n-π* Cotton effect in these diketopiperazines, which is realized, and (b) that the absolute magnitude of this Cotton effect increases with decreasing solvent dielectric constant. The latter prediction is not well realized. The discrepancy here may be possibly due to (i) association in dioxane and acetonitrile solutions, and (ii) small but finite mixing of the n-π* and π-π* transitions because of deviations from planarity of the ring. However, it is worth noting that since the potential terms that generate the n-π* Cotton effect are of the quadrupole type,[7] this partial rotation would show a sharper dependence on the distance of the perturbing group than on the solvent dielectric constant.

The results reported here suggest that neither the n-π* Cotton effect nor the exciton split of the degenerate π-π* transition of the peptide chromophore is unique to the α-helix, but can be achieved in cases where the proper molecular rigidity,[1] orientation of the vicinal groups, and also proper geometric disposition of identical peptide chromophores[8,9] are realized. Thus, the negative Cotton effect at 2250 A that Ruttenberg, *et al.*,[10] have observed in cyclic tyrocidine B and gramicidin S-A might be due to the activation of the Cotton effect of the n-π* transition by molecular rigidity imposed by cyclization.

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Received March 15, 1966

The Chromium(II)-Catalyzed Aquation of the Iodopentaaquochromium(III) Ion[1]

Sir:

Most studies of Cr^{2+}-CrX^{2+} (X^- = F^-, Cl^-, Br^-, N_3^-, $-NCS^-$, $-SCN^-$) exchange reactions are directed toward the elucidation of the role of the bridging ligand X^- in the electron-transfer process.[2-6] Such studies are usually conducted at high acid and low chromium(II) concentrations. Under these conditions, with the exception of the chromium(II)-catalyzed isomerization of $CrSCN^{2+}$, no net reaction is detected, and the rates of exchange are independent of $[H^+]$ in the concentration range studied.[3] A path inverse in $[H^+]$ is featured in the Cr^{2+}-$CrSCN^{2+}$ reaction,[6] but this path does *not* result in loss of thiocyanate from the coordination sphere of chromium(III).

In contrast with these observations, we have found that chromium(II) catalyzes the aquation of halogenopentaaquochromium(III) complexes *via* a path inversely proportional to $[H^+]$.

$$CrX^{2+} + Cr^{2+} = Cr^{3+} + X^- + Cr^{2+} \quad (X^- = Cl^-, Br^-, I^-) \qquad (1)$$

By using low $[H^+]$ and high $[Cr^{2+}]$, the reactions represented by eq 1 can be detected readily. The catalytic effect of chromium(II) is quite striking in the case of CrI^{2+},[7,8] and consequently we chose this system to provide a clear illustration of the lability of acidopentaaquochromium(III) complexes in the presence of chromium(II). In addition, kinetic studies of the CrI^{2+}-Cr^{2+} reaction are of special significance in view of the current interest in the reactions of CrI^{2+}.[9-13]

The disappearance of CrI^{2+} was followed spectrophotometrically at 475 or 306 mμ. Two sources of CrI^{2+} were used. In the majority of the experiments, CrI^{2+} was generated *in situ* by the reaction of *excess* chromium(II) with iodine[9,14] (which in turn was generated by the reaction of iodate with a sight excess of iodide). Following the rapid Cr^{2+}-I_2 reaction[15] ($k > 10^3\ M^{-1}\ sec^{-1}$), the slower chromium(II)-catalyzed aquation of CrI^{2+} was observed. Some experiments were carried out with CrI^{2+} prepared by the Cr^{2+}-I_2 reaction and purified by ion-exchange chromatography.[11] The kinetic measurements, summarized in Table I, were treated on the basis of the rate law

$$\frac{-d \ln [CrI^{2+}]}{dt} = k' = k_1 + \frac{k_2}{[H^+]} + \frac{k_3[Cr^{2+}]}{[H^+]} \qquad (2)$$

Values of the rate coefficient k_3 (*cf.* column 3 of Table I) were calculated from the observed pseudo-first-order rate coefficients k' using the known[11] values of k_1 and k_2 (the rate coefficients for spontaneous aquation of CrI^{2+} *via* $[H^+]$-independent and $1/[H^+]$-dependent paths, respectively). Under the experimental conditions used, the contribution of the spontaneous aquation (k_1 and k_2 paths) of CrI^{2+} to its over-all disappearance was less than 10% in all experiments. Although the values of k_3 scatter considerably, they remain reasonably constant when $[Cr^{2+}]$, $[H^+]$, and $[CrI^{2+}]$ are varied by factors of ∼10, ∼10, and ∼60, respectively, and we conclude that eq 2 provides an adequate description of the kinetics of the CrI^{2+}-Cr^{2+} system. It must be noted, however, that our data do not rule out an additional path of the form $k_4[CrI^{2+}]\cdot[Cr^{2+}]$. The present results indicate that $0 \leqslant k_4 < 1 \times 10^{-2}\ M^{-1}\ sec^{-1}$. Experiments in progress at higher

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[8] It is conceivable that chromium(II) is the catalytic impurity suggested by Swaddle and King[11] to explain the higher rates of aquation of CrI^{2+} observed by Espenson.[9] For example, the half-life for disappearance of CrI^{2+} at $[H^+] = 0.200\ M$ and 25° measured by Espenson[9] is 2.41×10^3 sec, to be compared with the calculated[7] value of 2.71×10^3 sec. If the difference between these values is ascribed to the catalytic effect of chromium(II), the necessary concentration of the catalyst is $3.0 \times 10^{-4}\ M$. This value may be sufficiently small to be attributed to slight stoichiometric inequalities in the Cr^{2+}-I_2 reaction used to generate CrI^{2+}.[9]

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[15] The reaction of $\sim 1 \times 10^{-4}\ M\ I_2$ with $\sim 5 \times 10^{-5}\ M\ Cr^{2+}$ (25°, $[H^+] = 1.0\ M$) is complete within 20 sec.

$[H^+]$(with $\Sigma[ClO_4^-] = 2.0\ M$) should reveal the presence or absence of such a path.

Table I. Kinetics of the Chromium(II)-Catalyzed Aquation of CrI^{2+} (25°, $\Sigma[ClO_4^-] = 1.0\ M$)[a]

$[H^+]$, M[b]	$[Cr^{2+}]$, M[c]	10^2k_3, sec^{-1} [d]
0.0483	0.0209	2.2
0.0715	0.0452	2.2
0.102	0.0314	2.0[e,f]
0.125	0.0452	2.2
0.125	0.0574	2.1[f]
0.130	0.0498	2.5
0.131	0.0502	2.1[e]
0.194	0.0209	2.4
0.194	0.0896	2.5[f]
0.194	0.117	2.0
0.194	0.200	2.2
0.197	0.0896	2.1[e,f]
0.500	0.123	2.1
0.502	0.0896	2.6[e,f]
		Av 2.2
0.0715	0.0452	0.86[g]
0.194	0.200	0.83[g]
0.500	0.162	0.84[g]

[a] Measurements at 475 mμ with CrI^{2+} ($3.5–5.0 \times 10^{-3}\ M$) prepared *in situ* by the reaction of iodine with excess chromium(II), except where noted. $\Sigma[ClO_4^-]$ maintained with $NaClO_4$. [b] Calculated from the $HClO_4$ added and the $HClO_4$ in the Cr(II) solution after allowing for the H^+ consumed in the IO_3^-–I^- reaction, except for measurements with purified CrI^{2+}. [c] Calculated as the difference between Cr(II) added and Cr(II) consumed in the reaction with I_2, except for measurements with purified CrI^{2+}. [d] Defined by the rate law $k_3[CrI^{2+}][Cr^{2+}]/[H^+]$. [e] Measurements at 306 mμ with $[CrI^{2+}] = 0.8–1.2 \times 10^{-4}\ M$. [f] CrI^{2+} purified by ion exchange. [g] Measurements at 15°.

The order of reactivity for the chromium(II)-catalyzed aquations of halogenopentaaquochromium(III) complexes is I^- ($k_3 = 2.2 \times 10^{-2}\ sec^{-1}$) > Br^- ($k_3 \sim 2 \times 10^{-3}\ sec^{-1}$) > Cl^- ($k_3 \sim 4 \times 10^{-4}\ sec^{-1}$). Undoubtedly, these reactions involve electron transfer from Cr(II) to Cr(III) by paths that do *not* make use of halide-bridged transition states. Therefore, it is noteworthy that the same order of reactivity applies to the spontaneous aquations of CrX^{2+} (for both $[H^+]$-dependent and $[H^+]$-independent paths[11]) and to the CrX^{2+}–Cr^{2+} exchange reactions that proceed *via* a halide-bridged transition state.[8] This correlation suggests that the same factors may be important in determining the order of the ligands in the three classes of reactions.

It is appropriate to compare the results for the CrI^{2+}–Cr^{2+} system with those for the related studies with $CrNH_3^{3+}$–Cr^{2+} [16] and $FeCl^{2+}$–Fe^{2+}.[17] The chromium(II)-catalyzed aquations of CrI^{2+} and $CrNH_3^{3+}$ [16] proceed predominantly *via* inverse acid paths, whereas only an acid-independent path was detected in the iron(II)-catalyzed aquation of $FeCl^{2+}$.[17,18] Moreover, the appreciable difference in rates between CrI^{2+} ($k_3 = 2.2 \times 10^{-2}\ sec^{-1}$) and $CrNH_3^{3+}$ ($k_3 = 5.92 \times 10^{-5}\ sec^{-1}$ [16]) suggests that substantial nonbridging ligand effects[6,19] are operative in these electron-transfer reactions.

Additional studies with CrI^{2+}, $CrBr^{2+}$, and $CrCl^{2+}$ as well as with other acidopentaaquochromium(III) complexes, and a discussion of the mechanism of these chromium(II)-catalyzed aquations, will be reported elsewhere.

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Received May 16, 1966

The Electronic Structures of Bis(β-ketoenolato)copper(II) Complexes

Sir:

The bis(β-ketoenolato)copper(II) complexes, as typified by the acetylacetonate, $Cu(acac)_2$, merit special interest because they occupy a pivotal position at the intersection of two important classes of complexes, namely, square complexes and β-ketoenolato complexes, both of which have been extensively studied in recent years.[1] Indeed the intimately related subjects of the order of "d" orbitals and the esr, the visible, and the ultraviolet spectra of the one compound $Cu(acac)_2$ have been the subject of a considerable number of publications.[2–12] However, despite these extensive efforts, the picture has remained obscure in several fundamental respects. Among the chief reasons for this are the unfortunate facts that the visible ("d–d") spectrum of $Cu(AcAc)_2$ is not well resolved in isotropic media[2] and the alignment of the molecules in the crystalline compound is such as to thwart the effort to obtain complete polarization information.[6]

In view of these circumstances we undertook the study of a closely related complex, $Cu(DPM)_2$,[13] in which the substituents on the chelate rings are *t*-butyl groups instead of methyl groups. The choice of this compound was dictated by three considerations: (1) its electronic structure should not differ in any essential way from its frustrating prototype, $Cu(acac)_2$; (2) its solution spectra show relatively good resolution and its crystal structure[14] is such that the molecules have an orientation which is exceptionally favorable for the measurement of polarizations; (3) the diamagnetic compound $Ni(DPM)_2$ is isomorphous[14] and thus

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