compositions for the transients. The former group contains those of the type $Pt(en)_2(X)^{n+}$ where X is Cl, OH, or H_2O. While their compositions would indicate a minimum coordination number of 5, we would propose that they may be of a six-coordinate type, with the sixth position occupied by water. The basis for this proposal resides in results obtained on the flash photolysis of $Pt(en)_2(Cl)_2^{2+}$ in the presence of millimolar amounts of free Cl^-.[5] Irradiation with wavelengths above 280 nm, for which photolysis of Cl^- is unlikely, produced a new and intensely absorbing transient (peak ca. 295 nm) suggestive of a possible reaction between $Pt(en)_2(Cl)^{2+}$ and Cl^-. Similar strongly absorbing products are also formed on electron reduction of $Pt(en)_2(Cl)_2^{2+}$ and on Cl_2^- oxidation of $Pt(en)_2^{2+}$ (0.5 M HCl).[16]

The second category is represented by $Pt(en)(en\text{-}H)^{2+}$, which has now been prepared by three different chemical routes. Consideration of these routes would imply a coordination number of 4, with the possible limiting forms of square-planar or tetrahedral geometries. Species having spectral and kinetic properties similar to those of $Pt(en)(en\text{-}H)^{2+}$ occur on reaction of OH with the glycine complexes *cis*-$Pt(gly)_2$ and *trans*-$Pt(gly)_2$.[17] The products associated with the cis compound are *not* the same as those of the trans complex. This difference precludes a tetrahedral form for the platinum glycine entities and presumably also for $Pt(en)(en\text{-}H)^{2+}$. Thus the systems may exhibit square-planar microsymmetry. Of note in this regard is the spectral similarity of these materials to those of the monoanionic complexes of Ni, Pd, and Pt containing dithiolene and related ligand systems.[11] The bis complexes possess spin-doublet ground states and square-planar geometry. These systems, while formally M(III), can be designated (depending upon the ligand) as a M(II) center stabilizing a ligand radical cation. In a similar vein, Whitburn and Laurence[46] have recently reported results on the reactions of nickel(II) macrocyclic complex ions with OH and dihalogen radical anions. They proposed that the transients which exhibit absorption peaks near 550 nm and which are derived from nickel(III) species are describable as nickel(II) complexes containing a nitrogen-based ligand radical. The amine nitrogen radical site is considered to have lost a proton in its formation. In the present context, an alternative description of $Pt(en)(en\text{-}H)^{2+}$ as a platinum(III) species containing an amido group would be that it is a platinum(II) entity with a nitrogen-based ligand radical where a proton has been lost from the radical site. Presumably charge delocalization between the platinum and nitrogen could lead to enhanced stability, and this may account for the apparent greater stability of $Pt(en)(en\text{-}H)^{2+}$ relative to the $Pt(en)_2(X)^{n+}$ forms. It is notable that this does not result in permanent degradation of the ligand. In this sense, the binding of ethylenediamine (and glycine) to a platinum(II) center has afforded some degree of radiolytic protection for the ligand toward OH, in contrast to its behavior as a free ligand.

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Registry No. *trans*-$[Pt(en)_2(OH)_2](ClO_4)_2$, 74643-96-2; $[Pt(en)_2](ClO_4)_2$, 28136-92-7; OH, 3352-57-6; H, 12385-13-6; $Pt(en)_2(OH)^{2+}$, 74592-11-3; $Pt(en)(en\text{-}H)^{2+}$, 74592-12-4; $Pt(en)_2(H_2O)^{3+}$, 74592-13-5; $Pt(en)_2(Cl)^{2+}$, 74592-14-6.

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Photoracemization of Δ- and Λ-Tris(ethylenediamine)chromium(III)

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The quantum yield (ϕ_R) for the photoracemization of $Cr(en)_3^{3+}$ at ambient temperature was determined. For the process $\Delta\text{-}Cr(en)_3^{3+} \rightleftharpoons \Lambda\text{-}Cr(en)_3^{3+}$ ϕ_R was found to be 0.015, independent of hydrogen ion concentration when varied from 0.08 to 1.0 M. Because extensive photolysis was necessary to obtain sufficient rearrangement for quantitative measurement, several methods of separation of $Cr(en)_3^{3+}$ from major photoproducts were utilized, and a method for determining quantum yield in the presence of a large quantity of other photoproducts was designed. Mechanisms consistent with experimental data are discussed with emphasis on one suggested by an orbital correlation diagram.

Introduction

Most investigations of the photochemistry of chromium(III)–amine complexes have dealt with photosubstitution[1,2] of a ligand by solvent, usually water. If the reaction coordinate for photoreaction is taken as one of the normal coordinates of the octahedral structure, models[3–6] of this process have considered almost exclusively the $E_g(S_2)$ symmetry vibration within the lowest excited quartet, a motion that causes elongation along the *z* axis or in the *xy* plane; such motion leads to species generally thought to be like d^4 or d^9 complexes and hence very fast to substitute.

Two possible fates of a molecule activated for substitution and containing chelated groups can be delineated: (1) The bond ruptured can be replaced by solvent in which case net photosubstitution occurs. This process is exemplified by many

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chromium(III)–amine complexes, *trans*-$Cr(en)_2F_2^+$ yielding $Cr(en)(enH)(H_2O)F_2^{2+}$[7] and $Cr(en)_3^{3+}$ yielding $Cr(en)_2(enH)(H_2O)^{4+}$.[8–10] (2) The ruptured chelate bond could close to show, under unfavorable circumstances, no net photochemistry or, under favorable ones, isomerization or racemization. In addition to this, however, another vibrational motion can be considered as a reaction coordinate for photoreaction: this is the $T_{2u}(S_6)$ vibration, a vibration that causes a twisting of the octahedral complex about the threefold axes. It is expected that this motion would lead to isomerization or racemization of appropriately chosen molecules.

Thus, although two different distortions of the excited quartet can lead to isomerization and/or racemization, no evidence to date can be used to distinguish these possibilities. From an experimental point of view, those systems that show photoracemization are just those that are not known to exist as "one-ended" species ($Cr(ox)_3^{3-}$,[11] $Cr(phen)_3^{3+}$[12]); thus either effective geminate recombination or reaction via the T_{2u} vibrations is a possible mechanism for racemization, and both mechanisms are consistent with the experimental data.

That the T_{2u} vibration might lead to photoracemization in a d^3 octahedral system is suggested by the studies of Burdett.[13] He has used an angular overlap approach within a one-electron orbital model that suggests there is some stability in a trigonal-prismatic intermediate relative to an *excited* ($t_{2g}{}^2e_g{}^1$) octahedral system. Therefore there is some theoretical justification to presume that an excited state of a d^3 system may lead to racemization by a "twist" mechanism.

The photoracemization of $Cr(en)_3^{3+}$ has been studied in order to test this possibility. This species is especially attractive for such a study because the "twist" mechanism can presumably be distinguished from a "bond rupture" mechanism for the process by introducing an efficient trap for the one-ended species $Cr(en)_2(en^*)(H_2O)^{3+}$, where en* is a monodentate ethylenediamine. This trap is H^+, which converts the pendant amine, a good entering group, into a pendant ammonium group, a very poor entering group. The results of a study on the photoracemization of $Cr(en)_3^{3+}$ are reported herein.

Experimental Section

Materials. $Cr(en)_3Cl_3 \cdot nH_2O$ was synthesized as described by Pedersen[14] and was resolved to provide pure Λ and Δ isomers.[15] Both of these isomers were used in the experiments, without any detectable difference in results. All other materials were of reagent grade and were used without further purification. All ion-exchange separations were performed on SP-Sephadex C-25 resin.

Techniques. Photolysis was performed by using a source of color temperature 5400 K, 1.5×10^8 km from the sample. The light was filtered through 16 km of ozone to remove most of the ultraviolet and then through 2.5 cm of a solution of $HCrO_4^-$ that removed photons of wavelength less than 400 nm. During photolysis the sample was cooled by an air current so that $T < 30$ °C. Photolysis times were always less than 1 h, short relative to that required for significant thermal aquation of $Cr(en)_3^{3+}$.

Photolyzed solutions were treated in the manner discussed in the Results. In all cases the final step in purification was by ion-exchange chromatography in a cold room held at 2–3 °C. Rotations were measured at 25 °C in a Perkin-Elmer polarimeter, Model 141, using the 436-nm region of the mercury arc lamp. Duplicate measurements indicated an error of about 1% is in these readings. All absorbance measurements were made on a Cary Model 14 recording spectrophotometer. Chromium analysis was by the method of Haupt.[16]

Results

When a solution of $Cr(en)_3^{3+}$ is photolyzed, the dominant products are the two isomers of $Cr(en)_2(enH)(H_2O)^{4+}$.[10] If photolysis of optically active $Cr(en)_3^{3+}$ is carried out to give a 10% yield of these photoproducts, no detectable change in the molar rotation is found for the remaining $Cr(en)_3^{3+}$. This result demands that photoracemization is inefficient compared to photoaquation; it further dictated that an unusual experimental approach had to be utilized to determine the quantum yield for photoracemization. This approach required extensive photolysis to obtain reasonable amounts of inverted material, a method to separate $Cr(en)_3^{3+}$ from large quantities of photoproducts, and a means of determining the number of photons absorbed by $Cr(en)_3^{3+}$ in the presence of photoproducts.

Solutions of optically active $Cr(en)_3^{3+}$ in 0.08 N HCl were photolyzed into the lowest lying quartet band (in some to the point where only 4% of the initial $Cr(en)_3^{3+}$ was left). Two parameters of these solutions were then measured: (1) the molar rotation of the remaining $Cr(en)_3^{3+}$ and (2) the fraction of total chromium in the form of $Cr(en)_3^{3+}, f$. To carry out these measurements we employed four different methods of separation of $Cr(en)_3^{3+}$ from the photoproducts. Direct separation in acid solution is not one of these. Under the conditions of the photolysis, a number of tripositive ions (*cis*- and *trans*-$Cr(en)_2(H_2O)_2^{3+}$, $Cr(en)(H_2O)_4^{3+}$) and several tetrapositive ions with reasonably high ion-exchange mobility are formed; separation of these from the small quantity of $Cr(en)_3^{3+}$ remaining was found to be very difficult in acid solution.

The first of the methods that was employed utilizes the observation of Mønsted and Mønsted[17] that all aquated descendants of $Cr(en)_3^{3+}$ in basic media (pH >9) exist as materials of charge less than 3. Therefore a photolyzed solution of $Cr(en)_3^{3+}$ can be loaded onto an ion-exchange column and eluted with Na^+ in an NH_3/NH_4^+ buffer; all materials are eluted more rapidly than the only tripositive ion, $Cr(en)_3^{3+}$, which can then be isolated as the only remaining band on the column. This method produces a clean separation of $Cr(en)_3^{3+}$ from the photoproducts but is potentially inaccurate because of reclosure of $Cr(en)_2(enH)(H_2O)^{4+}$ to $Cr(en)_3^{3+}$ *on* the column bed[17,18] when the column is made basic. Although this latter reaction is not too efficient (and hence will not influence f to any great extent), the fact that active *cis*-$Cr(en)_2(enH)(H_2O)^{4+}$ racemizes rapidly in base ($k \approx 6 \times 10^{-4}\ s^{-1}$ at 25 °C and pH 10.5)[10] implies that any racemization of *cis*-$Cr(en)_2(en^*)(OH)^{2+}$ would lead upon reclosure to a higher yield of racemized $Cr(en)_3^{3+}$. For minimization of this effect, which appears more efficient on the column than in heterogeneous solution,[18,19] the solution was made basic before loading on the column and the elutions carried out at low temperature.

The second method of separation employed was also designed to convert all photoproducts to ions of charge lower than 3. A photolyzed solution of $Cr(en)_3^{3+}$ was treated with sufficient sodium oxalate to make the medium about 0.1 M in total oxalate, buffered in the $HC_2O_4^-/C_2O_4^{2-}$ region. This

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(18) The reclosure to form $Cr(en)_3^{3+}$ is "catalyzed" by the column as comparison of the data in ref 17 and 19 demonstrates. We have attempted to measure the rate of the process on the column without much success. The production of $Cr(en)_3^{3+}$ seems to undergo a "burst" during the conversion of the column from pH 2.5 to 10.5. We have no explanation for this behavior.

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solution was heated at 45 °C for 10 min and then was cooled to ice temperature and loaded on an ion-exchange column. The majority of the Cr(III) in the sample was isolated as $Cr(en)(ox)_2^-$ or $Cr(en)_2(ox)^+$.[20] After elution of these materials a band of $Cr(en)_3^{3+}$ mixed with a reddish material remained on the column. Elution under basic conditions moved the reddish material, composed of two separate unidentified bands, away from $Cr(en)_3^{3+}$. (On the basis of a comparison of the values of its λ_{max} with those of $Cr(NH_3)_5(oxH)^{2+}$,[21] the presumption that $Cr(en)_2(enH)(oxH)^{3+}$ is the material responsible for the second tripositive component in acid solution is reasonable.) $Cr(en)_3^{3+}$ left on the column could then be eluted and analyzed.

The third technique used featured precipitation of the majority of the $Cr(en)_3^{3+}$. After photolysis of a solution of $Cr(en)_3^{3+}$, it was cooled to 0 °C, and a solution of Hg(II) in Br^- media was added. This causes precipitation of $[Cr(en)_3]_2(HgBr_4)_3$, which was removed from the other materials by filtration. After having been washed, the solid was redissolved in a large quantity of 0.1 N HCl, and the spectrum and optical rotation were recorded. The former establishes that only $Cr(en)_3^{3+}$ is precipitated, and the latter then measures the extent of racemization of this material. The filtrate from this solution was passed down a cation-exchange column at pH 2.5, washed with dilute NaCl to elute any mercuric species, and eluted with Na^+ in a NH_3/NH_4^+ buffered solution. The optical rotation and spectrum were again obtained as for the precipitate. With combination of the separate analyses of the two samples, the overall f value and the weighted average value of the molar rotation were determined. Although this method does not eliminate the possibility of reclosure, it does make experiments with low conversions (large f values) considerably easier to handle by reducing the overloading of the ion-exchange column.

The final method used unambiguously eliminates the problem of reclosure reactions but because of the additional steps offers greater possibility for experimental error. A photolyzed solution was eluted in acid solution (pH 2.5), slowly, to separate the various ions on the basis of charge; three broad and multicolored bands are found, corresponding to 3+, 4+, and 5+ charges. It is only within the band containing tetrapositive ions that molecules capable of reclosure to $Cr(en)_3^{3+}$, $Cr(en)_2(H_2O)(enH)^{4+}$, exist. The tripositive ion band was collected, and the solution was made basic and then subjected again to ion-exchange chromatography. In this tripositive ion band are the various isomers of $Cr(en)_2(H_2O)_2^{3+}$ and $Cr(en)(H_2O)_4^{3+}$, which are converted under basic conditions to ions of lower charge whereas the $Cr(en)_3^{3+}$ in the band remains tripositive. Separation is therefore straightforward. Separate experiments established that $Cr(en)_3^{3+}$ did not racemize on the column under any conditions used in any of the separation techniques.

The results of 31 experiments are shown in Figure 1 where the data are plotted as ln ($[R]/[R_0]$) vs. ln f, where $[R]$ is the observed molar rotation of $Cr(en)_3^{3+}$ recovered from a sample of initial rotation $[R_0]$. The data points show some scatter, but it must be noted that the observed change in rotation is slight; note especially the error bar on the graph at the left margin of the plot resulting from a 1% error in measurement of the molar rotation.

In addition to the experiments described above, two experiments were performed at higher $[H^+]$ in order to determine whether an $[H^+]$ dependence on the degree of racemization existed. Those experiments indicated, within the errors of measurement, no decrease in $[R]/[R_0]$ up to $[H^+]$ = 1.0 M.

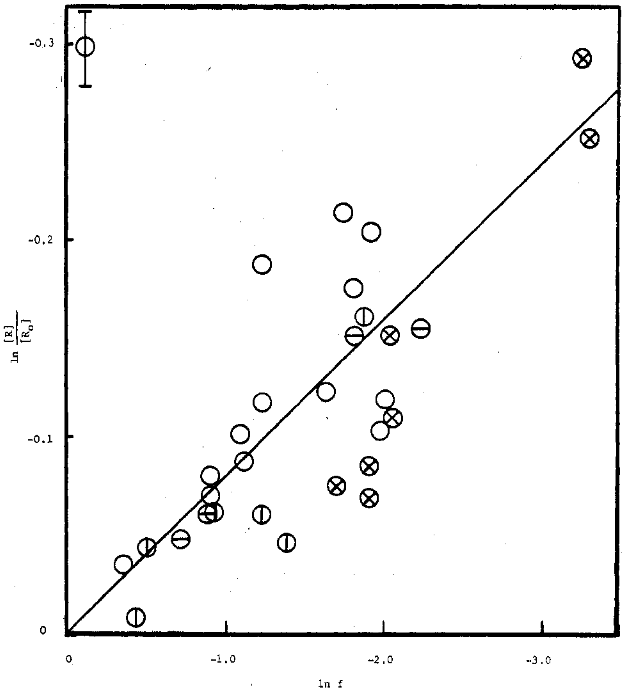
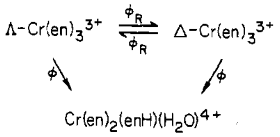


Figure 1. Plot of ln ($[R]/[R_0]$) vs. ln f for photoracemization of $Cr(en)_3^{3+}$ in dilute acid. The point at ln ($[R]/[R_0]$) = −0.3 and ln f = −0.1 is not a data point. It gives the error bars caused by manufacturers' stated error in reading of rotation; all points should have error bars of this size. Open circles are from experiments using precipitation followed by column separation. Experiments in which the solution was made basic prior to loading on the column are represented by circles with horizontal bars. Those in which two columns were used are represented by circles with vertical bars. For solutions treated with oxalate ion, the data points are shown with an "×" in the circle.

Scheme I



Discussion

In the previous section one of the two problems inherent in the measurement of racemization of $Cr(en)_3^{3+}$ was discussed: the separation problem. The second problem in determining a quantum yield for racemization is to obtain a means of counting the photons absorbed by $Cr(en)_3^{3+}$, especially when, during the course of carrying the reaction to 96% completion, other reagents absorb the majority of the incident photons. To do this, the known quantum yield for photoaquation of $Cr(en)_3^{3+}$ has been utilized; reference to Scheme I is instructive.

The appropriate differential equation governing the time dependence of Λ-$Cr(en)_3^{3+}$ is given by eq 1, where $[\Lambda]$ and

$$\frac{-d[\Lambda]}{dt} = [(\phi + \phi_R)[\Lambda] - \phi_R[\Delta]]\frac{\epsilon_\Lambda I_0}{\sigma}(1-10^{-\sigma}) \qquad (1)$$

$[\Delta]$ are used for the concentration of the respective enantiomers of $Cr(en)_3^{3+}$, [J] is the concentration of any colored species, and the ϵ_J's are the extinction coefficients of any colored species.[22] In this equation, $\sigma = \sum_J \epsilon_J[J]$. (It is to be noted that for broad-band irradiation this equation needs to be integrated over all wavelengths of irradiation; since in subsequent steps, on the assumption that ϕ and ϕ_R are

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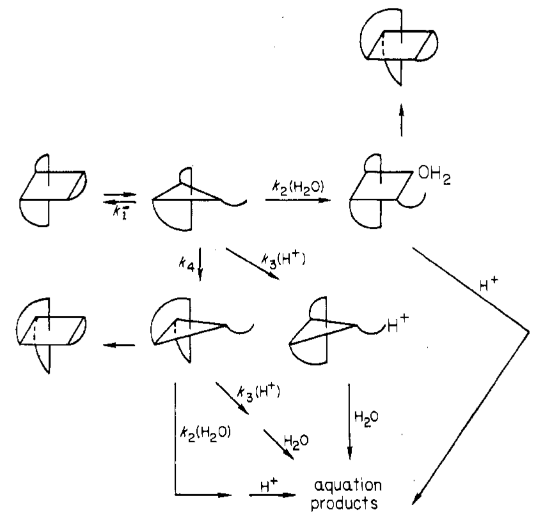
[21] T. Ramasami, R. K. Wharton, and A. G. Sykes, *Inorg. Chem.*, **14**, 359 (1975).

[22] Note that $\epsilon_\Lambda = \epsilon_\Delta$ for unpolarized light.

Scheme II



wavelength independent, this integration cancels, it will be neglected in the derivation.) The time dependence of the concentration of $Cr(en)_3^{3+}$ in both forms is given by eq 2.

$$\frac{-d([\Lambda] + [\Delta])}{dt} = (\phi[\Lambda] + \phi[\Delta])\frac{\epsilon_\Lambda I_0}{\sigma}(1-10^{-\sigma}) \qquad (2)$$

Equations 1 and 2 can be combined by using the chain rule to give eq 3, which, when integrated as a linear first-order equation under the limits that at $t = 0$, all chromium is in the form of one isomer, e.g., Λ-$Cr(en)_3^{3+}$, yields eq 4, where f is

$$\frac{d[\Lambda]}{d([\Lambda] + [\Delta])} = \frac{\phi + 2\phi_R}{\phi}\frac{[\Lambda]}{[\Lambda] + [\Delta]} - \frac{\phi_R}{\phi} \qquad (3)$$

$$\frac{[\Lambda]}{[\Lambda] + [\Delta]} = \frac{1}{2}(1 + f^{2\phi_R/\phi}) \qquad (4)$$

$([\Lambda] + [\Delta])/[\Lambda]_0$. This equation can be rewritten if the equality in eq 5 is used. The final result is eq 6. This is the

$$\frac{2[\Lambda]}{[\Lambda] + [\Delta]} - 1 = \frac{[R]}{[R_0]} \qquad (5)$$

$$\ln\frac{[R]}{[R_0]} = \frac{2\phi_R}{\phi}\ln f \qquad (6)$$

form in which the results are displayed in Figure 1. The slope of that plot is $2\phi_R/\phi$ from which, on the assumption that $\phi = 0.37$,[8,10] ϕ_R is 0.015.

There are two mechanisms which can cause racemization of $Cr(en)_3^{3+}$: (1) the "twist" mechanism, in which a pseudorotation of T_{2u} symmetry (O_h assumption) causes racemization without lowering the coordination number, and (2) the "bond rupture" mechanism, in which a bond breaks and racemization occurs either before or during re-formation of the bond. The second mechanism has two subsets; these are best described with reference to Scheme II. The first involves attack by water in a process (k_2) that is effective compared to the other pathways for reactions of the five-coordinate species (k_I, k_3, k_4). In this case, racemization occurs as the chelate recloses to expel water. The second involves successful competition with the other paths by the k_4 pathway for destruction of the five-coordinate species; racemization occurs within the five-coordinate species.

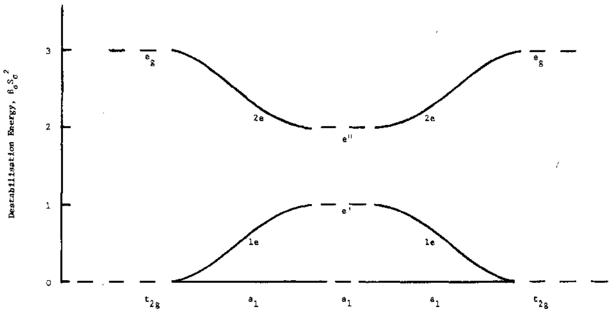


Figure 2. Pictorial representation of the change in one-electron energy levels upon a twist of an octahedral complex about the C_3 axis.

Consider the twist mechanism, and assume that reaction occurs only from the quartet. Although it is clear that the photosubstitution reaction of $Cr(en)_3^{3+}$ can occur "from or through" the doublet, there is no compelling argument for the former.[10,24,25] Because of the d-orbital argument to be given below, reaction only from the quartet is a plausible assumption. Further, electron–electron repulsion, ligand–ligand repulsion, and configuration interaction within the multielectronic states will be ignored in the simple one-electron orbital model presented. (A more complete treatment of a d^6 system has been given by Purcell.[26]) The resulting qualitative picture of a $T_{2u}(S_6)$ rotation leading to photoracemization can be had by inspection of the one-electron energy levels for a d^3-octahedral system quantized along the C_3 axis.[23] As twisting about C_3 begins, the t_{2g} set is split to a_1 + e in D_3 symmetry, and the e_g set goes to e—see Figure 2; extensive mixing between the e sets occurs as the $e(t_{2g})$ orbitals lose d_{xz} and d_{yz} character and obtain $d_{x^2-y^2}$ and d_{xy} character from the $e(e_g)$ orbitals. In the angular overlap approach used by Burdett,[13] motion toward the trigonal-prismatic structure from the $t_{2g}^3(a_1^1(1e)^2$ in $D_3)$ ground state of Cr(III) will not be allowed because of a d-electron energy barrier—consistent with lack of efficient thermal racemization processes—but from the $t_{2g}^2e_g^1$ excited quartet, net stabilization can occur if the $a_1^1(1e)^1(2e)^1$ state at near-octahedral geometry (stability of $9\beta_\sigma S_\sigma^2$) "jumps" at some point along the twisting motion coordinate to give the $(a_1)^1(e')^2$ state of the trigonal prism (stability of $10\beta_\sigma S_\sigma^2$). The momentum of this process will tend to carry the molecule through the trigonal-prismatic intermediate to the optically inverted $Cr(en)_3^{3+}$; Figure 2 illustrates this.

It is to be noted that in a tris-chelated species such as $Cr(en)_3^{3+}$, three of the four C_3 axes of the idealized octahedral symmetry used above disappear. If one of these three axes is chosen for the twist, the model has C_{2v} symmetry rather than D_3. This causes a further splitting of the 1e and 2e levels, a splitting that could lead to stability of the rhombic intermediate. Purcell[26] has done detailed calculations on $Fe(phen)_3^{2+}$, and his work should be consulted. The analysis presented above is not meant to choose between twisting about the C_3 or pseudo-C_3 axes but merely is meant to illustrate how from a d-electron model the excited state has the potential for twist.

With regard to the second mechanism (Scheme II), it is to be noted that, if reclosure to give racemization occurs after H_2O attacks the five-coordinate species ($k_2 > k_I$, $k_3(H^+)$, k_4), then since racemization is not the dominant process, an increase in $[H^+]$ will lower ϕ_R. This is not observed, and therefore racemization must occur by the k_4 path if the bond rupture mechanism pertains. This requires that k_4 be competitive with $k_3(H^+)$ and k_2. Since $k_3(H^+)$ is diffusion controlled, about 10^{11} s^{-1}, the pseudorotation with the one-ended ethylenediamine as pivot point, a rotation that gives racemization, must be comparable.

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(25) A. D. Kirk, private communication.

(26) K. F. Purcell, *J. Am. Chem. Soc.*, **101**, 5147 (1979).

Table I. Quantum Yield for Cr(III) Complexes

complex	ϕ_R (λ^a)	medium	ref
$Cr(ox)_3^{3-}$	0.045 (570)^b	aqueous	11
$Cr(phen)_3^{3+}$	0.018 (458)^c	aqueous	12
$Cr(aa)_3{}^d$	0.005 (546)	chlorobenzene	27
$Cr(en)_3^{3+}$	0.015 (br)^e	aqueous	this work

[a] Wavelength in nm. [b] This is the value consistent with the definition of ϕ_R in Scheme I. [c] ϕ_R is somewhat sensitive to vibronic level populated. [d] aa^- is 2,4-pentanedionato anion. [e] Broad band.

There are no definitive experimental data to discriminate between the two mechanisms noted above. There are, however, data that suggest that the twist mechanism might be preferable at this time. In Table I[27] are listed the quantum yields for isomerization of various Cr(III) complexes of octahedral microsymmetry. Note that the values are very similar; this is especially true if only the three systems studied in water are considered. If the bond-rupture mechanism were to hold, k_T would be expected to be an important parameter in determining ϕ_R. For the widely differing ligands listed in Table I, differing in rigidity, conjugation, and chain length, it would be expected that k_T would differ greatly from one to another. This change is not reflected insofar as ϕ_R depends on k_T. On the other hand, the constancy of ϕ_R can at least be rationalized by the "twist" mechanism if it is assumed that fractionation toward the S_6 pathway is determined at the vibronic level populated by absorption and that this fractionation is relatively independent of the nature of the coordination shell.

Registry No. Λ-$Cr(en)_3^{3+}$, 41509-53-9; Δ-$Cr(en)_3^{3+}$, 51002-41-6; $Cr(en)_3^{3+}$, 15276-13-8.

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2*n* Framework Electron Clusters: Preparation and Relative Thermal Stabilities of the Polyhedral Boron Subbromides

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Discharge of BBr_3 in the presence of mercury yields B_2Br_4 at rates of 200–300 mg/h. The decomposition of B_2Br_4 results in the formation of BBr_3 and a number of boron subbromides, B_nBr_n (n = 7–10), which are formed in combined yields of about 50% at ambient temperature. Under different conditions B_9Br_9 is isolated in 48% yield from the decomposition of B_2Br_4. The formation and subsequent decomposition of a paramagnetic species is observed by ESR. The boron NMR resonances of B_9Br_9 and $B_{10}Br_{10}$ in pentane solution are shown to be singlets at −60 °C, and the chemical shifts of the subhalides are found to be about 60–80 ppm deshielded relative to their electron-rich analogues which contain $2n + 2$ framework electrons. The nine-membered cage, B_9Br_9, is more stable both thermally and to air than the ten-membered cage, $B_{10}Br_{10}$. Preliminary investigations indicate that ligand substitutions proceed at ambient temperatures in the reaction of B_9Br_9 with $Pb(CH_3)_4$ although cage reduction also appears to occur.

Introduction

In many cluster compounds the geometric shape of the framework atoms is dictated by the number of electrons delocalized within the framework orbitals.[1] Polyhedral species with $2n + 2$ framework electrons frequently have deltahedral (closo) geometries while frameworks with only $2n$ electrons, e.g., $Os_7(CO)_{21}$ and $(C_5H_5)_3Co_3B_4H_4$, are often found as capped deltahedra.[2,3] There are a few exceptions, most notably Bi_9^{5+} and a growing number of metal-rich metalloboranes, like $(C_5H_5)_4Co_4B_4H_4$ and $(C_5H_5)_4Ni_4B_4H_4$[4,5] but typically main-group-containing clusters are found to have the structures expected on the basis of Wade's rules.

The polyhedral boron subhalides, which are compounds of the general formula B_nX_n (X = Cl, Br), however, appear to be an entire class of molecules that do not adopt the structures predicted by the framework count method. Each of these halides has only $2n$ framework electrons, yet the structures observed for, e.g., B_8Cl_8 (dodecahedral)[6] or B_9Cl_9 (tricapped trigonal prism),[7] are the structures usually associated with frameworks containing two additional electrons. Whether this apparent violation of the framework electron count–structural correlation by the boron subhalides results from ligand–framework interactions, which are ignored in the FEC method, or arises from other sources is, as yet, unknown.

The boron subhalides are also of interest because so little is known about them. The thermal decomposition of B_2Cl_4 has been variously reported to yield $B_{12}C_{11}$, $B_{11}Cl_{11}$, or, after recrystallization from (or possibly reaction with) BCl_3, B_8Cl_8 as the major polyhedral product.[6,8,9] The first named compound, $B_{12}Cl_{11}$, was reported to be paramagnetic although the adventitious addition of water to the sample was later held to be responsible for the formation of the free-radical species observed.[9] Irrespective of the source of the radical, however, it was reported to be extremely stable, persisting for years at ambient temperatures.[8,9] The decomposition of B_2Br_4 has been less studied although a mass spectral examination did indicate that, in addition to BBr_3, the compounds B_nBr_n (n = 7–10) were formed, but no indication of the amounts of these clusters produced in the reaction is available.[10]

In order to learn more of the boron subhalides and of the consequences of "electron hyperdeficiency", we have begun to study the formation, stability, and reactivity of these compounds. With the expectation that they might prove to be

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