C≡N Frequency Shifts in Dinitrilo Complexes of Cd^{2+}

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Reaction of $CdCl_2$ with $NC(CH_2)_nCN$, $n=1$, 3, 4 and 5 produced new complexes. The C≡N frequency red and blue shifts were noticed in them. These are explained in terms of interaction between the 5_pAO of Cd^{2+} and the MOs of the C≡N group.

It is well known that the vibration frequency of a nitrilo group changes on its coordination to a metal [1] and increases on its hydrogen bridge formation with a proton donating species [2]. Both frequency shifts were attributed to two different kinds of coordination; (a) coordination to the N-lone pair orbital causing an increase in the vibration frequency; (b) π-coordination to the C≡N bond causing a decrease in the vibration frequency [3]. Recent measurements of the vibration frequencies of the C≡N groups in alkyl dinitrile complexes showed the two types of shifts. It was noticed that if the ligand acts as a bridge between two metal ions and coordinates through the lone pair orbitals on the nitrogen atoms in the complex $[M(NC(CH_2)_nCN)_2Cl_2]_2$, (M = Co^{2+}, Ni^{2+}, Zn^{2+}; $n = -4$ [4]; $M(NC(CH_2)_nCN)_2ClO_4$, (M = Cu^{1+}, Ag^{1+}, $n = 1, 2$) [5, 6] and $(M(NC(CH_2)_nCN)Cl_4$, (M = Ti^{4+}, Sn^{4+}, $n = 1-4$); [6–8] an increase in the C≡N frequency is observed. On the other hand in the complexes $M(CO)_3(NC(CH_2)_nCN)X$ where the dinitrile coordinates via the triple bond as a bidentate ligand, a decrease in the C≡N frequency is observed, (M = Mn^{1+}, Re^{1+}; $n = 1-3$; X = Cl, Br) [9, 10]. We report here an extension of this study to the dinitrilo complexes of Cd^{2+} and a theoretical explanation for the observed frequency shifts.

Experimental Part

The infrared spectra were measured on a Perkin-Elmer model 137E infracord spectrophotometer using nujol mulls, and on a Perkin-Elmer spectrophotometer model 257 with a 2.5 fold wave number expansion. The C, H, N analyses were performed by the Alfred Bernhardt Microanalytisches Laboratorium- Mühlheim, West-Germany.

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Preparation of Bismalononitrile cadmium(II) chloride, hexahydrate

Twenty mmoles of malononitrile dissolved in the least amount of isobutanol were added to 10 mmoles of cadmiumchloride dissolved in the least amount of isobutanol also. The mixture was refluxed for 10 hours during which its colour changed from colorless to yellow. After cooling, the formed yellow precipitate was filtered, washed with ethanol and ether and dried under vacuum.

Anal. for $Cd[(NC-CH_2-CN)_2]Cl_2 \cdot 6\,H_2O$

Calc.	C, 17.0	H, 3,7	N, 13,2
Found.	C, 16.7	H, 1.25	N, 12.27

Preparation of Chlorocadmium(II)-μ-glutaronitrile, chlorocadmium(II)chloride

Sixty mmoles of glutaronitrile dissolved in the least amount of isobutanol were added to 30 mmoles of cadmiumchloride dissolved in ethanol and then refluxed for 25 hours. The solvent was then evaporated under vacuum. The formed white precipitate was filtered, washed with ethanol and ether and dried over calciumchloride under vacuum.

Anal. for $[ClCd\,NC-(CH_2)_3-CN\,CdCl]Cl_2 \cdot 1.4\,CdCl_2$

Calc.	C, 8.3	H, 0.83	N, 3.8
Found.	C, 7.6	H, 1.4	N, 3.5

Preparation of Chlorocadmium(II)-μ-adiponitrile, chlorocadmium(II)chloride

Fourty mmoles of adiponitrile dissolved in the least amount of isobutanol were added to a solution of 10 mmoles of cadmiumchlorid in a minimum amount of ethanol. The mixture was then refluxed for 24 hours. As then the solution was evaporated under vacuum and the resulting precipitate was filtered, washed with ethanol and ether and dried over calcium chloride under vacuum.

Anal. for $[ClCd\,NC-(CH_2)_4-CN\,CdCl]Cl_2 \cdot 1.4\,CdCl_2$

Calc.	C, 9.87	H, 1.1	N, 3.5
Found.	C, 9.40	H, 1.3	N, 3.56

Preparation of Chlorocadmium(II)-μ-pimelonitrile, chlorocadmium(II)chloride

The same above procedure was used for the preparation of this complex.

Anal for $[ClCd\,NC-(CH_2)_5-CN\,CdCl]Cl_2 \cdot 1.3\,CdCl_2$

Calc.	C, 8.08	H, 0.97	N, 2.6
Found.	C, 8.30	H, 1.6	N, 2.1

Theory and Discussion

The measured frequency values for the prepared complexes in Tab. 1 show the two types of shifts. Considering the C, H, N analysis of the experimental

Tab. 1. C≡N stretching frequencies (cm^{-1}) of the alkane dinitrile and their Cd^{2+} complexes.

n	1	3	4	5
Alkane dinitriles	2275	2255	2249	2248
Cd^{2+} complexes	2200 s	2300 s	2300 s	2300 s
$\Delta\nu_{C\equiv N}$	−75	+45	+51	+52

part and the IR values we suggest the following structure for the complex $[Cd(NC-(CH_2)-CN)_2]Cl_2 \cdot 6\,H_2O$, in which the dinitrile acts as a bidentate ligand that coordinates via the C≡N bond. Its frequency shift ($\Delta\nu_{C\equiv N} = -75\,cm^{-1}$) is similar to the shift ($-70\,cm^{-1}$) of the complex $TiNC-CH_2N(C_2H_5)_2 \cdot Cl_4$ in which the ligand coordinates through the C≡N bond also [12]. The values for the other complexes in the same table ($\Delta\nu_{C\equiv N} = +45\,cm^{-1}$, $+52\,cm^{-1}$) suggest a linear structure for them, i.e. of the type $Cd-N\equiv C-\ldots$, where the coordination occurs via the lone pair

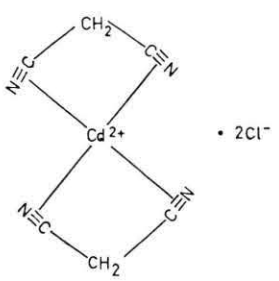


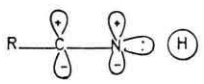
Fig. 1. The proposed structure for the $[Cd(NC-(CH_2)-CN)_2]Cl_2$ complex.

orbital of N. The measured shifts are similar in magnitude to the shifts of the complexes $2\,BCl_3 \cdot NC-CH_2N(C_2H_5)_2$ [12], ($\Delta\nu_{C\equiv N} = +60\,cm^{-1}$) and $[Ti(NC-CH_2-CN)Cl_4)]_2$, ($\Delta\nu_{C\equiv N} = +30\,cm^{-1}$) [7].

We discuss in the following a simplified MO explanation for the frequency shift in the nitrolo complexes and protonation products.

The Protonation of the Nitrilo Group

n-Type Protonation

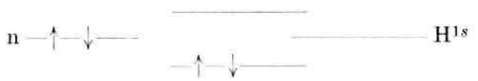


This type of protonation yields no bonding interaction between the H_{1s} orbital and the π-MO of the C≡N group ($S_{H1s,\,Npz} = 0$). The H_{1s}, N_{sp^2} interaction however should be significant due to their positive overlap,

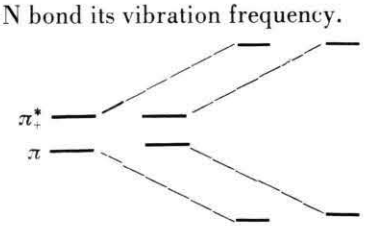
$$S_{H_{1s},\,N_{sp^2}} \neq 0\,.$$

This interaction creates two new MOs, one of them is bonding the other is antibonding,

$$\psi'_{bond} = a\,\Phi_{H_{1s}} + b\,\Phi_{N_{sp^2}}\,,$$
$$\psi'_{anti} = a\,\Phi_{H_{1s}} - b\,\Phi_{N_{sp^2}}\,.$$



The formation of the new bonding MO causes a release of electrons from the N-lone pair orbital, a decrease in the n-π and n-σ repulsion energy and consequently an increase in the π-bonding energy. This leads to the increase in the force constant of the C≡N bond its vibration frequency.



ΔE = decrease of the n-π repulsion energy.

π-Type Protonation of the Nitrilo Group

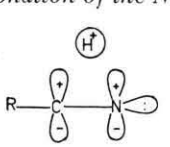


Fig. 2. π-type protonation of the nitrile group.

In this type of protonation there is a positive overlap between the H_{1s} orbital and the p_z orbitals of both C and N atoms,

$$S_{H_{1s},N_p} = 0 < S_{H_{1s},N_{sp^2}} .$$

In terms of the PMO treatment[13], the interaction between the H_{1s} and the π-MO is described by the second order perturbation formula,

$$\Delta E = (a_{u,N_z} + a_{u,C_z})^2 \beta^2 / E_{H_{1s}} - E_{\pi,C\equiv N}$$

a_{u,N_z} = MO coefficient of C≡N bond on N,
a_{u,C_z} = MO coefficient of the C≡N bond on C,
and forms two new MOs, one of which is bonding the other antibonding,

$$\psi_{bond} = c H_{1s} + d \Phi^{\pi}_{bond} ,$$
$$\psi_{anti} = c H_{1s} - d \Phi^{\pi}_{bond} .$$

Since electrons are transferred from the C≡N π-bond to the H_{1s} orbital, its bond order decreases. As a result the force constant decreases too and a red shift in the vibration frequency is expected.

All experimental data reveal a blue shift of the C≡N frequency as a result of the hydrogen bridge formation or protonation and therefore indicate the terminal protonation mode for all studied nitriles[9].

The Transition Metal Complexation

Chemical bonding between the ligand and the central metallic ion corresponds to the mutual interaction of the vacant orbitals of each partner with the filled orbitals of the other. The interaction energy depends on the magnitude of the overlap between the vacant AOs of Cd^{2+} (similarly Hg^{2+}) and the adjacent C_{p_z} or N_{p_z} orbitals.

The orbital exponents for the 4d and 5p orbitals (and 5d, 6p orbitals) of Cd^{2+} (and Hg^{2+}) are calculated according to the Slater rule to be as follows;

$$Cd^{2+}: \quad \alpha_{4d} = 3.97; \quad \alpha_{5p} = 1.77;$$
$$Hg^{2+}: \quad \alpha_{5d} = 3.60; \quad \alpha_{6p} = 1.14.$$

Since the overlap integral between any two AOs on different atoms is inversely proportional to their orbital exponents,

$$S \alpha [1/f(\alpha, \alpha')]$$

one may easily conclude that the overlap integrals between the vacant 5p(6p) AOs in Cd^{2+}(Hg^{2+}) and N_{p_z} as well as C_{p_z} are bigger than those of the 4d(5d) AOs with the same ligand AOs.

Accordingly the interaction energies of the 5p (6p) AOs of Cd^{2+}(Hg^{2+}) with the occupied MOs of the nitrile group should be greater than those of the corresponding vacant 4d(5d) AOs with the same MO.

The n-Coordination

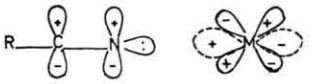


Fig. 3. n-Coordination of a metal to a nitrile group.

Of major importance for the discussion of bonding in this type of coordination are the following factors;

a) the n-d interaction, b) the n-5p interaction,
c) the π-d interaction.

By the n-d interaction the overlap between the n-orbital and a vacant 4d AO of Cd^{2+} or 5d AO of Hg^{2+} is either zero due to symmetry or, as in the case of an overlap with a single lope of the d AO, very small. The expected overlap interaction energy is consequently negligible.

By the n-5p (Cd^{2+}) or -6p(Hg^{2+}) interaction the overlap is bigger than in the previous interaction. The orbital exponents of the 5p (Cd^{2+}) or 6p(Hg^{2+}) AOs are comparable with that of N_{2p} AO (1.25). The overlaping interaction energy is bigger in magnitude than that of the n-d interaction. The formation of a new bonding MO,

$$\psi_{bond} = a' \Phi_n + b' \Phi_{5p}$$

causes a release of electrons from the n-orbital to the metal. As a result the n-π and n-σ repulsion energies decrease and the C≡N bonding energy as well as its force constant increase.

The π-d Interaction

Due to the big exponents of the d AOs their overlaps with the π-MOs should be small. The π-d interaction which causes the ligand-metal donation and the metal-ligand back donation of electrons should be weaker than the n-p interaction.

The n-coordination should cause an increase in the C≡N force constant and vibration frequency, due to the n-5p release of electrons.

The π-coordination

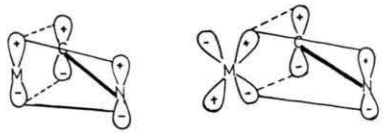


Fig. 4. π-Type coordination of a metal to the nitrile group.

One may distinguish between two terms of interaction in this type of coordination; (a) the p-π interaction and (b) the d-π interaction.

The p-π interaction of the 5p AO of Cd^{2+} with the occupied π-MOs of the C≡N group is strong due to the small orbital exponents of the ion. The resulting 3 centers bonding transfers electrons from the ligand to the ion and decreases the bond order of the C≡N bond. The electron density on the lone pair orbital remains constant.

The d-π interaction may not vanish due to symmetry, it should still be much weaker than the p-π interaction. Thus both π-d donation and d-π back donation of electrons should be weaker than the π-p electron release.

The overall result is then the transfer of electrons from the π-MO of the C≡N bond to the 5p AO of the ion, the decrease in the C–N bond order and force constant as well as the vibration frequency.

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