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LETTER

Higher stability constants for complexation of low valent, than of high valent, transition metal ions by saturated tertiary amine macrocyclic tetraaza ligands

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Recent results indicate that N-methylation of tetraaza macrocyclic ligands stabilizes low valent transition metal complexes [1–7]. It has been recently suggested [8] that at least for nickel$^{2+/1+}$ couples the redox potentials are in the order Ni(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradecane)$^{2+/1+}$ $<$ Ni$(H_2O)_6^{2+/1+}$ $<$ Ni(1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraaza-cyclotetradecane)$^{2+/1+}$. In this series the redox potential of Ni$(H_2O)_6^{2+/1+}$ could only be obtained as a rough estimate. This conclusion, if corroborated, suggests that tertiary amine ligands bind preferentially to the low valent nickel ion, and probably to other low valent transition metal ions. It was therefore decided to measure the redox potentials of *trans*-CrL$(H_2O_2^{3+/2+}$ ions with L = L^1 = 1,4,8,11-tetraza-cyclotetradecane and L^2 = 1,4,8,11-tetramethyl-1,4,8,11-tetraza-cyclotetradecane. The experimental results indeed corroborate the above suggested hypothesis.

The free ligands cyclam and tmc were synthesized according to the literature [9, 10]. *trans*-CrL$^1(H_2O)_2^{3+}$ was prepared via the steps *cis*-CrL^{1}Cl$_2^+$ [11] and *trans*-CrL$^1(CN)_2^+$ [12] which was treated with tetrafluoroboric acid. The synthesis of the novel complex *trans*-CrL$^2(H_2O)_2^{3+}$ was accomplished by a modification of a described procedure [13]. The spectral characteristics, including luminescence of the known *trans*-CrL$^1(H_2O)_2^{3+}$ are identical to those reported in the literature [11, 14, 15]. UV–Vis spectrum λ_{max}(nm) (ϵ(mol^{-1} dm^3 cm^{-1})) 510 (23); 405sh; 356 (51). The composition and configuration of the novel *trans*-CrL$^2(H_2O)_2^{3+}$ were verified by elementary analysis (C, H, N and Cr) as well as by IR and UV–Vis spectroscopy. The IR spectrum of *trans*-CrL$^2(H_2O)_2^{3+}$ has no absorption in the N–H region (3100 cm^{-1}) and has a singlet at 800 cm^{-1} for the CH$_2$ vibration in accord with expectations for a *trans* isomer, whereas the *cis* isomer should have a doublet at least. The UV–Vis spectrum showed the expected shift to lower ligand field and the characteristics of a D_{4h} configuration (λ_{max}(nm) (ϵ(mol^{-1} dm^3 cm^{-1})) 582 (28); 393sh; 334 (92)).

The redox potentials of the complexes were determined by cyclic voltammetry on a hanging mercury drop electrode (HMDE). Voltammograms of *trans*-CrL$^1(H_2O)_2^{3+}$ and *trans*-CrL$^2(H_2O)_2^{3+}$ are shown in Fig. 1. Besides the more anodic potential the L^2 complex exhibits a better reversibility of the redox process $E_{ox}-E_{red} = 0.08 \pm 0.01$ and 0.12 ± 0.01 V, respectively. The redox potentials determined depend on the pH as expected. For *trans*-CrL^1 the following potentials are measured: −0.90, −0.96 and −1.05 V versus SCE at pH 2.9, 4.2 and 7.2, respectively (accuracy ± 0.010 V). At these pHs the major forms of the complex present in the solution are *trans*-CrL$^1(H_2O)_2^{3+}$, *trans*-CrL$^1(H_2O)(OH)^{2+}$ and *trans*-CrL$^1(OH)_2^+$, respectively. For *trans*-CrL^2 the following potentials are measured: 0.250, 0.115 and 0.005 V versus SCE at pH 2.9, 5.2 and 7.9, respectively. (The measurement at pH 2.9 could not be carried out on the mercury electrode due to its oxidation at these potentials, therefore a solid gold electrode was used. The background current on this electrode at the required potentials was not negligible and the

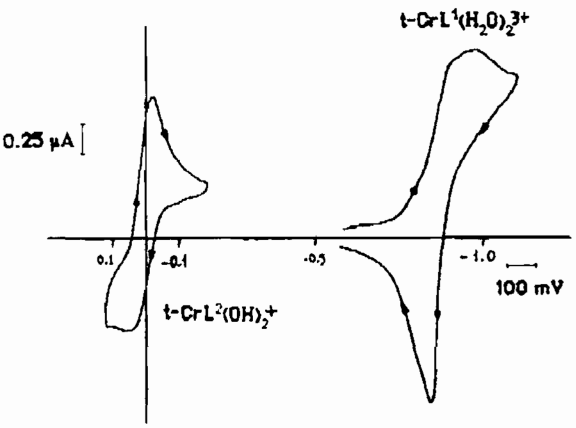

Fig. 1. Cyclic voltammograms of *trans*-CrL$^1(H_2O)_2^{3+}$ (1.8×10^{-3} mol dm^{-3} at pH 2.9) and *trans*-CrL$^2(OH)_2^+$ (1.5×10^{-3} mol dm^{-3} at pH 7.9 in aqueous media); room temperature, scan rate 20 mV/s; supporting electrolyte 0.45 mol dm^{-3} NaClO$_4$.

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error limit of the redox potential in this case is considerably larger, ±0.03 V). At these pHs the major forms of the complex present in the solution are *trans*-$CrL^2(H_2O)_2{}^{3+}$, *trans*-$CrL^2(H_2O)(OH)^{2+}$ and *trans*-$CrL^2(OH)_2{}^{+}$, respectively.

The redox potential for the $Cr(H_2O)_6{}^{3+/2+}$ couple is −0.41 V versus NHE, i.e. −0.68 V versus SCE. It is evident from these results that the relative equilibrium constants for the reactions

$$Cr(H_2O)_6{}^{3+} + L \rightleftharpoons trans\text{-}CrL(H_2O)_2{}^{3+} \qquad K_3 \qquad (1)$$

$$Cr(H_2O)_6{}^{2+} + L \rightleftharpoons trans\text{-}CrL(H_2O)_2{}^{2+} \qquad K_2 \qquad (2)$$

depend strongly on the nature of L. Thus for L^1 $K_3/K_2 > 10^3$ a result which is in accord with expectations. On the other hand for L^2 $K_3/K_2 < 10^{-15}$ a totally unexpected result.

The stabilization of low valent transition metal complexes by N-methylation of tetraaza macrocyclic ligands is commonly attributed to one of the following reasons.

1. The N-methylation increases the cavity of the macrocyclic ligand thus stabilizing the low valent complex [6]. Different results suggest [16] that this effect contributes to the observed stabilization, but suggest that this factor does not contribute the major effect to the stabilization. The present results cannot be explained by this effect as it would be difficult to argue on this basis that K_2/K_3 should be larger than 1 for L^2. (It should be noted that the ionic radii of Cr^{3+} and Cr^{2+} are 0.69 and 0.84 Å, respectively, whereas those for Ni^{2+} and Ni^{+} are 0.72 and 0.95 Å; the latter value is the radius of Cu^{+} [17]).

2. It has been pointed out that N-methylation decreases the ligand field of tetraaza macrocyclic ligands [1, 2, 6, 18]. This argument is equivalent to the statement that M–N bonds are inherently weaker for tertiary than for secondary amines [19]. It is evident that according to these arguments one would not predict that K_2/K_3 should be larger than 1 for L^2.

3. It has been pointed out that N-methylation increases the hydrophobicity of the complex thus stabilizing the low valent complexes [1, 2, 8]. Clearly this effect could explain the present results as one would predict that a hydrophobic ligand would form a more stable complex with a low valent cation than with a high valent one. On the other hand the bathochromic shift in the ligand field bands is rather large for a simple second sphere process. However the absence of hydrogen bonds in the tertiary amine may account for it.

In order of checking the validity of the latter argument we have determined $\Delta S^\circ = \Delta S_{red} - \Delta S_{ox}$ by measuring the temperature dependence of the redox potentials of *trans*-$CrL^1(OH)_2{}^{+}$ and *trans*-$CrL^2(OH)_2{}^{+}$ according to the technique by Weaver and co-workers [20]. The results are plotted in Fig. 2. From the slopes of the lines one calculates $\Delta S^\circ = 270 \pm 40$ and 52 ± 12 J mol^{-1} deg^{-1} for the two complexes, respectively. As the structure of the two complexes is similar the big difference in ΔS° has to stem from the difference in their degree of hydration. The difference in ΔS° contributes > 0.6 V of the difference in the redox potentials of *trans*-$CrL^1(OH)_2{}^{+}$ and *trans*-$CrL^2(OH)_2{}^{+}$. As differences in hydration also contribute considerably to ΔH° the results clearly suggest that the increase of the hydrophobic nature of the ligand is the major factor affecting the relative properties of transition metal complexes with secondary versus those with tertiary amine tetraaza macrocyclic ligands.

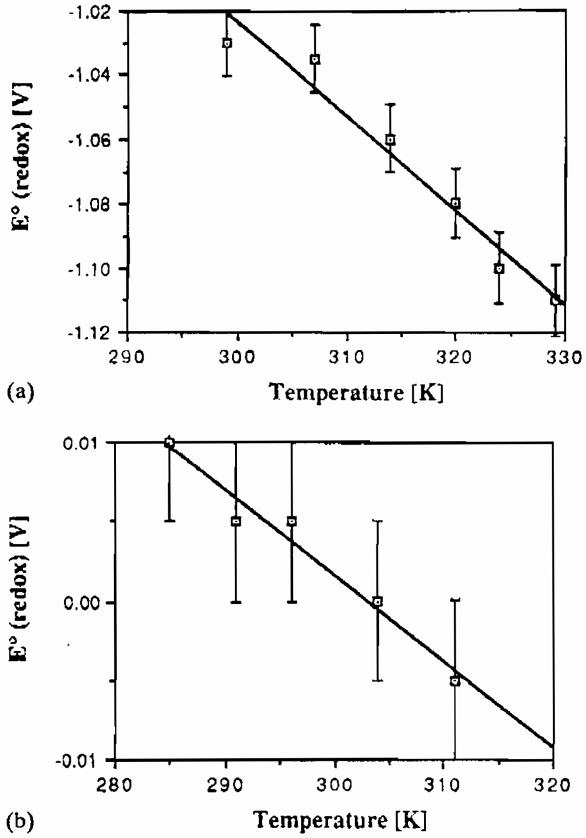

Fig. 2. Temperature dependence of the redox potentials: (a) *trans*-$CrL^1(OH)_2{}^{+}$, (b) *trans*-$CrL^2(OH)_2{}^{+}$.

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