the first member of a new class of diterpenes, and the gibberellins is immediately obvious; *i.e.*, an intermediate such as **11**, readily derivable from a gibberellin, could undergo facile rearrangement leading to the A_{An} skeleton with the correct absolute configuration and C–D configuration. Antheridium-inducing properties of gibberellins have indeed been previously noted, although at a much lower threshold activity, *i.e.*, 1 mg/l. for GA_3[18] and 0.3 μg/l. for A_{An}.[19,20]

[18] H. Schraudolf, *Nature* (*London*), **201**, 98 (1964).

[19] Physiological activity tests are being carried out by Dr. G. W. Keitt, Jr., Brooklyn Botanical Gardens, as well as by one of us (U. N.).

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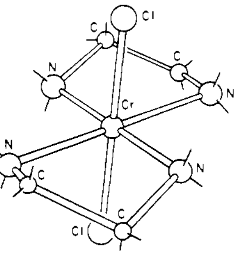
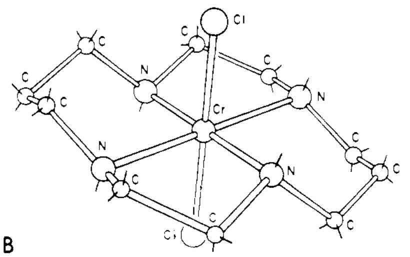
trans-Dichloro-1,4,8,11-tetraazacyclotetradecanechromium(III). A Photoinert Chromium(III)–Ammine Complex

Sir:

Some 25 Cr(III) complexes of the type MA_5X, MA_4X_2, and $M(en)_2X_2$ (X denotes a halogen, pseudohalogen, or water; A is NH_3; and en is ethylenediamine) have been investigated photochemically in various laboratories.[1–3] The general observation has been one of photosubstitution, with solvent (usually water) replacing selectively either the X or the ammine ligand with a quantum yield, ϕ, of 0.1–0.5. So consistent has been the pattern that a set of rules[4] ("Adamson's empirical rules"[2,5]) reliably predicts the course of the net photoreaction on irradiation of the L_1 (first) or L_2 (second) ligand-field band. Thus compound A, *trans*-$Cr(en)_2Cl_2^+$, is correctly predicted to show primarily chloride aquation; the observed ϕ_{Cl^-} value is 0.32–0.35.[6] Compound B, *trans*-$Cr(cyclam)Cl_2^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), should show essentially the same photochemistry as A, since the geometric and ligand-field environment is about the same. We consider it newsworthy and potentially very significant that B is in fact photoinert.



A



B

Adamson's rules are referenced to a pseudooctahedral framework of three mutually perpendicular axes, and designate the weak ligand axis as the one photolabilized; if this axis bears two different ligands, the stronger field one of the two is preferentially labilized. It has been inferred that the rules imply the stereochemical course of the photosubstitution;[2,5,7–9] this would follow *if* the octahedral framework remains rigid during the process. This inference need not be correct. If, for example, the mechanism is one of dissociation of the labilized ligand, the pentacoordinated residue need only collapse to a trigonal-bipyramidal geometry for stereospecificity to be lost on coordination of a solvent molecule. While retention of configuration may occur,[10] it now appears that stereomobility is more common.[2,5–9,11] An especially clear demonstration of stereomobility is that in the case of A the axial ligand aquates, yet the photoproduct is *cis*- rather than *trans*-$Cr(en)_2(OH_2)Cl^{2+}$;[6] there is experimental uncertainty in the $Cr(NH_3)_5X^{2+}$ series as to which ammonia is in fact replaced. It thus appears that the photoproduced reactive state is not usually stereorigid, and the present investigation was undertaken to test whether the *imposition* of such rigidity, as in B, leads to behavior differing from that of the nonrigid analog A.

Compound B was prepared as the perchlorate salt[12] and converted to the nitrate by ion exchange. We observe a spectrum showing absorption maxima at 568 nm (22) and 366 nm (37), with a shoulder at 407 nm (33) (numbers in parentheses are the extinction coefficients in M^{-1} cm^{-1}), in good agreement with the published values.[12] The chloride analysis showed 25.44% Cl (calculated, 25.16%); also, on prolonged heating, thermal aquation yielded two chlorides per chromium.

Solutions 1.1 × 10^{-3} *M* in B and acidified with nitric acid to a pH of 2.40 were irradiated at 22° either at 546 or at 408 nm, using a PEK lamp with suitable interference and blocking filters. Reineckate[13] and ferrioxalate actinometry[14] were used for the two wavelengths,

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[1] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

[2] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

[3] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, **49**, 375 (1971).

[4] A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

[5] A. D. Kirk, *J. Amer. Chem. Soc.*, **93**, 283 (1971).

[6] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, **49**, 1524 (1971).

[7] H. F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem.*, **57**, 282 (1968).

[8] M. F. Manfrin, L. Moggi, and V. Balzani, *Inorg. Chem.*, **10**, 207 (1971).

[9] P. Riccieri and H. L. Schläfer, *ibid.*, **9**, 727 (1970).

[10] E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, **91**, 1076 (1969).

[11] E. Zinato, private communication regarding $Cr(NH_3)_5X^{2+}$, where X denotes acetato or substituted acetato.

[12] J. Ferguson and M. L. Tobe, *Inorg. Chim. Acta*, **4**, 109 (1970). The cyclam ligand was prepared by G. Gokel and F. Jerome after the procedure of E. J. Bounsall and S. R. Koprich, *Can. J. Chem.*, **48**, 1481 (1970).

[13] E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, **88**, 394 (1966).

[14] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. Ser. A*, **235**, 518 (1956).

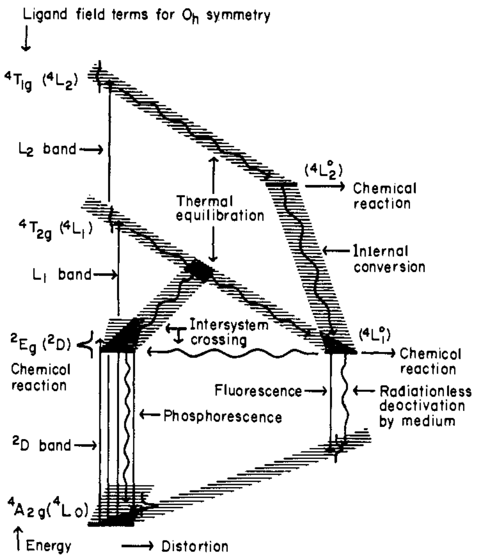

Figure 1. Energy level diagram (lowest levels) for a Cr(III) complex.

respectively. Released chloride ion was determined potentiometrically. Assuming that any Cr–N bond breaking would generate a weakly basic function, the upper limit to such bond breaking was inferred from the lack of detectable pH change on irradiation. The isomer composition of the product and the degree of isomerization of B were estimated from the spectral change on irradiation. The thermal aquation rate is negligibly slow at 22°.[15]

We find ϕ_{Cl^-} to be 6.9×10^{-4} and 7.7×10^{-4} on irradiation of the L_1 and L_2 bands, respectively, or about 400 times smaller than for A. The quantum yield for hydrogen ion uptake is $<10^{-3}$. More than 90% of the photoproduct is in the trans configuration (presumably *trans*-Cr(cyclam)(OH$_2$)Cl^{2+}); the quantum yield for *cis*-Cr(cyclam)Cl$_2^+$ is $<5 \times 10^{-4}$ at either wavelength. Preliminary results with 254-nm light are that only chloride aquation occurs, but now with a yield of about 0.2.

The photochemistry of non-O_h Cr(III) complexes appears to occur through reaction of the thermally equilibrated first excited quartet state, $^4L_1^0$,[16,17] rather than of the state immediately produced by light absorption, $^4L_1$, or the first doublet state, ^2D. A scheme of excited-state processes is shown in Figure 1.[16]

The photoinertness of B could have a photophysical explanation. Thus the radiationless deactivation $^4L_1^0 \rightarrow {}^4L_0$ might be unusually rapid; alternatively, the intersystem crossing $^4L_1 \rightarrow {}^2D \rightarrow {}^2D^0$ might be unusually efficient, with the latter state again rapidly deactivated. Preliminary observation, however, is that solid B at 77°K shows normal phosphorescence in about normal intensity;[18] there is thus no indication of unusual photophysical processes.

The second type of explanation is that the $^4L_1^0$ state is less reactive chemically in B than in A. The rigidity of the cyclam ring might have this effect in a dissociative mechanism, if collapse to a trigonal-bipyramidal intermediate were concerted with loss of the Cl$^-$ ligand. Simple dissociation to a square-pyramidal stage should be equally facile for the two compounds; in fact, the high yield at 254 nm suggests that at this wavelength the mechanism has shifted to one of a nonconcerted heterolytic bond fission. Our results are also explained if $^4L_1^0$ reacts by expanding its coordination sphere to a pentagonal-bipyramidal intermediate by addition of solvent, the unique axis being initially the weak-field one. Solvent would thus be coordinated in the plane perpendicular to this axis; loss of the appropriate ligand with rearrangement of the remaining ligands to an octahedron would yield the products observed in the various cases. A D_{5h} type of intermediate is not unreasonable. It has been pointed out that this geometry is stable relative to the first excited state in O_h on simple crystal-field stabilization grounds.[19] A mechanism of this second type not only allows explanation of stereomobility in photoaquation but now also accounts for the present observations. Compound B, of course, cannot undergo coordination expansion in the plane of the 4 ring. Investigations are continuing on both B and its cis isomer.

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[15] E. Campi, J. Ferguson, and M. L. Tobe, *Inorg. Chem.*, **9**, 1781 (1970).

[16] See J. Martin and A. W. Adamson, *Theor. Chim. Acta*, **20**, 119 (1971).

[17] S. Chen and G. B. Porter, *Chem. Phys. Lett.*, **6**, 41 (1970).

[18] P. Fleischauer, private communication.

[19] A. W. Adamson, *Pure Appl. Chem.*, **20**, 25 (1969).

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Nitrogen-Centered Free Radicals. III. Formation and Electron Spin Resonance Spectra of *N*-Alkoxy-*N*-alkylamino Free Radicals in Solution[1]

Sir:

In previous work[2] we have shown that dialkylamino free radicals are produced in sufficient quantities in solution for electron spin resonance (esr) studies by photolysis of appropriate 2-tetrazene compounds. As an alternate source of amino radicals we considered the possibility of photodecomposing solutions of *tert*-butyl peroxycarbamates (eq 1 and 2). This method appeared

$$R_2N\overset{\overset{\displaystyle O}{\|}}{C}OOC(CH_3)_3 \xrightarrow{h\nu} R_2N\cdot + CO_2 + \cdot OC(CH_3)_3 \qquad (1)$$

$$RNH\overset{\overset{\displaystyle O}{\|}}{C}OOC(CH_3)_3 \xrightarrow{h\nu} R\dot{N}H + CO_2 + \cdot OC(CH_3)_3 \qquad (2)$$

especially appealing since a variety of alkyl radicals have been observed recently by esr spectroscopy when solutions of *tert*-butyl peresters were photolyzed at reduced temperatures.[3,4]

In contrast to the results with the peresters, we wish to report that only *N*-*tert*-butoxy-*N*-alkylamino radicals were observed by esr spectroscopy when solutions of *tert*-butyl *N*-alkylperoxycarbamates were photolyzed (eq 3). There was no spectral evidence of monoalkylamino radicals. However, irradiation of solu-

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[1] Part II: W. C. Danen and T. T. Kensler, *Tetrahedron Lett.*, 2247 (1971).

[2] W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, **92**, 5235 (1970).

[3] J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3940 (1969).

[4] R. O. C. Norman, Ed., *Chem. Soc., Spec. Publ.*, No. 24, 147 (1970).