: C, 22.18; H, 1.84; N, 12.93; Cl, 32.81. Found: C, 22.28; H, 2.04; N, 12.86; Cl, 32.63.

When the reaction was carried out in methanol (3:1 ligand/metal ratio), a yellow color developed upon refluxing the solution for 3 hr. Concentration of the solution yielded a viscous yellow material.

Reactions with Glutaronitrile. Preparation of $[Co(NC(CH_2)_3CN)Cl_2]_2 . 4H_2O$. Fifty mmoles of glutaronitrile was added to a solution of 16.6 mmol of $CoCl_2 . 6H_2O$ in 100 ml of warm *t*-butanol. After the solution had been refluxed for 4 hr, half of the solvent was allowed to evaporate and the remaining solution kept at room temperature for 3 days, then filtered. The filtrate was concentrated to one-half of its original volume, then allowed to stand at room temperature for 2 days. Filtration yielded a pink precipitate which was washed with ethyl ether and dried *in vacuo* over calcium sulfate. The dehydrated form of the complex is blue in color.

Anal. Calcd for $C_{10}Cl_4Co_2H_{20}N_4O_4$: C, 23.20; H, 3.83; N, 10.80; Cl, 27.30. Found: C, 23.23; H, 3.81; N, 10.84; Cl, 27.53.

Preparation of $[Ni(NC(CH_2)_3CN)Cl_2]_2 . 4H_2O$. This green complex was prepared in the same manner as the succinonitrile derivative, with the exception that the solution was refluxed for one hr.

Anal. Calcd for $C_{10}Cl_4H_{20}N_4Ni_2O_4$: C, 17.02; H, 4.25; N, 9.93; Cl, 25.12. Found: C, 17.17; H, 4.57; N, 9.94; Cl, 25.45.

Reaction with Zinc(II) Chloride. Refluxing glutaronitrile and $ZnCl_2$ (3:1 ligand/metal ratio) in methanol for 24 hr, followed by the addition of ethanol, the reduction of the volume of the solution, and the addition of ethyl ether, yielded a viscous yellow material.

Reactions with Adiponitrile. Preparation of $[Co(NC(CH_2)_4CN)Cl_2]_2 . 4H_2O$. This pink complex was prepared in the same manner as the glutaronitrile derivative.

Anal. Calcd for $C_{12}Cl_4Co_2H_{24}N_4O_4$: C, 26.10; H, 4.36; N, 10.20; Cl, 25.80. Found: C, 26.18; H, 4.57; N, 10.31; Cl, 25.80.

Preparation of $[Ni(NC(CH_2)_4CN)Cl_2]_2 . 4H_2O$. This green complex was prepared in the same manner as the succinonitrile derivative, with the exception that the solution was refluxed overnight.

Anal. Calcd for $C_{12}Cl_4H_{24}N_4Ni_2O_4$: C, 26.28; H, 4.38; N, 10.22; Cl, 25.91. Found: C, 26.65; H, 4.58; N, 10.20; Cl, 26.10.

Preparation of $[Zn(NC(CH_2)_4CN)Cl_2]_2$. Thirty mmoles of adiponitrile was added to 10 mmoles of $ZnCl_2$ in 50 ml of ethyl alcohol. The solution was refluxed for 30 hr, during which time no change in color was noticed. It was concentrated on a steam bath until precipitation commenced, then allowed to stand overnight. Filtration yielded only crystals of unreacted starting material. The filtrate was reduced in volume until precipitation again commenced. Long white crystals formed upon standing overnight. These were isolated by filtration, washed with ethyl ether, and dried *in vacuo* over calcium chloride.

Anal. Calcd for $C_{12}Cl_4H_{16}N_4Zn_2$: C, 29.40; H, 3.21; N, 11.45; Cl, 29.05. Found: C, 29.30; H, 3.33; N, 11.32; Cl, 29.28.

Physical Measurements. Microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Mülheim, Germany. Infrared spectra were measured as Nujol mulls on a Perkin Elmer 421 spectrophotometer, using a five-fold wavenumber scale expansion in the $\nu_{C\equiv N}$ region. The $\nu_{C\equiv N}$ frequencies for both the complexes and the free dinitriles are shown in Table I.

Molar conductances at 25° of 10^{-3} *M* solutions of

Table I. $\nu_{C\equiv N}$ Frequencies[a] of Alkyl Dinitriles and the $[M(NC(CH_2)_nCN)Cl_2]_2 . xH_2O$ Complexes

Dinitrile/M	x	$\nu_{C\equiv N}$, cm^{-1}	$\Delta\nu_{C\equiv N}$[b], cm^{-1}
succinonitrile	—	2275 sh, 2253 s	—
Co^{II}	0	2302 s, 2289 s	+49, +36
	6	2300 s, 2287 s	+47, +34
Ni^{II}	0	2310 s, 2300 sh	+57, +47
	8	2308 s, 2298 s	+55, +45
Zn^{II}	0	2313 s, 2283 sh, 2265 sh	+60, +30, +12
glutaronitrile	—	2255 s	—
Co^{II}	0	2288 s	+33
	4	2300 s, 2288 s	+45, +33
Ni^{II}	4	2287 s	+32
adiponitrile	—	2249 s	—
Co^{II}	4	2292 s	+43
Ni^{II}	4	2292 s	+43
Zn^{II}	0	2292 s	+43

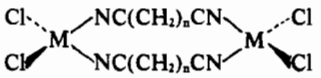
[a]Measured as Nujol mulls; s, strong; m, medium; sh, shoulder. [b] Relative to free ligand.

the complexes in Spectrograde N,N-dimethylformamide were determined with an Industrial Instruments, Inc. Model RC-16B2 conductivity bridge and a cell with platinized electrodes. The cobalt(II) and zinc(II) complexes behave as non-electrolytes in DMF solution, whereas the nickel(II) complexes exhibit considerable chloride ion dissociation (Λ_m values of 63-76 ohm^{-1} cm^2 mol^{-1}).

Discussion

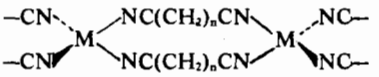
The differing coordination behavior exhibited by alkyl dinitriles is reflected in the different frequency shifts of the $\nu_{C\equiv N}$ band resulting from coordination which have been observed. The N-bonded bridging dinitriles all exhibit[3-7] increased $\nu_{C\equiv N}$ frequencies, relative to those of the uncomplexed dinitriles. Blue shifts have generally been observed[12,13] for N-bonded nitriles, and an explanation of this effect, based on the results of normal coordinate analyses and molecular orbital calculations, has been presented in the recent literature.[14,15] Coordination of the dinitriles *via* their CN triple bonds invariably results[8,9] in a diminution of the $\nu_{C\equiv N}$ frequency. The same effect has been observed for a series of diethylaminoacetonitrile complexes,[16,17] wherein the molecule functions as a bidentate chelating ligand, bonding *via* the lone pair of the amino group and the CN triple bond. The red shift may generally be attributed to a combination of ligand→metal σ-bonding, involving the π-bonding electrons of the CN group, and metal→ligand π-bonding, involving the π^* orbitals of the CN group, both of which serve to lower the CN bond order, much in the same manner as alkene and alkyne π-complexes.

The dinitriles utilized in this study were chosen such that, with the possible exception of adiponitrile, the number of methylene groups present in each would be insufficient to permit chelation through both nitrogen lone pairs to the same metal ion. Since all of the anhydrous succinonitrile, glutaronitrile, and adiponitrile complexes shown in Table I exhibit *only* blue-shifted $\nu_{C\equiv N}$ bands, a common structure involving N-bonded bridging dinitriles and tetrahedral geometry about the metal atoms is most probable:



$[M=Co^{II}, Ni^{II}, Zn^{II}]$

This structure is analogous to that observed for the previously reported[1-5] copper(I) and silver(I) complexes, with the exception that the presence of a coordinating anion (Cl^-) prevents the formation of the polymeric structure observed for the latter



$[M=Cu^{I}, Ag^{I}]$

That the metal-nitrile bonds are quite weak is seen in the fact that even the nitrate ion has been found to successfully compete with the dinitriles for coordination sites, as in the complex $2AgNO_3 . NC(CH_2)_2CN$.[4]

The color changes observed for the cobalt(II) and nickel(II) complexes upon hydration are undoubtedly due to a switch to octahedral geometry, with water molecules occupying *trans* positions on each metal, the process being reversible. The $\nu_{C\equiv N}$ bands shown for the hydrated complexes in Table I are those exhibited by the complexes when they are initially prepared as hydrates. Dehydration and rehydration yields complexes which, in addition to the $\nu_{C\equiv N}$ bands shown, exhibit new $\nu_{C\equiv N}$ bands of medium intensity at frequencies lower than those of the free dinitriles, *e.g.*, 2160 and 2171 cm^{-1}, respectively, for the reconstituted $[Co(NC(CH_2)_2CN)Cl_2]_2 . 6H_2O$ and $[Ni(NC(CH_2)_2CN)Cl_2]_2 . 8H_2O$ complexes. This suggests concurrent rearrangement of some of the dinitrile groups to accommodate bonding *via* their CN triple bonds.

An overview of the different types of complexes formed by the $NC(CH_2)_nCN$ and $NC(CH_2)_nNR_2$ molecules reveals the importance of the charge on the metal, the energy level of the d orbitals of the metal, the geometry

(12) R. A. Walton, *Quart. Rev.*, *19*, 126 (1965).
(13) Two recent exceptions involving cobalt(I) and ruthenium(II) complexes containing N-bonded nitriles have been reported [A. Misono, Y. Uchida, M. Hidai, and T. Kuse, *Chem. Commun.*, 208 (1969); R. E. Clark and P. C. Ford, *Inorg. Chem.*, *9*, 227 (1970)]. The small $\nu_{C\equiv N}$ frequency decreases observed may be attributed to the fact that the metal coordination centers are exceptionally good π-donors, as evidenced by the fact that they coordinate molecular nitrogen.
(14) K. F. Purcell and R. S. Drago, *J. Amer. Chem. Soc.*, *88*, 919 (1966).
(15) K. F. Purcell, *J. Amer. Chem. Soc.*, *89*, 247 (1967).
(16) S. C. Jain and R. Rivest, *Inorg. Chem.*, *6*, 467 (1967).
(17) S. C. Jain and R. Rivest, *Inorg. Chim. Acta*, *3*, 249 (1969)

of the ligand, and the nature of the reaction medium in determining the bonding fate of the molecules. Low positive charge, coupled with soft metal character, *i.e.*, filled d orbitals of appropriate symmetry and energy, favor coordination through the CN triple bond, since metal→ligand π-bonding can be optimized under these conditions. A low charge on the metal is not sufficient unto itself to result in this type of bond, as is demonstrated by the manganese(I)[9] and copper(I)[1-5] complexes. However, if the geometry of the ligand is such that the CN group is constrained by its position to coordinate *via* its triple bond, as in diethylaminoacetonitrile,[16,17] this can be accomplished even with a metal having a high positive charge and no d electrons, *e.g.*, $[Ti(NCCH_2N(C_2H_5)_2)Cl_4]$[16] ($\Delta\nu_{C\equiv N} = -70\ cm^{-1}$). If this constraint is removed, either by increasing the chain length, *e.g.*, $[Ti(NC(CH_2)_3N(CH_3)_2)Cl_4]$[16] ($\Delta\nu_{C\equiv N} = +45\ cm^{-1}$); switching to a coordination center with only one bonding site available, *e.g.*, $2BCl_3 . NCCH_2N(C_2H_5)_2$[16] ($\Delta\nu_{C\equiv N} = +60\ cm^{-1}$); or switching to a dinitrile, *e.g.*, $[Ti(NCCH_2CN)Cl_4]_2$[6] ($\Delta\nu_{C\equiv N} = +30\ cm^{-1}$); chelation or bridging by N-bonded groups results.

In addition to providing further evidence supporting the trends described above, the results of this study have revealed the importance of the solvent, coupled with the chain length of the dinitrile and the nature of the metal, in determining the result of the reaction. Thus, zinc(II), but not mercury(II),[11] catalyzes an addition/condensation/cyclization reaction between malononitrile and ethanol. Based on the appearance of viscous yellow products, zinc(II) apparently initiates similar reactions between succino- and glutaronitrile and methanol. However, no reaction between glutaronitrile and ethanol takes place in the presence of zinc(II). Neither 2- nor *t*-butanol reacts with the nitriles in the presence of any of the metal ions employed.

The effectiveness, relative to mercury(II), of zinc(II) as a catalyst for the reaction may be explained[11] on the basis of zinc(II) being a harder coordination site.[18-20] As a result, it would be expected to coordinate more strongly to the nitrogen atom of a nitrile group, polarizing the group to a greater extent, and thereby making it more susceptible to the addition of the ethanol molecule. The lack of reactivity of glutaronitrile may be attributed to its greater chain length, which would make ring closure more difficult. The rather surprising lack of reactivity of both 2- and *t*-butanol may be due to steric hindrance, although this does not appear to be very large in the former case.

The coordination chemistry of the corresponding diisocyanides, $CN(CH_2)_nNC$, is currently being investigated in our laboratory.

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(20) G. Klopman, *J. Amer. Chem. Soc.*, *90*, 223 (1968).