(410 mμ), 21.2 (577 mμ)), and to that of the acetato complex, $(H_2O)_5CrOAc^{2+}$ (ϵ_{max} 20.7 (406 mμ), 21.6 (568 mμ)).[3]　Apparently, then, the N–Cr bond does not survive, but the N-coordinated Cr(III) complex is rapidly re-equilibrated, possibly by Cr(II) catalysis, to the more stable carboxylato-coordinated complex.

The much higher absorbance of the product derived from reduction of the 2-carboxylato complex (ϵ_{max} 50.8 (406 mμ), 32.8 (553 mμ)) indicates that here the product is chelated and thus features a Cr(III)–N bond.　Because Cr is bound both to oxygen and nitrogen, the identity of the product does not identify the atom through which electron transfer has occurred.　The very high rate of reduction, i.e., about one million times that associated with the pentaamminemalonato complex (which also forms a chelated product) indicates transfer through nitrogen.

Reductions of the complexes of pyridine-2,5-dicarboxylic and 2,6-dicarboxylic acids, even in 3 M HClO$_4$, are immeasurably fast under our conditions.　Almost certainly, these proceed predominantly by the basic path.　Our lower limits for the rate constants fall so much below the values for the 2- and 4-monocarboxylato complexes because the dicarboxylato complexes are much the weaker bases.　Both complexes appear to yield chelated chromium products (ϵ_{max} for the 2,5-derivative: 40.9 (403 mμ), 29.2 (562 mμ); ϵ_{max} for the 2,6-derivative: 44 (428 mμ), 102 (557 mμ)).　It is likely that the 2,6-derivative is reduced in the same manner as the 2-carboxylate complex, but another route must be considered for the 2,5-complex.　The nonprotonated form of the 2,5-complex is twice as strongly basic as the corresponding form of the 2,6-complex (pK_A values of 3.80 and 3.45, respectively), suggesting that the acid-strengthening Co^{3+} ion is coordinated to the 5-, rather than the 2-, carboxyl group.　Since the coordinated and noncoordinated carboxy groups lie para to each other, remote attack, as has been demonstrated for reduction of the terephthalato complex in this series,[1] may occur, but in this case it is facilitated by chelation to nitrogen.

Remote attack, but not chelation, is possible also in reduction of the N-methylated 2,5-dicarboxylato derivative, and the specific rate for this complex is significantly greater than for reductions of the other N-methylated complexes.　It is, however, only about one tenth as rapid as reduction of the terephthalato complex, probably because the α-carboxyl is pushed out of the plane of the ring by interference with the N-methyl group, thus diminishing conjugative effects between the two carboxyls.

The specific rates for reduction of the N-methylated and the protonated 4-carboxylato derivative[4] lie well above those for the corresponding 2- and 3-carboxylato species, and also above those for the large majority of ring-substituted pentaamminebenzoato complexes which undergo reduction by adjacent attack at specific rates clustering between 0.09 and 0.25 l. mole^{-1} sec.$^{-1}$.　It is possible that this effect is associated with transitory reduction of the pyridine ring, forming a radical-like intermediate.[5]　In our experience, the ring in the pyridine-4-carboxylato system is more easily reduced than in the 2- or 3-carboxylato systems.

(3) R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, J. Am. Chem. Soc., 80, 4469 (1958).

(4) Dr. R. T. M. Fraser (private communication) reports specific rates for these reductions (0.2 M HClO₄, μ = 1) as 1.2 (methylated) and 0.95 (non-methylated).　Since, in our experience, raising μ from 1.0 to 3.0 accelerates reactions of this sort by about 15%, his values are in reasonable agreement with ours.

(5) N-Ethyl-4-carbethoxypyridinyl, a stable free radical related to our N-substituted-4-carboxypyridine complexes, has been isolated:　E. M. Kosower and E. J. Poziomek, J. Am. Chem. Soc., 85, 2035 (1963).

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Radical Anions of Adamantane and Hexamethylenetetramine[1]

Sir:

The prediction and observation of the radical anion of the highly strained hydrocarbon, cyclopropane, has recently been reported.[2]　We now wish to report the observation of the radical anions of two bicyclic, strain-free systems, adamantane and hexamethylenetetramine.　Adamantane in tetrahydrofuran–dimethoxyethane (2:1) containing sodium–potassium alloy[2,3] at $-150°$ affords an electron paramagnetic resonance spectrum[4] consisting of five broad lines of approximately binomial intensity with a line separation $a_H = 3.9$ oersteds and a g value of 2.0029.　The five-line spectrum is ascribed to principal interaction of the electron with the four equivalent bridgehead protons.　This pattern seems reasonable if one assumes that the odd electron is "located" inside the molecular cavity of adamantane.　The methine carbon–hydrogen bonds are oriented normal to the molecular sphere and are in best position for exchange interactions involving the back side of the sp^3 hybrid orbitals.　The methylene carbon–hydrogen bonds, on the other hand, are oriented nearly tangential to the molecular sphere and might be expected to be in a less favorable position for exchange interactions.　Support for this interpretation is found in the e.p.r. spectrum of the radical anion of hexamethylenetetramine (1,3,5,7-tetraazaadamantane), nine broadened lines ($a_N = 4.2$ oersteds, g value of 2.003) that approximately fit the intensity ratio of 1:4:10:16:19:16:10:4:1, expected for interaction of the electron with four equivalent nitrogen nuclei.

The significance of these results to questions of bonding and transmission of electrical effects[5] in these and related systems are under investigation.

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(1) This work was supported under contract No. AT(30-1)-905 with the Atomic Energy Commission.　Reproduction is permitted for any purpose of the United States Government.

(2) K. W. Bowers and F. D. Greene, J. Am. Chem. Soc., 85, 2331 (1963).

(3) J. R. Bolton, Mol. Phys., 6, 219 (1963).

(4) A Varian Associates V-4500 spectrometer with 100-kc. modulation was used for this work.

(5) E.g., see J. D. Roberts and W. T. Moreland, Jr., J. Am. Chem. Soc., 75, 2167 (1953).

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