Table II. Band Maxima, *Dq*, and *B* Values for Some Octahedrally Coordinated Nickel(II) Halide Compounds

Compd	σ_1	σ_2	σ_3[b]	*Dq*	*B*	Ref
$CsNiCl_3$	7.10	11.8	22.2	710	845	27
$NiCl_2$	7.40	12.8	21.8	740	780	27
$NiBr_2$	7.15	12.1	(20.3)[a]	715	695	27
$xdtcNi_5Cl_8Br_3$	7.08	11.8	21.4	708	787	This work

[a] Shoulder on a charge-transfer band. [b] Values in kK; *Dq* and *B* in K. σ_1 is the assigned transition $^3A_{2g} \rightarrow {}^3T_{2g}$; σ_2 is the assigned transition $^3A_{2g} \rightarrow {}^3T_{1g}(F)$; σ_3 is the assigned transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. [c] Mineral oil mull between quartz plates.

using large excesses of DBX when alkylating complexes in chlorinated solvents.

Characterization of $xdtcNi_5Cl_8Br_3$ (most likely mixed with $xdtcNi_5Cl_9Br_2$) allows some generalizations concerning the structure of this new compound. The nickel ions appear to be octahedrally coordinated based on the electronic spectrum (Table II) and the magnetic moment of 3.54 BM/nickel (assuming the Curie law). This moment is quite in agreement with that observed for octahedral $CsNiCl_3$ (3.50 BM at 300 K).[24] Such a high value for the moment suggests a spin–orbit coupling constant of about −375 K.[25] An additional peak at 26.6 kK in the electronic spectrum of $xdtcNi_5Cl_8Br_3$ is assigned as a cation (xdtc) transition. Several known 1,3-dithiolium ions have adsorbances in the 25–42 kK range.[26]

When $Ni(dtc)_2$ and DBX were allowed to stand in 1,2-dichoroethane at room temperature, blue crystals of $(xdtc)_2NiBr_4$ appeared within several days. Analysis and the visible spectrum confirmed the nature of the anion in this salt. It was found to be the typical tetrahedral $NiBr_4^{2-}$ observed by others.[28]

Yields of $(xdtc)_2NiBr_4$ and $xdtcNi_5Cl_8Br_3$ are inversely related in that one appears to form at the expense of the other. At room temperature $(xdtc)_2NiBr_4$ is isolated while at reflux (and with longer reaction time) $xdtcNi_5Cl_8Br_3$ is the product. Thus it appears that $NiBr_4^{2-}$ is first formed and then interacts with 1,2-dichloroethane producing the ultimate product. No reaction is observed between $Ni(dtc)_2$ and 1,2-dichloroethane in the absence of DBX, while $(xdtc)_2NiBr_4$ with fresh 1,2-dichloroethane (reflux) forms $xdtcNi_5Cl_8Br_3$.

Thus, to summarize, we have a complex and interesting reaction between a chlorinated solvent and a nickel(II) complex. The reaction of $Ni(dtc)_2$ with DBX is different from reactions previously reported. Studies utilizing dithiocarbamato complexes of other metal ions should lead to some interesting products and further information concerning the metal–sulfur bond.

Acknowledgment. The authors wish to thank the National Science Foundation for partial support of this work under Grants GP-5993 and GP-20457. We also wish to thank Professor F. Wassmundt for helpful discussions.

Registry No. $(xdtc)Ni_5Cl_8Br_3$, 57594-29-3; $xdtcClO_4$, 57484-17-0; $(xdtc)_2NiBr_4$, 57527-41-0; $Ni(dtc)_2$, 14267-17-5; DBX, 91-13-4; 4, 57484-18-1; Na(dtc), 148-18-5.

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Effects of Quenchers on the Emission and Photoracemization of Tris(1,10-phenanthroline)chromium(III)

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Received May 13, 1975 AIC50333Z

The observation that several Cr(III) complexes of O_h and D_3 symmetries exhibit room-temperature solution phosphorescence[1] has assisted considerably in elucidating mechanistic details of their photochemistry. For the majority of these systems, selective doublet ^2E_g quenching agents have been found, thus enabling a distinction to be made between the quartet $^4T_{2g}$ and doublet ^2E_g as excited-state precursors to photochemical reaction.[2,3] The case of $Cr(phen)_3^{3+}$ (phen = 1,10-phenanthroline)[3] is of particular interest because of the marked influence of the medium on its photochemical and photophysical behavior.

We have previously discussed the highly efficient quenching of $(+)_{589}$-$Cr(phen)_3^{3+}$ phosphorescence and photoracemization in aqueous solution by iodide ion.[3] We have recently noted[4] the unusual emission behavior of $Cr(phen)_3^{3+}$ and the 2,2′-bipyridine analogue in dimethyl sulfoxide solution. In this note, we reexamine iodide quenching and extend our earlier discussion of the photoracemization of $(+)_{589}$-$Cr(phen)_3^{3+}$ in aqueous solution, based on an analysis of new quenching data for the anions SCN^- and OH^- and for molecular oxygen. The O_2 data elucidate and correct our earlier report. The OH^- data present an interesting mechanistic puzzle not yet resolved.

Experimental Section

$(+)_{589}$-$Cr(phen)_3(ClO_4)_3$ was isolated according to the literature method.[5] All other reagents used were of analytical grade quality. Stock solutions of the chloride salt used in the investigation were prepared by ion-exchange chromatography of the perchlorate salt using a Dowex 1-X4 resin (Cl^- form).

Racemization and luminescence data were collected using equipment described before.[1] The *T* dependence of phosphorescence

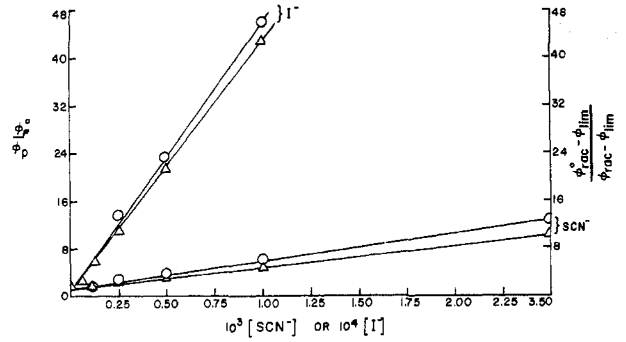

Figure 1. Stern–Volmer plots for iodide and thiocyanate quenching in aqueous solution at 25°C: $Cr(phen)_3{}^{3+}$ phosphorescence, ϕ_p (△); quenchable part of $(+)_{589}$-$Cr(phen)_3{}^{3+}$ photoracemization, $\phi^\circ_{rac} - \phi_{lim}$ (○).

(decreasing intensity with increasing T) was analyzed as in ref 1. A plot of log (intensity (relative)) vs. $1/T$ was sufficiently linear to allow for assignment of an apparent activation energy. The quantum yield for racemization (ϕ_{rac}) is derived from the relationship $\phi_{rac} = k_{rac}[\text{complex}]V/I$, where V is the cell volume in liters, I is the light intensity in einsteins per second, and k_{rac} is the first-order racemization rate constant under the given conditions, obtained from the plot of log (optical rotation) vs. time. Kinetic plots were accurately linear over 3 or more half-lives. (Since reactant and product in a racemization process have identical absorptivities, excellent first-order kinetics are observed for several half-lives of reaction. Thus, quantum yields may be determined with unusual precision.) Note that ϕ_{rac} is twice the primary yield if the mechanism is inversion and not racemization via a symmetrical intermediate.

Deaeration was achieved by purging solutions for a minimum of 30 min with an oxygen-free nitrogen stream.

Results and Discussion

SCN^- and I^- Quenching. Examination of Figure 1 indicates that on a concentration basis iodide ion is approximately 100 times more effective than thiocyanate as a quenching agent. Iodide has been reported before.[2] The SCN^- results are parallel. However, for both anions in aerated solution at 25°C, 16% of the racemization yield (ϕ_{rac}) at 350 nm remains nonquenchable under conditions of total phosphorescence quenching. These observations clearly imply that the main role of *both* ions is selective deactivation of a common excited state, namely, the doublet, ^2E_g. The conclusion is reinforced by the near equivalence of the phosphorescence and quenchable racemization Stern–Volmer slopes for each individual ion (Figure 1).

As noted previously by us and by other authors, an unquenchable reaction component (ϕ_{lim}) may be assigned to direct reaction out of the $^4T_{2g}$ level prior to intersystem crossing (ISC) to the doublet. In contrast, for the quenchable portion of racemization (84%) a choice must be made between two possible paths: (a) direct doublet reaction or (b) $^4T_{2g}$ reaction, subsequent to thermal repopulation via back ISC. The principal evidence cited before in support of the latter pathway was the unusually high apparent activation energy (10.1 kcal mol^{-1}) for the quenchable part of reaction.[2] Reaction originating directly out of the doublet should *probably* be characterized by a relatively small activation energy, while back ISC will be associated with an activation barrier near the energy gap between the ^2E_g and $^4T_{2g}$ states.[6]

However, should *back* ISC proceed with unit efficiency, this would mask the energy requirement for racemization via this pathway because the increase of temperature could not increase the *fraction* of doublets returning to quartet. The experimental activation energy of 10.1 kcal mol^{-1} reported[2] therefore requires efficient $^2E_g \rightarrow {}^4A_{2g}$ deactivation, in *contrast* to the situation reported for $Cr(NH_3)_6{}^{3+}$ and $Cr(en)_3{}^{3+}$ (en = ethylenediamine).[1] This requirement is consistent with the low apparent activation energy (4.5 kcal mol^{-1}) associated with

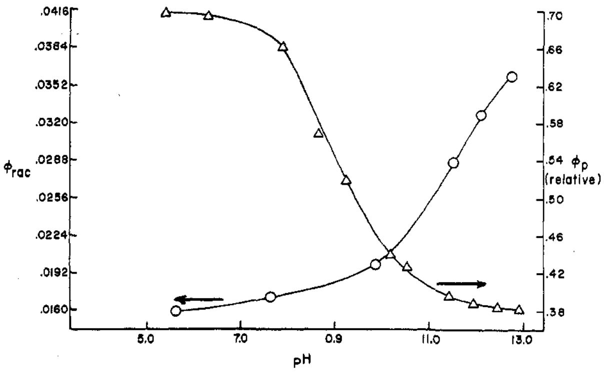

Figure 2. pH dependence in aqueous solution at 25°C: $Cr(phen)_3{}^{3+}$ phosphorescence, ϕ_p (△); $(+)_{589}$-$Cr(phen)_3{}^{3+}$ photoracemization, ϕ_{rac} (○).

the decrease of the phosphorescence intensity of $Cr(phen)_3{}^{3+}$, as compared with previously reported values of 10.4 and 10.5 kcal mol^{-1} for $Cr(NH_3)_6{}^{3+}$ and $Cr(en)_3{}^{3+}$ (en = ethylenediamine), respectively.[1] As reported in the following section, quenching by molecular O_2 provides the efficient relaxation path of ^2E of $Cr(phen)_3{}^{3+}$ which is required. This clarifies and corrects our earlier observations while supporting the mechanistic conclusion.

Oxygen Quenching. An approximate threefold increase in phosphorescence intensity[7] and ϕ_{rac} at 350 nm results from nitrogen purging of an aerated solution of $(+)_{589}$-$Cr(phen)_3{}^{3+}$. (ϕ_{rac}: aerated 0.016; deaerated 0.048). In addition, the enhanced phosphorescence quantum yield (ϕ_p) is accompanied by a corresponding increase in the lifetime of phosphorescence.[7] These observations are consonant with bimolecular quenching of the long-lived ^2E_g level of $Cr(phen)_3{}^{3+}$ by dissolved oxygen. In accord with this interpretation, the iodide nonquenchable reaction component decreases from the 16% value in aerated solution to 5% in oxygen-free solution. Further, values for nonquenchable ϕ_{rac} correspond closely in the presence and absence of oxygen. We infer from these data a lower limit of 0.95 for the quantum efficiency of $^4T_{2g} \rightarrow {}^2E_g$ ISC because 95% of the reaction is quenchable and therefore involves the system passing through the doublet.

The oxygen-quenching results so far presented do not differentiate between a doublet racemization component proceeding by either path a or b. However, trends in the activation energies for phosphorescence intensity and quenchable racemization in deaerated solution provide additional support for path b except in the presence of OH^-. While the apparent activation energy associated with decrease of phosphorescence intensity increases from the aerated solution value of 4.5 to 7.3 kcal mol^{-1}, the activation energy for the quenchable reaction component decreases from 10.1 to 6.7 kcal mol^{-1}. (E_a values derived from ϕ at three temperatures from 25 to 45°C.) These trends are precisely those anticipated for mechanism b if bimolecular oxygen quenching contributes significantly to doublet deactivation because, crudely put, an increase in the fraction of doublets returning to quartet at 25°C decreases the possible fractional increase with increasing temperature.

Influence of OH^- Ion. High hydroxide ion concentrations result in partial phosphorescence quenching accompanied by an increase in ϕ_{rac} (Figure 2). Despite this increase in ϕ_{rac}, the reaction portion nonquenched by iodide remains constant at ~16% for 350-nm irradiation. (At pH 12, $\phi_{rac} = 0.033$; $\phi_{rac} = 0.0051$ when $[I^-] = 0.001$ M). The situation is more complex than that in acid or neutral solution, since visible spectral changes indicate base hydrolysis makes a contribution to loss in rotation.

With regard to phosphorescence, the emission intensity approaches, at pH 13, a limiting value nearly half that in acid solution. The quenching process is obviously different from that present for the complexes $Cr(NH_3)_6{}^{3+}$ and $Cr(en)_3{}^{3+}$, where total phosphorescence quenching was observed at pH values ≥11. For the latter compounds we have suggested[8] involvement of an amine–hydrogen deprotonation step, a mechanism unavailable to $Cr(phen)_3{}^{3+}$. The pH profile for phosphorescence intensity (Figure 2) is suggestive of hydroxide ion addition to either ground- or excited-state $Cr(phen)_3{}^{3+}$, resulting in the equilibrium formation of a Meisenheimer-type complex.[9] Since phosphorescence occurs between levels predominantly metal in character, the absence of a spectral shift in the basic emission spectrum is consistent with this model of peripheral hydroxide attack on an aromatic ring.

One way to account for an increase in ϕ_{rac}, on a decrease in phosphorescence, and a continuing small fraction of nonquenchable reaction would be to suggest that a *reaction* from the doublet has been observed; with our results, this conclusion cannot be regarded as firm. However, Moggi, Balzani, and Bolletta[10] have very recently developed a strong case for bimolecular reaction between OH^- and the doublet of $Cr(bpy)_3{}^{3+}$.

Racemization Mechanism in Acid or Neutral Solution. Although the ultimate product of $(+)_{589}$-$Cr(phen)_3{}^{3+}$ photolysis is $(\pm)$-$Cr(phen)_2(H_2O)_2{}^{3+}$, loss of optical activity proceeds at a rate well in excess of photoaquation for pH ≤7. Thus, after 2.5 half-lives of racemization at 350 nm in the presence of Fe(II), no evidence for free phenanthroline was obtained. Rotation loss is therefore attributed to direct racemization, $(+)_{589}$-$Cr(phen)_3{}^{3+} \rightarrow (\pm)$-$Cr(phen)_3{}^{3+}$.

Direct racemization could proceed by either intermolecular or intramolecular mechanisms.[11] Of these pathways, an intermolecular mechanism is considered the less probable. Although the lack of a ferroin color test is by no means unequivocal, it does require that the steady-state concentration of free phenanthroline be exceedingly small if an intermolecular scheme is operative. A variety of twist and one-ended dissociation mechanisms of intramolecular racemization have been suggested for tris-bidentate complexes.[12] Basolo and others[13,14] have pointed out that a one-ended dissociation pathway for phenanthroline chelates is also unlikely. Owing to the rigid nature of the ligand, any "half-bonded" structure should normally be expected to undergo ring closure with retention of configuration. However, it is noteworthy that after 2.5 half-lives for racemization, a small decrease (~8%) in phosphorescence intensity is observed. Since this change cannot be attributed to photoaquation or to a twist pathway, it is possible that some racemization proceeds through the intermediacy of the ring-opened species *cis*-$Cr(phen)_2phen(H_2O)^{3+}$.

Registry No. $(+)_{589}$-$Cr(phen)_3{}^{3+}$, 41587-82-0; SCN^-, 302-04-5; I^-, 20461-54-5; O_2, 7782-44-7; OH^-, 14280-30-9.

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Convenient Preparations of 1,2,3,4,5-Pentamethylcyclopentadiene and 1-Ethyl-2,3,4,5-tetramethylcyclopentadiene

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Received May 19, 1975 AIC50344S

Pentamethylcyclopentadienyl (Me_5Cp) anion is a useful cyclopentadienyl congener in transition metal chemistry.[1,2] Investigation of Me_5Cp–metal compounds has been hindered by the inaccessibility of pentamethylcyclopentadiene (**1**).[1,3] The most commonly used synthesis[3] (Scheme I) is inconvenient and expensive and the optimal experimental conditions[4] have not been widely disseminated. Although specialized reactions yield Me_5CpM derivatives,[5,6] no general, large-scale preparation of pentamethyl- or other polyalkylated cyclopentadiene derivatives has been available.

Burger et al. recently reported two short syntheses of Me_5Cp which are practical for large-scale preparations (Scheme II).[7] The starting material in the first of these syntheses, hexamethyl(Dewar benzene) (**2**) is expensive and sensitive. We have repeated the cleavage of **3** to **1** following the reported method[7] on a preparative scale and found it to be an efficient and convenient method. The second procedure provides an inexpensive route to tetramethylcyclopentenone (**4**), an intermediate also used in the previous synthesis.[3] We have not reproduced the second route.

Here we describe a fourth route to **1** and a particularly convenient preparation of 1-ethyl-2,3,4,5-tetramethylcyclopentadiene (**9**) (Scheme III). This synthesis of **1** is based on the work of Conia[9] and Eaton.[10] 2-Butyl tiglate (**6**) is prepared either by acid-catalyzed esterification of tiglic acid (**5**) or by allowing tigloyl chloride to react with 2-butanol. Compound **6** is cyclized and dehydrated to tetramethylcyclopentenone (**4**) using 1:10 solution of P_2O_5 in methanesulfonic acid.[10] This medium proved superior to PPA for this cyclization (see the Experimental Section). Addition of methyllithium to **4** and dehydration of the resulting alcohol to **1** follow previous syntheses.[3,7] The synthesis of **9** begins with dimerization of 3-pentanone to 4,5-dimethyloctane-3,6-dione (**7**) by refluxing with lead dioxide.[11] This procedure is both more convenient and safer than that requiring acetyl peroxide,[12] and it is not necessary to isolate **7**. After simple distillation of excess 3-pentanone, a base-catalyzed internal aldol condensation converts **7** to **8**; addition of methyllithium and dehydration affords **9**. Compound **9** was characterized by NMR spectroscopy and by conversion to ethyltetramethylcyclopentadienyl ($EtMe_4Cp$) derivatives of titanium and iron ($(EtMe_4Cp)_2TiCl_2$ and $(EtMe_4Cp)_2Fe$).

The relative merits of these new methods for preparation of pentaalkylcyclopentadienes are based on cost and convenience. The most convenient of these four preparations for large-scale work is that leading from 3-pentanone to **9** (method