Quenching of the Tris(ethylenediamine)chromium(III) Phosphorescence by Some Transition Metal Ions in Aqueous Solutions

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The intensity and lifetime quenchings of the $Cr(en)_3^{3+}$ phosphorescence have been investigated in aqueous solution at room temperature. It has been found that Mn_{aq}^{2+}, whose lowest excited state is at 18.9 kK, does not exhibit any quenching effect, whereas Fe_{aq}^{2+} and Co_{aq}^{2+}, which have very low lying excited states (<10 kK), do quench the $Cr(en)_3^{3+}$ phosphorescence. The quenching action of $CoCl_2$ has been investigated under various experimental conditions. It has been found that (i) the emission intensity and lifetime are quenched in parallel, (ii) the Stern–Volmer plots (I^0/I or τ^0/τ against $[CoCl_2]$) show a positive curvature, and (iii) the quenching effect increases with increasing Cl^- concentration. The results obtained are quantitatively accounted for considering the relative abundances and the different quenching abilities of the various Co(II) species (e.g., $Co(H_2O)_6^{2+}$, $Co(H_2O)_5Cl^+$, etc.) that are present in aqueous solutions containing Co^{2+} and Cl^- ions.

Introduction

The quenching of the luminescence emission of coordination compounds in fluid solutions has been scarcely investigated. However, recent studies have pointed out that the nature of the ligands,[2] the charges of the complex and the quencher,[2-5] and several parameters of the medium (ionic strength, viscosity, etc.[5,6]) play important roles in determining the value of the quenching constants. The possibility of carrying out systematic investigations in this field is somewhat limited because of the difficulty of finding suitable quenchers. This is particularly true in the case of the Cr(III) complexes which have low absorption bands and emit at very low energies (12–15 kK). In this paper, we wish to report the results of an investigation on the quenching of the $Cr(en)_3^{3+}$ phosphorescence by some transition metal ions in aqueous solution, under various experimental conditions. Some of these ions are very suitable for quenching experiments since they have low lying (<10 kK) excited states, low absorption, and high solubility in aqueous solutions. However, it will be shown that the quenching ability of these ions strongly depends on the actual nature of the species (e.g., $M(H_2O)_6^{2+}$, $M(H_2O)_5Cl^+$, etc.) that they are incorporated in.

Experimental Section

Materials. Tris(ethylenediamine)chromium(III) chloride dihydrate, $[Cr(en)_3]Cl_3 \cdot 2H_2O$, was prepared following the procedure indicated in the literature.[7] The corresponding perchlorate salt was obtained by adding concentrated perchloric acid to an aqueous solution of the chloride salt. $FeCl_2 \cdot 3H_2O$, $CoCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, and all the other chemicals used were of reagent grade.

Apparatus. The emission spectra were recorded by means of a Hitachi-Perkin-Elmer MPF-3 spectrofluorimeter equipped with a high sensitivity cell assembly and a red sensitive (R-446) photomultiplier. Luminescence lifetimes were obtained by exciting with a frequency doubled ruby laser (104 TRG/Control Data Corp.). The arrangement used has been described elsewhere.[8]

Procedures. A weighed amount of the complex was dissolved in the selected medium so as to obtain a 2.5×10^{-2} M solution. This operation was carried out in red light. The media used were as follows: (i) aqueous solutions which contained the desired concentration of the quencher and which had been slightly acidified with HCl so as to have a pH of about 2.5; (ii) the same solutions as above, except that their total Cl^- concentration[9] was adjusted to 2.0, 4.0, or 5.2 M by adding KCl or $MgCl_2$; (iii) aqueous solutions which contained the desired concentration of the quencher and whose total Cl^- concentration was adjusted to 2.0, 4.0, or 5.2 M by adding HCl. For the study of the intensity quenching, the excitation was carried out at 365 nm when using $CoCl_2$ or $MnCl_2$ and at 464 nm when using $FeCl_2$, in order to minimize the fraction of exciting light absorbed by the quencher (see Figure 1). Because of the low phosphorescence quantum yield, large excitation and emission slits ($\sim$30 nm) had to be used. In order to obtain reliable I^0/I values (see Results), the measured emission intensities had to be corrected for each one of the following factors: (a) the fraction of the exciting light absorbed by the quencher (maximum values: 8% for $CoCl_2$, 4% for $FeCl_2$, and 5% for $MnCl_2$); (b) the change in the emission intensity due to the change of the total absorbance of the solution at the wavelength of irradiation (maximum changes of absorbance for 1 cm of optical path: from 1.16 to 1.26 for $CoCl_2$, to 1.21 for $FeCl_2$, and to 1.22 for $MnCl_2$); (c) the "trivial" reabsorption of the emission by the quencher (minimum transmittance for 1-cm optical path: 0.42 for $CoCl_2$, 0.68 for $FeCl_2$, and 0.94 for $MnCl_2$). The correction for point a is a simple one. The other corrections are much more complicated since they also depend on the optical geometry of the spectrofluorimeter. The methods used for such corrections were based on experimental calibration plots and they will be fully described elsewhere.[10] No correction had to be made for the lifetime measurements since absorption by the quencher reduces the luminescence intensity but, obviously, does not affect the luminescence lifetime. All experiments were performed at room temperature ($\sim$20°).
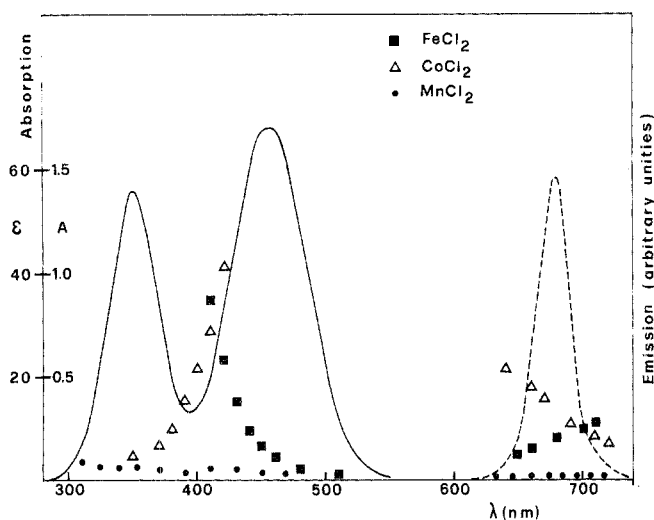
Figure 1. Molar extinction coefficients (solid line) and relative emission intensity (dotted line) of Cr(en)$_3$$^{3+}$. The absorbances of 1.7 M FeCl$_2$, 1.6 M CoCl$_2$, and 2.0 M MnCl$_2$ are also shown.

Since it is known that under these conditions neither the intensity[11] nor the lifetime[2] of the Cr(en)$_3$$^{3+}$ phosphorescence are affected by oxygen, all experiments were carried out in air equilibrated solutions.

Results

Quenching of the Phosphorescence Intensity. We found that the luminescence intensity of Cr(en)$_3$$^{3+}$ in aqueous solution was not affected by the presence of KCl (up to 4 M) and MgCl$_2$ (up to 5.2 M), whereas HCl exhibited some quenching action (I^0/I = 1.2 for [HCl] = 4). We also found that MnCl$_2$ did not quench the Cr(en)$_3$$^{3+}$ luminescence (see Figure 2). In contrast, CoCl$_2$ and FeCl$_2$ were found to exhibit a quenching effect. The Stern–Volmer plot for the quenching by CoCl$_2$ is shown in Figure 2. The quenching by FeCl$_2$ showed a very similar behavior.

Using CoCl$_2$ as a quencher, other experiments were carried out in order to find the reason for the positive curvature of the Stern–Volmer plot of Figure 2. It was found that the addition of Cl$^-$ ions to solutions containing a fixed amount of [Co^{2+}]$_{tot}$[9] strongly enhanced the intensity quenching. As is shown in Figure 3, for [Cl$^-$]$_{tot}$ = 2 or 4[9] this effect was the same regardless of whether HCl, KCl, or MgCl$_2$ was used for adjusting the Cl$^-$ concentration. Some experiments were also carried out in solutions containing [Cl$^-$]$_{tot}$ = 5.2 (adjusted with MgCl$_2$). Under these conditions, I^0/I was 1.9 and 4.1 for [Co^{2+}]$_{tot}$ = 0.1 or 0.3, respectively.

Quenching of the Phosphorescence Lifetime. The emission lifetime of Cr(en)$_3$$^{3+}$, τ^0, was found to be 1.33 ± 0.03 μsec in aqueous solution at room temperature. This value is in agreement with a previously reported one[12] and is also similar to the values obtained in different media.[2,8] We found that the presence of 1.1 M MnCl$_2$ or MgCl$_2$ (up to 5.2 M) did not affect the emission lifetime of Cr(en)$_3$$^{3+}$. When the complex was dissolved in concentrated HCl solutions, only a very small decrease in lifetime was observed (τ = 1.26 μsec for HCl 5.2 M). We found that the emission lifetime of Cr(en)$_3$$^{3+}$ was quenched by CoCl$_2$. The most important results obtained are shown in Figures 2 and 3. As one can see from Figure 2, the Stern–Volmer plot for the lifetime quenching coincided with that of the intensity quenching. Moreover, the effect of Cl$^-$ addition was the same as that found for the
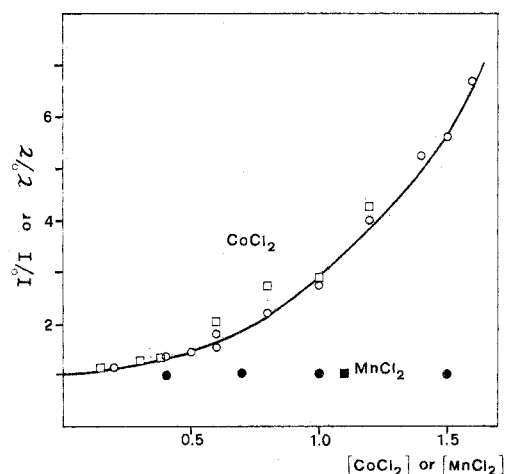

Figure 2. Quenching of the Cr(en)$_3$$^{3+}$ phosphorescence intensity (O) and lifetime (□) by CoCl$_2$. The curve represents the values calculated on the basis of eq 2 (see text). The lack of quenching by MnCl$_2$ (● and ■) is also shown.
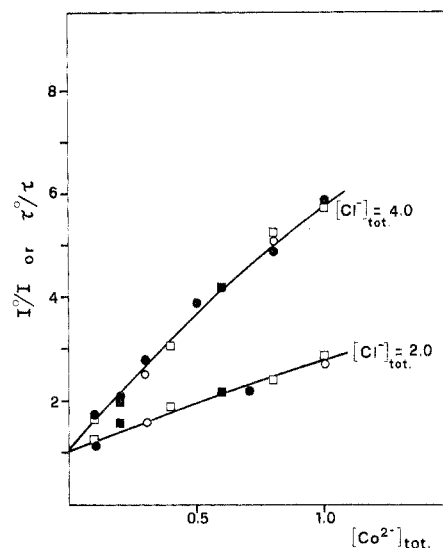

Figure 3. Quenching of the Cr(en)$_3$$^{3+}$ phosphorescence intensity (O) and lifetime (□) by Co^{2+} for solutions having constant Cl$^-$ concentration. Open symbols refer to solutions whose Cl$^-$ concentration was adjusted with MgCl$_2$ or KCl; solid symbols refer to solutions whose Cl$^-$ concentration was adjusted with HCl. The curves represent the values calculated on the basis of eq 2 (see text).

intensity quenching, at least for [Cl$^-$]$_{tot}$ = 2 or 4 (Figure 3). A few experiments were also carried out at [Cl$^-$]$_{tot}$ = 5.2. Using MgCl$_2$ to adjust the Cl$^-$ concentration, the τ^0/τ values were 2.2 and 4.15 for [Co^{2+}]$_{tot}$ = 0.1 and 0.3, respectively. Using HCl, τ^0/τ was 2.4 for [Co^{2+}]$_{tot}$ = 0.1.

Discussion

The results obtained may be summarized as follows: (i) KCl, MgCl$_2$, and MnCl$_2$ do not quench the Cr(en)$_3$$^{3+}$ emission, whereas CoCl$_2$ and FeCl$_2$ exhibit a quenching effect; (ii) the Stern–Volmer plots for the quenching by CoCl$_2$ or FeCl$_2$ show a positive curvature; (iii) the quenching effect of CoCl$_2$ increases with increasing Cl$^-$ concentration; (iv) at least for [Co^{2+}]$_{tot}$ ≤ 1.0, and [Cl$^-$]$_{tot}$ ≤ 4.0, the effect due to the increase in [Cl$^-$] does not depend on whether MgCl$_2$ or HCl are used for adjusting the chloride ion concentration; (v) at least under the
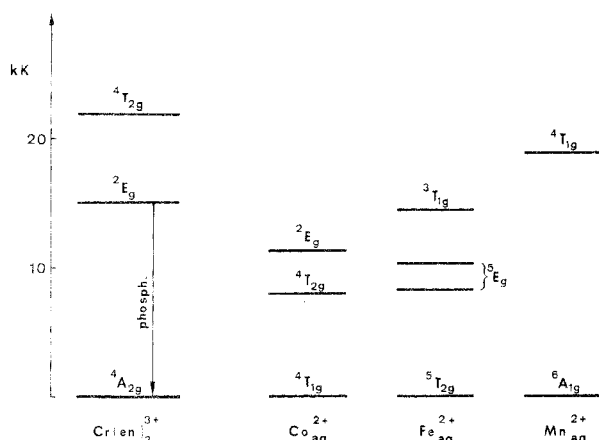
Figure 4. Energy level diagram for Cr(en)$_3$$^{3+}$ and the hexaaquo ions used as quenchers. The Co(II) and Fe(II) species which are present in concentrated Cl$^-$ solutions are also expected to exhibit energy levels lower than the ^{2}E$_g$ of Cr(en)$_3$$^{3+}$.

Figure 5. Quenching of the Cr(en)$_3$$^{3+}$ phosphorescence by Co(II) species. Open and solid circles refer to the experiments previously shown in Figures 2 and 3, respectively. For the meaning of k', see text.

experimental conditions given above, the emission intensity and lifetime are quenched in parallel.

The results mentioned in point i seem to indicate that the quenching of Cr(en)$_3$$^{3+}$ emission involves electronic energy transfer to the low lying excited states of Co$_{aq}$$^{2+}$ and Fe$_{aq}$$^{2+}$ (or to some other Co(II) or Fe(II) species, see later). As shown in Figure 4, Mn$_{aq}$$^{2+}$ has no excited state lying at lower energy than that of the Cr(en)$_3$$^{3+}$ emitting state. Of course, the same is true for KCl and MgCl$_2$. It does not seem likely that the quenching by Co$_{aq}$$^{2+}$ and Fe$_{aq}$$^{2+}$ is due to electron transfer. The doublet state of Cr(en)$_3$$^{3+}$ is not expected to exhibit remarkable redox properties. Moreover, if Co$_{aq}$$^{2+}$ acted as an electron donor toward excited Cr(en)$_3$$^{3+}$, Mn$_{aq}$$^{2+}$ would exhibit a similar quenching action since the ionization and oxidation potential of Co$_{aq}$$^{2+}$ and Mn$_{aq}$$^{2+}$ are practically equal. The lack of quenching by Mn$_{aq}$$^{2+}$ also shows that the presence of a paramagnetic ion does not enhance the ^{2}E$_g$ → ^{4}A$_{2g}$ intersystem crossing of Cr(en)$_3$$^{3+}$. As far as the small quenching action of HCl is concerned (see Results), the most plausible explanation is that of an acid catalysis on the Cr(en)$_3$$^{3+}$ photolysis which is known to take place, at least in part, from the lowest quartet excited state.[13]

The positive curvature of the Stern–Volmer plots of Figure 2 cannot be due to the quenching of two excited states or to some static quenching.[14] Such phenomena, in fact, could account for the curvature in the plot of the *intensity* quenching, but they cannot account for the nonlinearity of the *lifetime* plot and for the fact that intensity and lifetime are quenched in parallel. For a dynamic quenching, when the excited state and the quencher have ionic charge of the same sign, a positive curvature of the Stern–Volmer plot is expected because of the ionic strength influence.[15] However, for high ionic strengths (0.4 < μ < 3.4, for the experiments plotted in Figure 2) this effect is expected to be very small,[15] in agreement with the experimental results mentioned in point iv. Therefore, the most important cause for the observed behavior (Figure 2) seems to be a change in the nature of the quenching species with increasing CoCl$_2$ concentration. Actually, it is well known that different species may be present in CoCl$_2$ solutions, depending on its concentration and on the addition of other compounds which contain Co^{2+} or Cl$^-$ ions. To our knowledge, the most complete investigation on this problem was that carried out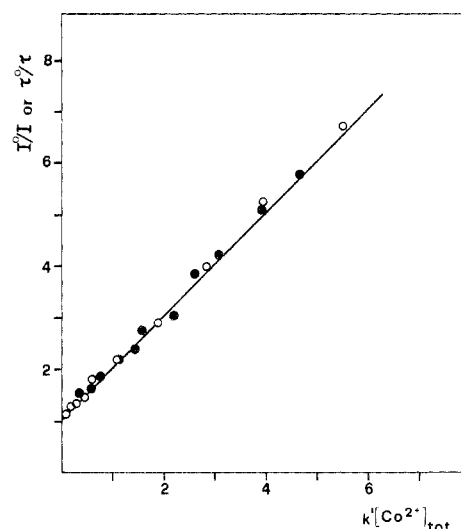 by Zeltmann, et al.,[16] who identified the following important species for Co^{2+} in hydrochloric acid solutions: Co(H$_2$O)$_6$$^{2+}$, Co(H$_2$O)$_5Cl^+$, Co(H$_2$O)$_2Cl_2$, Co(H$_2$O)Cl$_3$$^-$, and CoCl$_4$$^{2-}$.[17] In diluted aqueous solutions of CoCl$_2$, Co(H$_2$O)$_6$$^{2+}$ is the dominant species. When the concentration of CoCl$_2$ or of added Cl$^-$ increases, the chloride containing species become important. Then, the positive curvature of the plot in Figure 2 and the positive effect of added Cl$^-$ on the quenching constant (Figure 3) may be qualitatively accounted for assuming that the Stern–Volmer quenching constant increases with increasing number of Cl$^-$ present in the Co(II) species. Since the substitution of water by Cl$^-$, which is a weaker ligand, is expected to decrease the reducing ability of Co$_{aq}$$^{2+}$, the positive effect of added Cl$^-$ is another evidence against an electron-transfer quenching mechanism.

In order to consider the problem from a quantitative point of view, let us assume that all the above-mentioned Co(II) species can act as quenchers. The Stern–Volmer equation for the emission quenching can thus be written as follows

$$I^0/I = \tau^0/\tau = 1 + k_1[\text{Co(H}_2\text{O)}_6^{2+}] + k_2[\text{Co(H}_2\text{O)}_5\text{Cl}^+] +$$
$$k_3[\text{Co(H}_2\text{O)}_2\text{Cl}_2] + k_4[\text{Co(H}_2\text{O)Cl}_3^-] + k_5[\text{CoCl}_4^{2-}] \quad (1)$$

or

$$I^0/I = \tau^0/\tau = 1 + (k_1\alpha_1 + k_2\alpha_2 + k_3\alpha_3 + k_4\alpha_4 +$$
$$k_5\alpha_5)[\text{Co}^{2+}]_{\text{tot}} \quad (2)$$

where α's are the relative abundances of the various Co(II) species. By means of a nmr study, Zeltmann, et al.,[16] were able to obtain the α values for hydrochloric acid solutions. The results in point iv suggest that Zeltmann's α values can be used to discuss our experiments, at least for [Co^{2+}]$_{\text{tot}}$ ≤ 1.0 and [Cl$^-$]$_{\text{tot}}$ ≤ 4.0. Under such conditions, only Co(H$_2$O)$_6$$^{2+}$, Co(H$_2$O)$_5Cl^+$, and Co(H$_2$O)$_2Cl_2$ are present, i.e. α_4 and α_5 are practically zero. By means of the least-squares method, we found that our experimental results are best explained by the following Stern–Volmer quenching constants: $k_1 = 0.2$ M^{-1}, $k_2 = 7$ M^{-1}, and $k_3 = 1 \times 10^2$ M^{-1}. Using these values and eq 2, the curves shown in Figures 2 and 3 were obtained. As one can see,

the agreement with the experimental values is excellent. A more direct comparison between the results obtained under various experimental conditions and the proposed interpretation is given in Figure 5, where the line with unitary slope and intercept represents the plot of the first member of eq 2 against $k'[Co^{2+}]_{tot}$ (where $k' = k_1\alpha_1 + k_2\alpha_2 + k_3\alpha_3$). As one can see, the agreement with the experimental values (which are all those previously shown in Figures 2 and 3) is again excellent.[19]

For $[Cl^-]_{tot} = 5.2$, α_4 is still very small (0.005 for $[Co^{2+}]_{tot} = 0.1$) but, in eq 2, the term $k_4\alpha_4$ can no longer be neglected. By using the few results of the experiments carried out under such conditions, we obtained a value of about $3 \times 10^2 M^{-1}$ for k_4.

Dividing each one of the above Stern–Volmer quenching constants by the lifetime of Cr(en)$_3^{3+}$ in the absence of Co(II) ($\tau^0 = 1.33$ μsec), one may obtain the following values for the bimolecular quenching rate constants of the various Co(II) species: $k_{q1} = 1.5 \times 10^5 M^{-1}$ sec^{-1}, $k_{q2} = 5 \times 10^6 M^{-1}$ sec^{-1}, $k_{q3} = 8 \times 10^7 M^{-1}$ sec^{-1}, and $k_{q4} \sim 2 \times 10^8 M^{-1}$ sec^{-1}. As is expected for the quenching of a cationic species,[3-5] these constants increase as the positive charge of the quencher is decreased. It can be noted that all these values are much lower than the diffusion rate constants calculated by means of the Debye equation.[20] As already observed, the energy transfer between complex ions seems to have a scarce efficiency especially when the ions have electric charge of the same sign.[3-5] In this regard, it is to be noted that the ratio between the calculated diffusion rate constant[20] and the experimental quenching rate constant for our system progressively decreases as the charge of the quencher passes from +2 to −1 (e.g., such a ratio is 3000 for Co(H$_2$O)$_6^{2+}$ and about 90 for Co-(H$_2$O)Cl$_3^-$). In line with this trend, it has recently been found[6] that the Ru(bipy)$_3^{2+}$ phosphorescence is quenched by Cr(CN)$_6^{3-}$ with a rate constant very close to the diffusion controlled one.[21] It should be noted, however, that the role played by the ionic charge in determining the quenching ability cannot be unequivocally established, since the change in the ionic charge is accompanied by a change in the nature of the ligands, which is also known to play an important role in this regard.[2,23]

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