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Tertiary-poly-amine ligands as stabilisers of transition metal complexes with uncommon oxidation states

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Tertiary-amine ligands are known to be poorer σ donor ligands than the corresponding primary- or secondary-amine ligands. They are known to shift the redox potentials of given couples to the anodic direction relative to the corresponding complexes with primary- or secondary-amine ligands. A review of data in the literature and of recent results on nickel complexes with tetra-aza-macrocyclic ligands and copper complexes with open chain poly-amine ligands suggests that the major source for these effects is the poorer solvation of the complexes with the tertiary-amine complexes due to the lack of hydrogen bonding between the complexes and the solvent, or the counter ions. Thus the stabilisation of low valent transition metal complexes by tertiary-amine ligands is due to thermodynamic reasons. On the other hand, tertiary-amine-macrocyclic ligands stabilise high valent complexes because the route to the formation of imine groups is kinetically inhibited in these complexes.

INTRODUCTION

The stabilisation of transition metal complexes with uncommon oxidation states by ligands is due either to thermodynamic or to kinetic factors.

Thermodynamic stabilisation of complexes with uncommon oxidation states by ligands might be due to one, or more, of the following factors:

1. Electronic factors, *e.g.* good σ donors stabilise complexes with high oxidation states whereas π acids stabilise complexes with low oxidation states.

2. Steric factors, *e.g.* the ligand might impose a coordination geometry which is preferred by the transition metal ion in its uncommon oxidation state.

3. Entropic factors, *e.g.* the ligand imposes a smaller coordination number in the complex with the uncommon oxidation state.

4. Solvation energies, *e.g.* in aqueous solutions the hydrophobic and hydrophilic nature of the ligand, *i.e.* ligands which are hydrophobic, while bound to the central cation, stabilise low valent transition metal complexes whereas hydrophilic ligands stabilise high valent transition metal complexes. Though this factor is in principle important only in aqueous solutions it is often also applicable to aprotic solvents due to the role of ion-pairing.

Kinetic stabilisation of complexes with uncommon oxidation states by ligands is caused when the ligands inhibit, or slow down, the common path of decomposition of the complex with the uncommon oxidation state. This might be due to one, or more, of the following factors:

1. The ligand is less susceptible towards redox processes.

2. The ligand inhibits, often via steric hindrance, the approach of two central ions to each other thus inhibiting two-electron processes.

Amine ligands are pure σ donors and are therefore in principle expected to stabilise high valent complexes. However, it is commonly accepted[1] that the M-N bond is inherently weaker for tertiary amines than for primary or secondary ones. Furthermore, data in the literature point out that tertiary-amine ligands, many of them macrocyclic ones, stabilise thermodynamically and often also kinetically low valent complexes, *e.g.* those of Ni(I)[2], Pd(I)[3], Cu(I)[4], Cr(II)[5], Co(II)[6] and Ru(II)[7].

These ligands also inhibit the common mechanism of oxidation of amine ligands by the central cation, *i.e.* the formation of imines. Indeed they stabilise kinetically complexes of Ru(III)[7] and of Ni(III)[8].

In the present paper the factors contributing to the stabilisation of transition metal complexes with uncommon oxidation states by tertiary-poly-amine ligands are analysed in detail.

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DISCUSSION

It is the purpose of this short review to sum up the data obtained to date concerning the factors which contribute to the thermodynamic and kinetic stabilisation of transition metal complexes with uncommon oxidation states by macrocyclic and open chain tertiary-poly-amine ligands. The effect of the different factors which might contribute to the stabilisation will be analysed separately.

Electronic effects: Tertiary-amines are generally considered to be poorer σ donors than the corresponding primary- and secondary-amines. This is somewhat surprising as alkyl substituents are electron donating groups. However, the experimental data, *e.g.* spectroscopic data,[2a,b;4b-d;5] clearly point out that indeed the ligand field splitting caused by tertiary-amine ligands is smaller than that caused by the corresponding primary- and secondary-amines. Two factors probably contribute to this property of tertiary-amines:

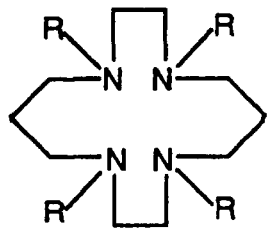
1. Due to steric hindrance, the M-N bond is elongated in complexes of tertiary-amines and is therefore weaker.[2a,4c] This effect clearly does not explain all the observations, *e.g.* the observation that β_2 for the complexation of Ag^+ by trimethylamine is considerably smaller than that for ammonia and methylamine.[9]

2. In the complexes of tertiary-amine ligands there is no hydrogen bonding with the solvent which exists in complexes of primary- and secondary-amine complexes. The hydrogen bonds, M-N-H···O, increases the electron density on the nitrogen thus making it a better σ donor. In solvents with a low dielectric constant a similar effect is observed; here, it is explained by contact ion pairing the complex with its counter ion which is weakened by the alkyl substituents.

Furthermore, as tertiary-poly-amine ligands are pure σ donor ligands, the weakening of the latter property cannot explain the observation that the binding constants of some of these ligands to Cu(I),[4c] Cr(II)[5a] and probably Ni(I) are larger than those to Cu(II),[4c] Cr(III)[5a] and Ni(II), respectively. Thus, though clearly N-alkylation decreases the σ donating properties of poly-amine ligands, this cannot be the only, or even the major, factor contributing to the stabilisation of low valent complexes by tertiary-poly-amine ligands.

Steric effects: The stabilisation of low valent transition metal complexes with macrocyclic or linear poly-amine ligands by N-per-methylation was attributed to two types of steric effects:

1. N-per-methylation of tetra-aza-macrocyclic ligands increases, due to steric hindrance, somewhat the cavity formed by the ligand thus stabilising the complex of the larger, low valent, cation. Thus it was proposed that the difference in the redox potentials of $[NiL^1]^{2+}$ and $[NiL^2]^{2+}$ is due to this effect.[4a] On the other hand, it was argued that the observation that the redox potentials of

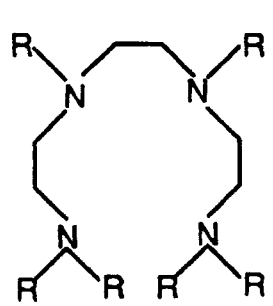


R = H L^1 R = $CH_2CO_2^-$ L^3

R = CH_3 L^2 R = CH_2CH_2OH L^4

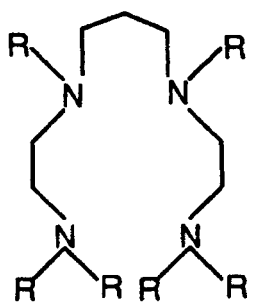
$[NiL^1]^{2+}$ and of 1,4,8,12-tetraazacyclopentadecane-Ni(II) are similar points out that this effect is not the major effect causing the large difference in the redox potentials of $[NiL^1]^{2+}$ and $[NiL^2]^{2+}$.[2d] Furthermore the observation that the redox potentials of the trans-I and the trans-III isomers of $[NiL^2]^{2+}$ are similar[10] seems also not to be in accord with this explanation. In order to check this point further the redox potentials of $[NiL^3]^{2+}$ and $[NiL^4]^{2+}$ were recently determined.[11] The results clearly point out that the redox potential of $[NiL^1]^{2+}$ and $[NiL^3]^{2+}$ are similar whereas that of $[NiL^4]^{2+}$ is about half way between those of $[NiL^1]^{2+}$ and $[NiL^2]^{2+}$.[11] As the steric hindrance in $[NiL^3]^{2+}$ and $[NiL^4]^{2+}$ is clearly considerably larger than in $[NiL^2]^{2+}$ these results point out that the increase in the cavity of the macrocyclic ligands caused by N-alkylation is not the major factor affecting the redox potentials of their complexes.[11]

2. It was argued[3] that the N-alkylation of the tetra-aza-macrocyclic ligands causes a tetrahedral distortion of the complexes and that this distortion is the source of the stabilisation of the low valent complexes. It seems difficult to reconcile this argument with the observation that N-methylation stabilises complexes of Ni(I)[2], Pd(I)[3], Cu(I)[4], Cr(II)[5], Co(II)[6] and Ru(II)[7] which are expected to prefer different coordination spheres.[4b] Furthermore, this argument can clearly not explain the observation that the



R = H L^5

R = CH_3 L^6



R = H L^7

R = CH_3 L^8

redox potentials of the trans-I and the trans-III isomers of $[NiL^2]^{2+}$ are similar.[10]

It is expected that tetrahedral distortion of the complex induced by N-methylation will be maximal for complexes with open chain ligands. As the ligands L^6 and L^8 stabilise Cu(I) in aqueous solutions[4b-d] it was decided[4c] to measure the E.S.R. spectra of the Cu(II) complexes with the ligands L^5, L^6, L^7 and L^8. The A_{II} values of these complexes point out that N-methylation does not induce a considerable tetrahedral distortion of these complexes.[4c]

Thus, the data in the literature point out that though clearly N-methylation of poly-amine ligands causes some steric hindrance in their complexes this is not the only, or even the major, factor contributing to the stabilisation of low valent complexes by tertiary-poly-amine ligands.

Entropic effects: If the ligand causes a decrease in the coordination number upon reduction, as exemplified in the following equation:[12]

$$Cu(NH_3)_4^{2+} + e^- \rightleftharpoons Cu(NH_3)_2^+ + 2NH_3 \quad (1)$$

the equilibrium is shifted to the right and the redox potential to the anodic direction due to the increase in entropy. If, on the other hand, the ligand is bound mainly to the reduced ion, *e.g.*:[13]

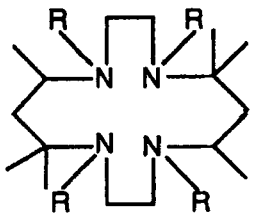
$$Cu_{aq}^{2+} + e^- + 4CH_3CN \rightleftharpoons Cu(CH_3CN)_4^+ + 6H_2O \quad (2)$$

the reaction is accompanied by an entropy decrease and this factor will shift the redox potential to the cathodic direction.

It is difficult to envisage situations where N-alkylation of poly-amine ligands will cause either of these effects. Therefore entropic effects, with the exclusion of effects on the outer coordination spheres discussed below, are not expected to contribute to the stabilisation of low valent complexes by tertiary-poly-amine ligands.

Hydrophobic effects: The redox potential of a complex is strongly dependent on its solvation energy. In principle, the ionisation potential of the central cation from the low valent oxidation state to the high valent one has to be compensated by the increase in the bonding energy of the inner sphere and the increase in the solvation energy due to the increase in the charge of the complex and the decrease in its radius. N-methylation of poly-amine ligands clearly increases the radii of their complexes and is therefore expected to destabilise the high valent complexes. Furthermore N-methylation of the ligands rules out hydrogen bonding of the type M-N-H····O-H····O thus also decreasing outer sphere solvation.

In accord with expectations, indeed the reduction of $[NiL^{10}]^{2+}$,[11] of $[CrL^2]^{3+}$,[5a] and of $[CuL^6]^{2+}$ [4c] is accompanied by a significantly smaller $\Delta S°$ than that of $[NiL^9]^{2+}$,[4c] of $[CrL^1]^{3+}$ [5a] and of $[CuL^5]^{2+}$ [4c] respectively. The most striking result is that for the copper system where $\Delta S° = 29 \pm 10$, 230 ± 20 and 145 ± 15 J/deg·mol for the reduction of $[CuL^6]^{2+}$ and for equations (1) and (2) respectively.[4c] The process described in equation (1) is expected to be accompanied by a $\Delta S°$ somewhat larger than that for the reduction of Cu_{aq}^{2+} whereas the process described in equation (2) is expected to be accompanied by a $\Delta S°$ somewhat smaller. The observation that $\Delta S°$ for the reduction of $[CuL^6]^{2+}$ is considerably smaller than that described in equation (2) clearly stems from the decreased outer sphere solvation of $[CuL^6]^{2+}$. The 100 J/deg·mol attributable, at least, to the outer sphere solvation correspond to an effect of ~30 KJ/mol on $\Delta G°$ of the reduction of $[CuL^6]^{2+}$. Clearly, the outer sphere solvation contributes also to $\Delta H°$. Thus, the results indicate that the hydrophobic nature of the complexes with the N-methylated-poly-amine ligands contributes considerably to the stabilisation of their low valent complexes.



R = H L^9
R = CH_3 L^{10}

Another way to estimate the effect of N-methylation of the ligands on the outer sphere solvation energy is by applying the Bohr equation. A computer model simulation,[4c] indicates that the radii of $[CuL^5]^{2+}$ and of $[CuL^6]^{2+}$ are ~3.3A° and ~3.8A°, respectively. Such an increase by N-methylation decreases $\Delta G°$ of solvation by 100 KJ/mol and 25 KJ/mol for the divalent and monovalent complexes, respectively.[4c] Clearly, such a difference in the solvation energies has a major effect on the redox potential of the complexes.

Effect of N-per-methylation of poly-amine ligands on the binding constants of the ligands to transition metal ions at different oxidation states: The observation that N-per-methylation of poly-amine ligands stabilises low valent complexes points out that the ratio of the equilibria constants K_{n+1}/K_n is smaller for the N-methylated ligands.

$$M^{(n+1)+}_{aq} + L \rightleftharpoons [ML]^{(n+1)+} \qquad K_{n+1} = [ML^{(n+1)+}]/[M^{(n+1)+}_{aq}]\cdot[L] \quad (3)$$

$$M^{n+}_{aq} + L \rightleftharpoons [ML]^{n+} \qquad K_n = [ML^{n+}]/[M^{n+}_{aq}]\cdot[L] \quad (4)$$

In some cases, *e.g.* for CrL^{2} [5], CuL^{10} [4a] and for CuL^{8} [4c] $K_{n+1}/K_n < 1$ is observed. To the best of our knowledge, this is the first type of pure σ donor ligands for which such a ratio is observed.

In principle, the decrease in K_{n+1}/K_n can be achieved by a decrease in the value of K_{n+1}, by an increase in the value of K_n or by a decrease of both equilibria constants where the value of K_n decreases less than that of K_{n+1}. The results for the copper complexes with L^6 and L^8 when compared with those with L^5 and L^7 point out that indeed both equilibria constants decrease upon N-methylation.[4c] However that for Cu(I) decreases considerably less than that for Cu(II).[4c] This observation is in accord with the effect of N-methylation on $\Delta G°$ of the solvation of these complexes.

The only other complexes for which both K_2 and K_1 can be estimated are those of Ni with L^1 and L^2. The stability constants for the binding of these ligands to Ni(II) are $K_2 = 10^{22.2}$ [14] and $10^{11.8}$ [15] M^{-1}, respectively. The redox potentials of these complexes are -1.34 and -0.91 V vs, NHE, respectively.[2b] For the calculation of the K_1 values we need an estimate of the redox potential of $Ni_{aq}^{2+/+}$ which is not known. For this purpose we note that the redox potential of $[NiL^9]^{2+/+}$ is -1.18V,[2b] as L^9 is a ligand with four secondary amines it is expected to have $10^3 < K_2/K_1 < 10^{10}$. From these values the redox potential of $Ni_{aq}^{2+/+}$ is calculated to be -0.8 ± 0.2 V vs. NHE in very good agreement with an earlier estimate based on a totally different set of assumptions.[16] From this value we calculate $K_1 = 10^{13}$ and 10^{10} M^{-1} for L^1 and L^2 respectively. For L^{10} this assumption suggests that $K_2/K_1 < 1$ as the redox potential of $[NiL^{10}]^{2+/+}$ is -0.75 V vs. NHE.[2b]

The self exchange rates of the $Ni_{aq}^{2+/+}$ and $[NiL^i]^{2+/+}$ couples, i = 1; 2; 9 and 10, were calculated using these redox potentials and the rates of reaction of Ni_{aq}^{+} [16] and $[NiL^i]^{+}$ [2b] with $Ru(NH_3)_6^{3+}$ and the Marcus cross relation. The results are $3.8 \cdot 10^2$, $1 \cdot 10^{-3}$, $1 \cdot 10^{-1}$, $3 \cdot 10^{-2}$ and 3 $M^{-1}s^{-1}$, respectively. The observation that the self-exchange rates for all the macrocyclic complexes are slower than for the aquo complex is surprising. This result suggests that the redox process of the $[NiL^i]^{2+/+}$ couples requires considerable rearrangement of the macrocyclic ligands, a quite unexpected conclusion.

Effect of N-per-methylation of poly-amine ligands on the acidity of the central transition metal ions: The decrease in the σ donating properties of the ligands due to N-methylation increases the charge density on the central cation. As a result the equilibria constants of the reactions:

$$[ML^i]^{n+} + OH^- \rightleftharpoons [L^iM(OH)]^{(n-1)+} \quad (5)$$

or

$$[L^iM(H_2O)_m]^{n+} \rightleftharpoons [L^iM(OH)(H_2O)_{m-1}]^{(n-1)+} + H_3O^+ \quad (6)$$

are expected to be shifted to the right. This expectation was indeed experimentally verified for a variety of $[NiL^i]^{2+}$ [17] and for $[L^iCu(H_2O)_2]^{2+}$, $L^i = L^5$ and L^6.[4c] More interesting is the observation that the equilibrium constant of the reactions:

$$[L^iCu(H_2O)_2]^{2+} + X^- \rightleftharpoons [L^iCuX(H_2O)]^{+} + H_2O \quad (7)$$

where X^- is a halide increases along the series $X^- = F^-$; Br^- and I^- for $L^i = L^5$ whereas it decreases along the same series for $L^i = L^6$.[4c] These results indicate that the copper ion in $[L^5Cu(H_2O)_2]^{2+}$ is a relatively soft acid whereas it is a relatively hard acid in $[L^6Cu(H_2O)_2]^{2+}$.[4c] This observation is a further proof to the major effect of N-methylation of poly-amine ligands on the properties of the central cation via the loss of the M-N-H...O hydrogen bonds.

Kinetic stabilisation of low valent transition metal complexes via N-methylation of complexes with tetra-aza-macrocyclic ligands: The results obtained for the $[NiL^i]^{+}$ complexes suggest that two kinetic factors contribute to the kinetic stabilisation of these complexes via N-methylation:

1. The N-methylation slows down the rate of the ligand exchange reaction:[2,10]

$$[NiL^i]^{+} \rightarrow Ni^{+}_{aq} + L^i \quad (8)$$

which is followed by:[18]

$$2Ni^{+}_{aq} \rightarrow Ni_2^{2+}{}_{aq} \rightarrow \text{products} \quad (9)$$

and or by:

$$Ni^{+}_{aq} + Ni^{2+}_{aq} \rightarrow Ni_2^{3+}{}_{aq} \rightarrow \text{products} \quad (10)$$

2. The N-methylation probably inhibits reactions of the type:

$$Ni^{+}_{aq} + [NiL^i]^{+} \rightarrow L^iNi_2^{2+}{}_{aq} \rightarrow \text{products} \quad (11)$$

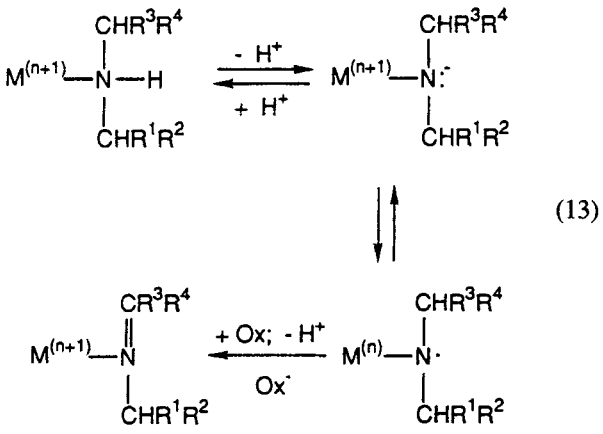
or via:

$$Ni^{+}_{aq} + [NiL^i]^{2+} \rightarrow L^iNi_2^{3+}{}_{aq} \rightarrow \text{products} \quad (12)$$

which are analogous to reactions (9) and (10). Reactions of two $[NiL^i]^{+}$ complexes, in the trans-I or trans-III configurations, are already inhibited by the unmethylated tetra-aza-macrocyclic ligands.

Though no information is available on the kinetic stabilisation of other low valent transition metal complexes in aqueous solutions via N-methylation of their tetra-aza-macrocyclic ligands, similar effects are expected.

Kinetic stabilisation of high valent transition metal complexes via N-methylation of complexes with tetra-aza-macrocyclic ligands: Though N-methylation of transition metal complexes with tetra-aza-macrocyclic ligands destabilises their high valent oxidation states this process is expected to stabilise them kinetically as it inhibits the common mechanism of their decomposition, *i.e.* via:[19]



(13)

Indeed, it was recently shown that the electrochemical oxidation of $[NiL^2]^{2+}$ and of $[NiL^{10}]^{2+}$ at potentials which are above the potentials at which water is oxidised yields also some of the corresponding trivalent nickel complexes.[10] These complexes are strong single electron oxidising agents and have half life times of 6.7 and 23.5 min. at room temperature and pH 3.0.[10]

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