# Influence of Nephelauxetic Effect on Thermodynamic and Kinetic Stability of Octahedral Cobalt(III)–Amine Complexes

*Sir:*

In the course of the structural and mechanistic studies of octahedral Co(III) complexes containing a macrocyclic quadridentate amine ligand, 1,4,8,11-tetraazacyclotetradecane, abbreviated as cyclam, a few spectacular properties have been observed which differ markedly from those of the corresponding bisethylenediamine, en, complexes.[1,2] (I) *trans*-[Co(cyclam)ACl]$^+$, where A = Cl, NCS, NO$_2$, and CN, is thermodynamically more stable than *trans*-[Co(en)$_2$ACl]$^+$ with respect to the corresponding *trans*-[Co(cyclam)A(H$_2$O)]$^{2+}$ and *trans*-[Co(en)$_2$A(H$_2$O)]$^{2+}$, respectively. The cyclam complexes, even supplied as the nitrates, only partially release the chloride at equilibrium,[1,2] whereas under similar conditions the corresponding bisethylenediamine complexes aquate with complete loss of the chloride.[3–5] (II) *trans*- and *cis*-[Co(cyclam)(H$_2$O)$_2$]$^{3+}$ are more acidic than *trans*- and *cis*-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$, respectively.[6,7] This effect is most pronounced for the first p$K_a$ of these aquo complexes. (III) The acid hydrolysis of *trans*-[Co(cyclam)ACl]$^+$ is slower than those of the corresponding *trans*-[Co(en)$_2$ACl]$^+$.[1,2,8] (IV) The base hydrolyses of *trans*-[Co(cyclam)Cl$_2$]$^+$ and *trans*-[Co(cyclam)OHCl]$^+$ are faster than those of *trans*-[Co(en)$_2$Cl$_2$]$^+$ and *trans*-[Co(en)$_2$OHCl]$^+$, respectively.[2,4,9] This communication attempts to correlate these seemingly unrelated facts and to explain them in terms of the "thermodynamic" and "kinetic" nephelauxetic effects of various amine ligands on the central Co(III) ion.

The energy separation between the two excited singlets, $^1T_{1g}$ and $^1T_{2g}$, of octahedral Co(III)–amine complexes, [Co(Am)$_6$]$^{3+}$, is given by $\Delta\bar{\nu} = [16 - (84B/10Dq)]B$. For the series of most saturated alkylamine ligands, such as Am = NH$_3$ and $^1/_2$(en), since $10Dq$ and the Racah interelectronic parameter $B$ are of the order 23,000 and 600 cm$^{-1}$, respectively,[10] it is quite safe to infer that the larger the $\Delta\bar{\nu}$, the larger is the value of $B$. In order to estimate the relative position of cyclam in the nephelauxetic series as defined by Jorgensen,[10] *trans*-[Co(cyclam)(NH$_3$)$_2$]$^{3+}$ proved to be the best model closest to a "perfect" octahedral Co(III) complex containing cyclam. As will be shown in Table I, since $\Delta\bar{\nu}$ in *trans*-[Co(en)$_2$(NH$_3$)$_2$]$^{3+}$ (8300 cm$^{-1}$)[11] is midway between those in [Co(NH$_3$)$_6$]$^{3+}$ and [Co(en)$_3$]$^{3+}$, it is reasonable to suggest that the value of $B$ for cyclam differs even greater from that for NH$_3$ than the average value as observed in *trans*-[Co(cyclam)(NH$_3$)$_2$]$^{3+}$. From the subsequent Table I, it is clear that some of the common amine ligands could be arranged in the following order in the nephelauxetic series: cyclam > en ≥ pn > NH$_3$. Therefore, the 3d electrons of Co(III) are delocalized to the largest extent in cyclam and least in ammine complexes. This seems to indicate a gradual decrease of donor lone-pair donation to Co(III) along the series. In other words, the metal ion tends to attract the donor lone-pair electrons to itself closest in the cyclam and least in the ammine complexes. This deduction is reasonable since all octahedral Co(III) complexes containing saturated alkylamines are structurally, electronically, and energetically fairly similar.

The earlier mentioned differences in properties between cyclam and bisethylenediamine complexes could now be explained in terms of the greater expansion of the 3d shell and hence a greater demand of donor lone-pair elections by Co(III) in cyclam complexes. Consequently, in these complexes, the metal–ligand bonds are strengthened. This idea is strongly supported by the observed greater acidity of aquo–cyclam complexes than of the corresponding aquo–en complexes. The relatively greater attraction of water lone-pair electrons by Co(III) in cyclam complexes indirectly weakens the O–H bond of the aquo ligand and, therefore, increases the acidity of their aquo complexes. This effect of metal–ligand bond strengthening would be more pronounced for negatively charged ligands, such as Cl$^-$ and OH$^-$, than for neutral molecules, such as OH$_2$, since the electron pairs from the former donors are relatively more "basic." This immediately explains the observation that chloro–cyclam complexes are more stable with respect to their aquo complexes than the corresponding bisethylenediamine analogs. That hydroxo–cyclam complexes would be more stable with respect to their aquo counterparts would, therefore, be responsible for the greater acidity of the latter than the corresponding bisethylenediamine analogs. This effect would be more obvious for a triply charged diaquo complex than for a lower positively charged hydroxo–aquo complex, thus explaining the pronounced difference in the first p$K_a$ of the diaquo complexes. These are "thermodynamic nephelauxetic effects."

A "kinetic nephelauxetic effect" is realized when the aquation rates of *trans*-[Co(cyclam)ACl]$^+$ are found slower than those of the corresponding bisethylenediamine analogs. Ethylenediamine complexes, which have a smaller reduction in the Racah electronic repulsion parameter $B$, would have a greater demand to expel the leaving group in order to gain a greater delocalization of the 3d electrons into the vacated orbital so that the ground-state electronic repulsion could be reduced in the transition state. The reaction rate is therefore faster.[12] In both series, the labilizing power of A follows the same pattern:[1] NH$_2$ > OH > NO$_2$ > Cl ∼ CN > NCS. Since Cl and CN are so vastly different in their $\pi$-conjugative ability, being operative in opposite directions, and in their ligand field strength, one of the obvious factors for grouping these two ligands together in their labilizing power is their similarity in their nephelauxetic effect on Co(III).[10]

The faster base hydrolysis of *trans*-[Co(cyclam)Cl$_2$]$^+$ and *trans*-[Co(cyclam)OHCl]$^+$ could also be predicted.

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**Table I.** Some Thermodynamic and Kinetic Data of Octahedral Co(III)–Amine Complexes

| Amine ligand,[a] Am | $\Delta\bar{\nu}$,[b] $cm^{-1}$ | $pK_{(1)}$[c] | $pK_{(2)}$[c] | $k_{H_2O}$[d] (25°), $sec^{-1}$ | $k_{ex}$[e] (25°), $M^{-1}$ $sec^{-1}$ | $k_{OH}$[f] (25°), $M^{-1}$ $sec^{-1}$ |
|---|---|---|---|---|---|---|
| $NH_3$ | 8500 | 5.79[g] | ... | $1.8 \times 10^{-2}$ | $1.6 \times 10^{6}$ | $1.8 \times 10^{3}$ |
| $^1/_2$(m-bn) | ... | ... | ... | $4.2 \times 10^{-3}$ | ... | $9.8 \times 10^{3}$ |
| $^1/_2$(*dl*-bn) | ... | ... | ... | $1.5 \times 10^{-4}$ | $5.0 \times 10^{6}$ | $2.1 \times 10^{3}$ |
| $^1/_2$(pn) | 8200 | ... | ... | $6.2 \times 10^{-5}$ | $4.5 \times 10^{6}$ | $2.3 \times 10^{3}$ |
| $^1/_2$(en) | 8100 | 4.45[h] | 7.94[h] | $3.2 \times 10^{-5}$ | $2.5 \times 10^{6}$ | $3.0 \times 10^{3}$ |
| $^1/_2$(N-me·en) | ... | ... | ... | $1.7 \times 10^{-5}$ | $3.0 \times 10^{8}$ | $1.1 \times 10^{4}$ |
| $^1/_4$(cyclam) | 8000[i] | 2.82[j] | 7.22[j] | $1.1 \times 10^{-6}$ [k] | $3.0 \times 10^{9}$ [l] | $6.7 \times 10^{4}$ [k] |

[a] m-bn = *meso*-butylenediamine, *dl*-bn = *dl*-butylenediamine, pn = propylenediamine, N-me·en = N-methylethylenediamine. [b] $\Delta\bar{\nu}$ = energy separation between $^1T_{1g}$ and $^1T_{2g}$ of $[Co(Am)_6]^{3+}$ in aqueous solution. In the case of cyclam, $\Delta\bar{\nu}$ is for *trans*-$[Co(cyclam)(NH_3)_2]^{3+}$. Data were taken from M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **266,** 49 (1951); **271,** 101 (1952), except as indicated. [c] $pK_{(1)}$ and $pK_{(2)}$ are the first and second $pK_a$, respectively, for *trans*-$[Co(Am)_4(H_2O)_2]^{3+}$ in aqueous solution. Complicated by *cis–trans* isomerization reactions, not many reliable data have been reported. [d] $k_{H_2O}$ = first-order aquation rate constant for *trans*-$[Co(Am)_4Cl_2]^+$. Data were taken from R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, **78,** 709 (1956), except as indicated. [e] $k_{ex}$ = second-order amine-proton exchange rate constant for $[Co(Am)_6]^{3+}$ in $D_2O$. In the case of cyclam, $k_{ex}$ is the estimated value for the complex *trans*-$[Co(cyclam)(H_2O)_2]^{3+}$. Data were taken from F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Amer. Chem. Soc.*, **82,** 1073 (1960), except as indicated. [f] $k_{OH}$ = second-order base hydrolysis rate constant for *trans*-$[Co(Am)_4Cl_2]^+$ in aqueous solution. Data were taken from Pearson, *et al.*, footnote *d*, except as indicated. [g] The gross acid dissociation for the *cis–trans* equilibrium. The equilibrium *cis*/*trans* ratio is 0.17; Pearson, *et al.*, footnote *d* and R. G. Yalman and T. Kuwana, *J. Phys. Chem.*, **59,** 298 (1955). [h] Reference 7. [i] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4,** 1102 (1965). [j] Reference 6. [k] Reference 2. [l] Estimated from ref 6.

Assuming an SN1cb mechanism,[13,14] the rate constant is directly proportional to the product of $k_a$ and $k_{cb}$, where $k_a$ is the acid ionization constant of the conjugate acid and $k_{cb}$ is the rate constant for the dissociation of the conjugate base. The greater tendency by Co(III) to attract donor electron density in cyclam complexes, on one hand, indirectly weakens the N–H bond and, therefore, increases the value of $k_a$ while, on the other hand, promotes $k_{cb}$ by enhancing the $\pi$-donating ability of the amido group in the conjugate base. Both effects jointly increase the rate of base hydrolysis of the two cyclam complexes. The second-order amine proton exchange rate constant for *trans*-$[Co(cyclam)(H_2O)_2]^{3+}$ could be estimated to be $3 \times 10^9$ ($M^{-1}$ $sec^{-1}$) at 25°.[15] This is very much faster than that of the equally charged $[Co(en)_3]^{3+}$ (Table I).

Similarly, both "thermodynamic" and "kinetic" nephelauxetic effects could also explain satisfactorily the properties of other Co(III)–amine complexes and to correlate them with the cyclam and bisethylenediamine analogs. Some of these properties are collected in Table I.

It is obvious from Table I that as $\Delta\bar{\nu}$ decreases down the amine series $pK_{(1)}$ and $k_{H_2O}$ decrease while $k_{ex}$ and $k_{OH}$ increase. This systematic variation is fully consistent with the above discussion. In the absence of available data on $\Delta\bar{\nu}$ and $pK_{(1)}$ for m-bn, *dl*-bn, and N-me·en, these ligands are inserted into the series according to a decreasing order of $k_{H_2O}$.

As a conclusion, it seems worthwhile noting that the nephelauxetic effect is still only one of the many factors affecting the thermodynamic and kinetic stability of coordination compounds. Its importance may be relatively more pronounced in octahedral low-spin $d^6$ systems, such as Co(III)–amine complexes. It is in these systems that there are a maximum number of electrons in the nonbonding or antibonding $\pi$ orbitals to display the maximum benefit out of this d electron repulsion effect. Even in this Co(III)–amine system, however, other factors, under favorable conditions, may overshadow the nephelauxetic effect. A higher $k_{H_2O}$ and $k_{OH}$ for (m-bn) than for (*dl*-bn) is a good indication of the influence of steric effect in the reactions of these two compounds. The two amine ligands are electronically similar but sterically different. In the *meso* form, the methyl groups are *cis* and very nearly maximally opposed. Consequently, the dissociative rate constants of the complex and of the conjugate base are higher than those in the corresponding *dl* isomers. The steric effect, however, cannot be more important than the nephelauxetic effects in Co(III)–cyclam complexes; otherwise, both $k_{H_2O}$ and $k_{OH}$ of these complexes would be changed in the same direction when compared to those of the bisethylenediamine analogs.

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## Synthesis and Characterization of a Nitrogen-Bridged [12]Annulene

*Sir:*

Oth and Schröder and coworkers[1a,b] have recently reported the synthesis of [12]annulene in which the *cis* and *trans* double bonds alternate. Farquhar and Leaver[2] have described the preparation of the related cycl[3.3.3]azine. We now wish to report the synthesis of the [12]annulene derivative 8b,8c-diazacyclopent[*fg*]acenaphthylene (**4**) in which, because of the presence of a central N–N bridge, the double bonds are situated *trans–trans–cis–trans–trans–cis*.

Scheme I delineates the reactions which have led to the formation of this compound and its structural interrelationship with the starting compound 3,4,7,8-tetrahydro-8b,8c-diazacyclopent[*fg*]acenaphthylene (**2**).

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