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Second Sphere Photochemistry and Photophysics in $Cr(NH_3)_6{}^{3+}$ Polycarboxylate Associates

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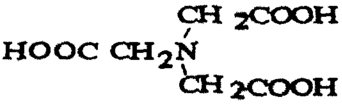
Abstract

Adding polycarboxylates to alkaline aqueous solutions of $(Cr(NH_3)_6)^{3+}$ affects the photochemical quantum yield for ammonia release in a complex way. The quantum yield was found to increase at low carboxylate concentrations, then to pass a maximum and finally to decrease below the value of the quantum yield observed in the absence of carboxylate ions. The effect may be explained by (i) hindering the doublet quenching by hydroxide, which opens a path for photoreaction via the doublet state and (ii) a cage effect that impedes the bond breaking.

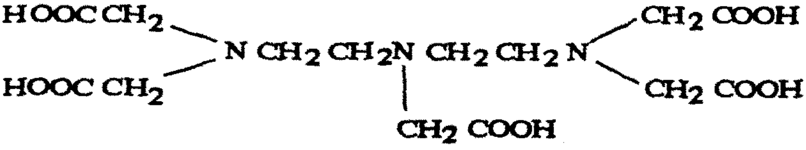
1. INTRODUCTION

$(Cr(NH_3)_6)^{3+}$ seemed to us a likely candidate for studying second sphere effects on account of its highly positive charge and its capacity to form hydrogen bonds. The effects should be more evident , if polyfunctional counter ions as the aminopolycarboxylates (AP) of the EDTA type were used. In this contribution we report the effects of ethylenediaminetetraacetate (EDTA), nitrilotriacetate (NTA) and diethylenetriaminepentaacetate (DTPA) on the phosphorescence and photosubstitution of $(Cr(NH_3)_6)^{3+}$.

H_4EDTA



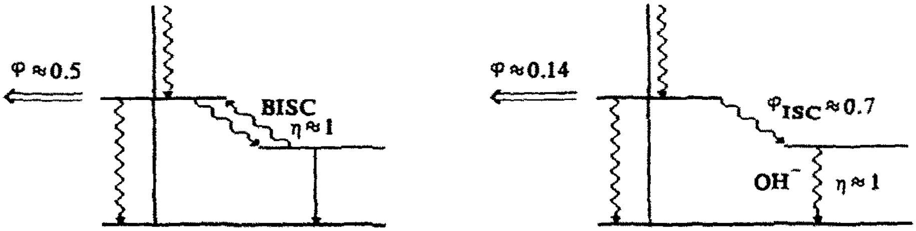
H_3NTA



H_5DTPA

$(Cr(NH_3)_6)^{3+}$ photoaquates on irradiation into the ligand field bands with a quantum yield of 0.5 ± 0.05 in acid solution ($pH < 4$) (1, 2).

The diagram, Figure 1, shows the deactivation channels that occur after excitation (3). Experimental evidence points to only one photoactive state (4). The metastable doublet state acts only as an excitation buffer, which deactivates almost quantitatively to the photoactive state by backintersystem crossing (bisc). The radiative deactivation channel is negligible at room temperature because the phosphorescence quantum yield is 10^{-5} (5). In alkaline solution, the doublet is efficiently quenched by OH^- (6), bisc is negligible. There remains a non quenchable quantum yield $\varphi_{nq} = 0.14$, which is supposed to originate in a prompt photoreaction without passing the doublet state.



a) acid solution

b) alkaline solution

Figure 1. Deactivation channels of excited hexammine chromium(III) at room temperature.

2. RESULTS

The crystalline salts $(Cr(NH_3)_6)_2Na_3(NTA)_3 \cdot 2H_2O$, $(Cr(NH_3)_6)Na(EDTA) \cdot 4H_2O$, $(Cr(NH_3)_6)Na_2(DTPA)_4 \cdot 5H_2O$ were prepared from hexammine chromium perchlorate and the sodium salts of the aminopolycarbonic acids in H_2O - dimethylsulfoxide mixtures. We had confidence in the stoichiommetry, if repeated preparations or repeated crystallisations produced identical chemical analysis.

The solid salts showed significant differences in the ${}^2E_g - {}^4A_{2g}$ phosphorescence of the chromium moiety (Figure 2). The rich vibrational fine structure in the NTA salt points to several crystallographically different chromium centers.

Interactions between the hexammine chromium and the aminopolycarboxylates manifest themselves in rather dilute aqueous solutions. Figure 3 compares the molar conductivities of the EDTA salt and the perchlorate. The EDTA salt behaves like a weak electrolyte.

The phosphorescence spectra in aqueous solution at room temperature were almost unchanged by adding aminopolycarb-

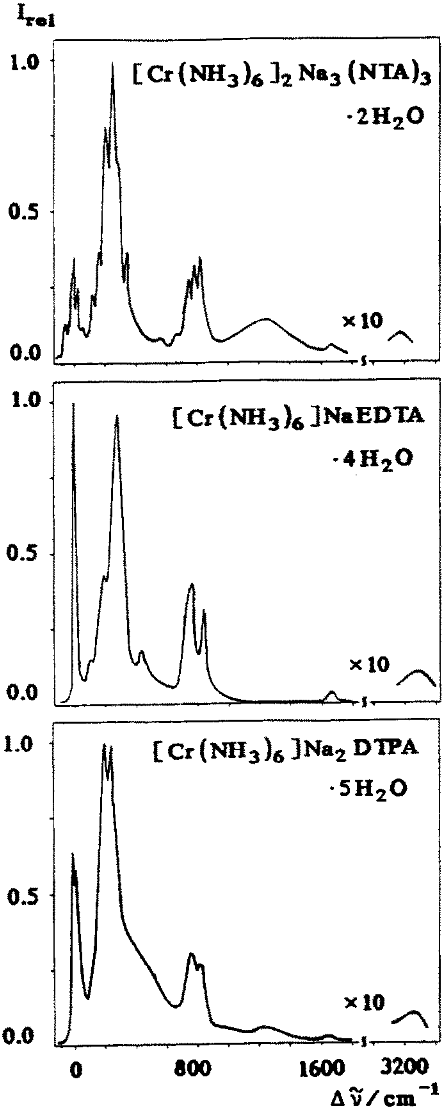


Figure 2. Phosphorescence spectra of hexammine chromium(III) polycarboxylates relative to the 0-0-transitions.

oxylates. There was only a small bathochromic shift with Δν < 30 cm^{-1}. In alkaline solution, however, where the phosphorescence is almost quantatevely quenched (> 95% at pH 13), the phosphorescence reappeared, when aminopolycarboxylates were added. We found a sharp rise at low AP concentrations and a less steep increase that levelled off at high concentrations(Figure 4). The latter effect apparently is caused by the concentration of the carboxylate groups present in solution $c = nc_{AP}$ with $n=3$ for NTA, $n=4$ for EDTA and $n=5$ for DTPA.

The photochemical quantum yield for ammonia release was also effected by adding aminopolycarboxylates. Figure 5 shows the effects in the EDTA system: a rise at low c_{AP} concentrations that corresponds to the sharp increase in phosphorescence intensity but a decrease at higher concentrations. The spectral changes were consistent with photosubstitution producing $(Cr(NH_3)_5OH)^{2+}$ in the low concentration region. With NTA and DTPA we observed similar effects. The maxima of the quantum yields were 0.15±0.01 at 0.05M Na_3NTA and 0.23±0.01 at 0.20M Na_5DTPA.

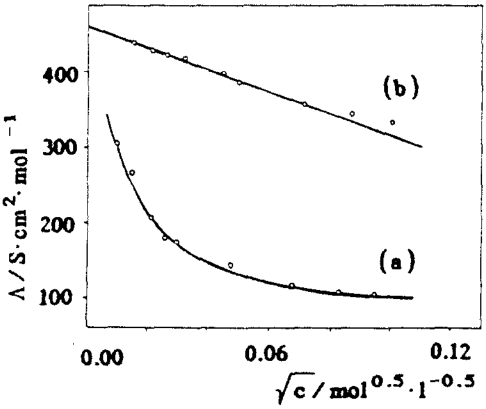


Figure 3. Molar conductivity of a) the EDTA salt and b) the perchlorate of hexamminechromium(III).

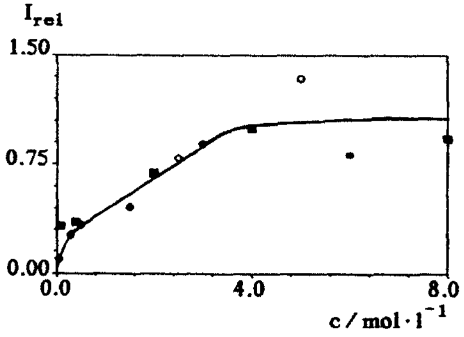


Figure 4. Phosphorescence intensity versus concentration of acetate groups; intensity relative to acid solution

● NTA, ■ EDTA
○ DTPA

3. DISCUSSION

The different effects on phosphorescence and photoreaction can be explained by ion pairing. Solvent separated ion pairs are formed at low concentrations, that contain the chromium complexes with intact solvation shells, whereas at higher concentrations contact ion pairs are formed in which the close polyacetates impede the ammonia dissociation.

According to the deactivation scheme (Figure 1) the efficiency for reaction from the photoactive state is $\eta \approx \varphi_{acid} \approx 0.5$. Assuming that all complexes that went through backintersystem crossing react with this efficiency, the photochemical quantum yield would be

$$\varphi_{calc} = \varphi_{nq} + \varphi_q I_{rel} \qquad (1)$$

with $I_{rel} = I/I_{acid}$ the phosphorescence intensity, relative to an acid solution of $(Cr(NH_3)_6)^{3+}$ and $\varphi_{cal} - \varphi_{exp}$ gives the quantum yield for quenching by contact ion pairing. Figure 6 shows that approximately 4-5 sixths of the photoreaction in acid solution were quenched at the highest carboxylate concentrations.

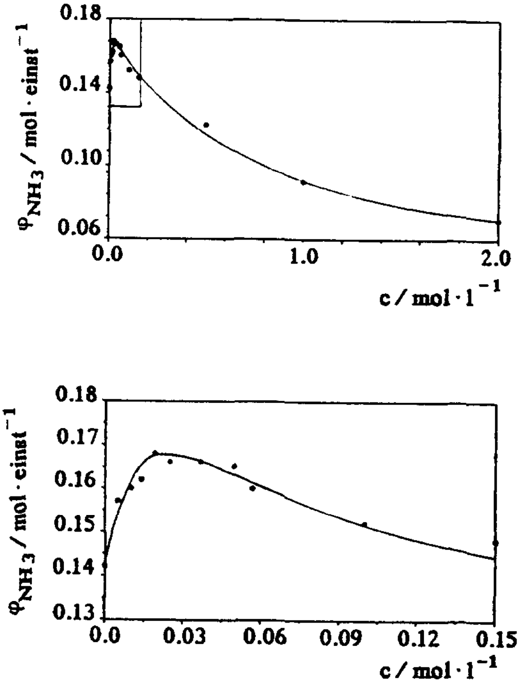


Figure 5. Plot of photochemical quantum yield versus concentration of added sodium EDTA salt

If each carboxylate group fixes one ammonia ligand in the contact ion that it cannot dissociate and the ethylenediamine bridge shields another ammonia, the observed reduction in the photochemical quantum yield in the presence of large amounts of EDTA seems feasible as shown in Figure 7.

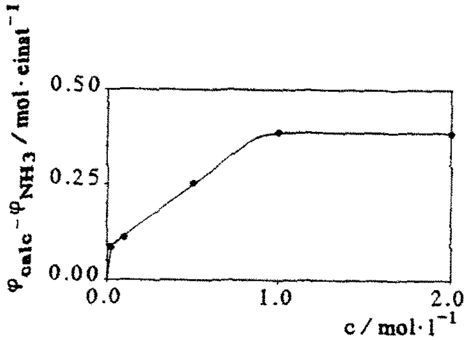


Figure 6. Quantum yields for quenching by contact ion pairs with EDTA.

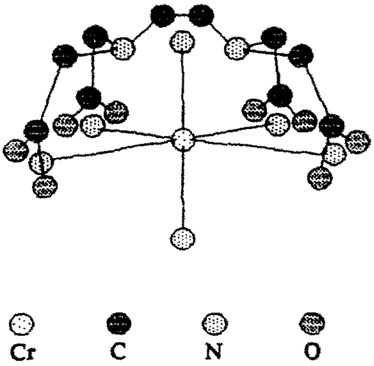


Figure 7. Molecular model for contact ion pair with EDTA.

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