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Are M–N bonds indeed inherently weaker when N is a tertiary rather than a primary or secondary nitrogen atom?

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Contents

Abstract

N-alkylation of amine ligands decreases the stability constants of their metal ion complexes, stabilizes low valent complexes, increases the acidity of the central cation and turns it into a harder acid. The major source of these effects is the decrease in the outer sphere solvation energy induced by the *N*-alkylation. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

It is commonly accepted that metal–nitrogen bonds are inherently weaker when the nitrogen is a tertiary rather than a primary or a secondary nitrogen atom [1]. This notion is based on three main observations:

1. The stability constants of complexes with tertiary amines are considerably lower than those with the analogous primary or secondary amines [2–10].

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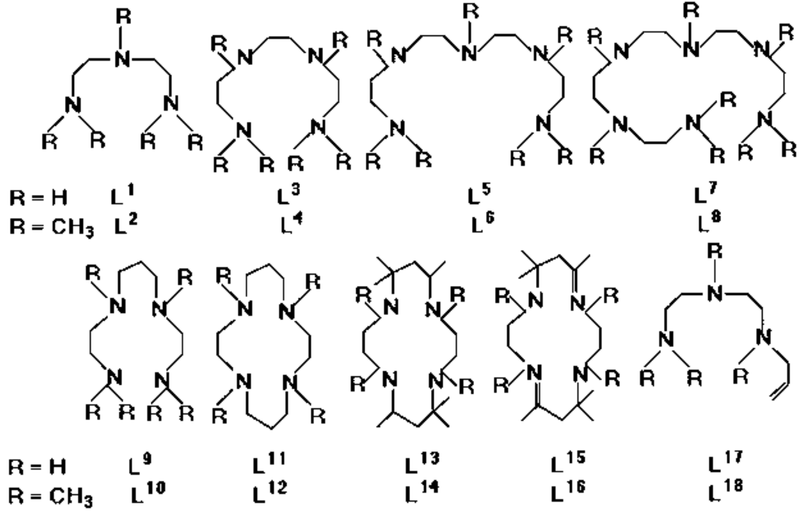
2. The ligand field induced by tertiary amines, as deduced from the energies of the d → d transitions of their complexes, is considerably lower than that induced by the analogous primary or secondary amines [4,6,10–14][1]. This phenomenon is usually significant only when several amines are ligated to the same central cation [2,3].
3. *N*-alkylation of amine ligands shifts the redox potentials of the couples $M^{n+1/n}L_m$ anodically relative to those of the corresponding non-alkylated complexes [4–6,10,11,13–27].

These observations are surprising as alkyl substituents are electron donors, and are therefore expected to increase the σ donating properties of the N atom. Usually this discrepancy is attributed to steric hindrance imposed by the tertiary amines which causes an elongation of the M–N bond and or affects the angles in the coordination sphere [17–19]. This argument clearly does not explain the observation that β_2 is smaller for $Ag(N(CH_3)_3)_2^+$ than for $Ag(NH_3)_2^+$ or $Ag(NH_2(CH_3))_2^+$ [28]. It should be noted that tertiary amine ligands are weaker bases than the analogous primary and tertiary amines. This phenomenon is commonly attributed to the loss of solvation stabilization via hydrogen bonds to the solvent, induced by the *N*-alkylation. Therefore, it seemed of interest to check whether the properties of tertiary amines as ligands have a similar origin.

2. Discussion

For this purpose the properties of first row transition metal complexes with the following ligands were studied recently:



$N(CH_2CH_2NR_2)_3$ L^{19} R = H; L^{20} R = CH_3

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[1] It should be noted that the suggestion made in Ref. [14] that the observations in Ref. [4] are due to a mixture of two different ligands cannot be true as the analytical, spectrophotometric and potentiometric data in Ref. [4] point out. Furthermore if a Cu(I) complex is formed as agreed in Ref. [14] it clearly will be reduced electrochemically somewhere.

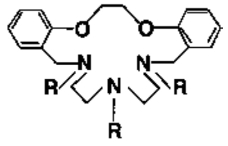
the results point out the following general conclusions.

1. *N*-methylation decreases the stability constants of the corresponding complexes, thus for all systems studied $K^n(L^{2n-1}) > K^n(L^{2n})$ is observed [2–4,6–10,16,29–31]; where $K^jL^i = [M^jL^i]/[M^j_{aq}][L^i]$ and j is the oxidation state of the central metal cation M.

2. The effect of *N*-methylation on the stability constants of the complexes is much larger for central ions with higher oxidation states, i.e. $K^{n+1}(L^{2n-1})/K^{n+1}(L^{2n}) > K^n(L^{2n-1})/K^n(L^{2n})$ [4–6,10]. This effect causes the significant stabilization of low valent complexes by the *N*-alkylation of their saturated amine complexes.

Surprisingly, this effect in extreme cases results in $K^n(L^{2n}) \geq K^{n+1}(L^{2n})$, e.g. for the $Cu^{II/I}L^{14}$ [20], $Cu^{II/I}L^{10}$ [4], $Cr^{III/II}L^{12}$ [21,22] and $Ni^{II/I}L^{14}$ [5] couples. This result is extraordinary as all these ligands are pure σ donors and are therefore expected to form complexes with $K^{n+1}(L^i) > K^n(L^i)$. Thus, this result alone points out that the effect of *N*-alkylation of amine ligands on the properties of their complexes does not stem from pure electronic factors.

3. The effect of *N*-alkylation on the stability constants of Pb(II) complexes is considerably smaller than that on the stability constants of the corresponding complexes of first row divalent transition metal cations [9]. This result suggests that the effect decreases with the increase in the radius of the central cation. In the extreme case of Ag^+, a large and monovalent central cation, *N*-alkylation of the ligand L^{21} increases, as expected from the electronic effects, the stability constants of the silver complexes, which are $\log(K) = 8.7$, 10.3 and 9.3 for R = H, CH_3 and $CH_2C_6H_5$, respectively [9].



L^{21}

4. *N*-methylation shifts to the red both the d → d bands [4–6,11,15] and the ligand-to-metal charge transfer (LMCT) bands [4–6,8,14] of the corresponding complexes. The shift of the d → d bands clearly points out that the tertiary nitrogens are poorer σ donors than primary or secondary ones. Therefore, the shift of the LMCT bands has to be attributed to the anodic shift of the redox potential of the central cation [4–6].

All these observations are in accord with the notion that a major factor in the effect of *N*-alkylation of amine ligands on the properties of their metal complexes is due to their effect on the interaction of the complexes with the solvent. Two major factors have to be considered.

1. *N*-alkylation increases the radii of the complexes and therefore decreases their outer sphere solvation energy. The magnitude of this effect can be roughly estimated using the Born equation $\Delta G_s = -686Z^2/R_{eff}$ kJ mol^{-1}; where 686, Z and R_{eff} are the constant for aqueous solutions, the charge of the complex and its effective radius, respectively. Clearly a given increase in R_{eff} has a greater effect the larger Z and the smaller R_{eff} are. Thus, the calculated contribution of the effect of

N-methylation on the outer sphere hydration energy of Cu(II) and Cu(I) complexes is larger than the observed shift in the redox potentials [4].

The effect of *N*-alkylation on the outer sphere solvation energy of the complexes is clearly the major contribution to the observed effect of *N*-alkylation on the stability constants of the corresponding complexes.

2. *N*-alkylation inhibits the formation of hydrogen bonds of the type M–N–H···O with the solvent, or with the counter anions in aprotic solvents. These hydrogen bonds affect the properties of the complexes with primary and/or secondary amine ligands in several ways:

1. They contribute to the outer sphere solvation energy.
2. They increase the electron density on the nitrogen atom thus transforming it into a better σ donor. Their absence in complexes of tertiary amines explains the observation that tertiary amines are poorer σ donors and that therefore *N*-alkylation shifts $d \rightarrow d$ bands to the red. Similar arguments concerning the effect of such hydrogen bonds on the location of $d \rightarrow d$ bands [32] and LMCT bands [33] were discussed recently.
3. They enable charge delocalization from the complex to the solvent.

If indeed the effect of *N*-alkylation of amine ligands on the properties of their complexes is due mainly to their effect on the outer sphere solvation energies as outlined above then several other effects, which can be checked experimentally, are expected:

1. If the complexes $M^{n+1}(L^{2n})$ have smaller solvation energies than the complexes $M^{n+1}(L^{2n-1})$ then $\Delta S°$ of the reduction of the former complexes should be smaller than that of the latter ones. This prediction was indeed verified experimentally for complexes of Cr(III) [22]; Ni(II) [27] and Cu(II) [4].

2. If the complexes $M^{n+1}(L^{2n})$ have smaller solvation energies than the complexes $M^{n+1}(L^{2n-1})$ then the rate of the self exchange reaction

$$M^{n+1}(L^{i}) + {}^{*}M^{n}(L^{i}) \rightarrow M^{n}(L^{i}) + {}^{*}M^{n+1}(L^{i})$$

is expected to be faster for the couples $M^{n+1/n}(L^{2n})$ than for the couples $M^{n+1/n}(L^{2n-1})$ as the activation energy of these self exchange processes involves equilibration of the outer sphere solvation shells of the complexes in the two oxidation states. This prediction was indeed verified for $Ni^{II/I}L^{12}$ and $Ni^{II/I}L^{11}$ and for $Ni^{II/I}L^{14}$ and $Ni^{II/I}L^{13}$ [11].

3. The lack of hydrogen bonds of the type M–N–H···O in the complexes $M^{j}(L^{2n})$ is expected to increase the charge density on the central metal cation. This is expected to have the following effects:

1. The stability constants for OH^- binding, $K_{OH} = [L^iM^j(OH)^{(j-1)+}]/[(M^jL^i)^{j+}][OH^-]$ is expected to be larger for complexes with the ligands L^{2n} than for those with the ligands L^{2n-1}. This expectation was verified for a variety of Ni(II) [11,12,27] and Cu(II) [4,6,7,29,31] complexes.
2. The central cation is expected to be a harder acid in the *N*-alkylated complexes. This was verified for the Cu(II) complexes with L^{19} and L^{20} [7].
3. The charge localization on the central cation induced by *N*-alkylation might also explain the observation that the O–H···F hydrogen bond in

$[\{CuL^2F(H_2O)\}_2[BF_4]_2$ 'is the shortest ligand fluoride–ligand water hydrogen bonding interaction in any Cu(II) complex' [34].

4. It was demonstrated recently that 1,4,7-triisopropyl-1,4,7-triazacyclononane–copper(II)Cl_2 is a better catalyst for the anaerobic catalyzed hydrolysis of DNA than 1,4,7-triazacyclononane–copper(II)Cl_2 [35]. This observation might tentatively be also attributed to the increased charge density on the central copper cation induced by *N*-alkylation.

Clearly the effect of *N*-alkylation of amine ligands on the properties of the corresponding complexes is not limited to outer sphere solvation effects and one has to consider also electronic effects and the role of steric hindrance, which might cause M–N bond elongation; affect the bond angles; induce strain in the skeleton of chelating ligands and cause steric distortions, e.g. tetrahedral distortions, which might be preferred by a given oxidation state of a given central cation. It is of interest to note that semi empirical MO calculations in the gas phase suggest that it easier to reduce CuL^3 and CuL^5 than CuL^4 and CuL^6, respectively, i.e. the situation in the gas phase is opposed to that observed in solutions [4]. Thus, the results presented clearly suggest that the major factor causing the large change in the properties of complexes with amines by *N*-alkylation is the large change in the outer sphere solvation energy. Thus the effect of *N*-alkylation on the basicity of amine ligands and on their properties as ligands originate mainly from analogous effects.

3. Concluding remarks.

The results obtained in recent years point out that *N*-alkylation of amine ligands affects the properties of their metal ion complexes via several, often opposing, effects:

1. It decreases the outer sphere solvation energy of the complexes.
2. It eliminates the M–N–H···O hydrogen bonds, thus turning the nitrogen a poorer σ donor.
3. It elongates the M–N bonds due to steric hindrance.
4. The alkyl substituents are electron donating groups which turn the nitrogen into a better σ donor.
5. It often induces skeleton strain and bond angle distortions due to steric hindrance.

The first three effects all cause decrease in the stability constants of the corresponding complexes and stabilization of low valent complexes whereas effect (4) has the opposite effect. In most complexes the transformation of all the nitrogen donor atoms into tertiary ones decreases the stability constants in solution and stabilizes low valent complexes mainly due to the first two effects. However, for large monovalent cations, e.g. Ag^+, under some conditions effect (4) is the major contributing factor. This effect seems to be also the governing factor in gas phase calculations.

4. Note added in proof

Recently (H. Deng, P. Kebarbe, J. Am. Chem. Soc. 120 (1998) 2925) reported that ΔG°_{393} for the reaction $CuL_2^{+} \rightleftarrows Cu^{+} + 2L$ in the gas phase equals 82.7, 93.1 and 98.7 kcal/mol for $L = NH_3$; $NH_2{-}C_3H_7$ and $N(m\text{-}C_4H_9)_3$, respectively, i.e. *N*-alkylation stabilizes the complexes in the ga phase.

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