described by those authors. The spectra of the complexes in methylene chloride solution were recorded on a Bruker HFX-90 MHz spectrometer with 5- and 13-mm spinning sample tubes. The experimental method employed was to observe the phosphorus spectrum while applying a small irradiation field which perturbed the ^{183}W ($I = {}^1/_2$, abundance 14.3%) satellites. A capillary of H_3PO_4 was used for an external reference. The ligand protons were decoupled during the experiments in order to improve the signal:noise ratio of the spectra.[7] Thus the tungsten shifts are accurate to ±1 ppm and the coupling constants to ±1 Hz. Also for the tungsten shifts the difference in bulk susceptibility between samples in the two sized tubes was found to be less than 2 ppm when referred to the phosphorus-31 capillary. The tungsten shifts were calculated from our measured frequency and the reported ratio of tungsten to proton frequencies in tungsten hexafluoride and water, respectively.[1]

The tungsten chemical shifts reported in Table I exhibit a few general trends which deserve discussion. First, the tungsten resonances of these carbonyl complexes are found to higher field than those of the higher oxidation state complexes previously measured. This parallels the trend noted for the variation in chemical shift between the different oxidation state compounds of several other transition metal elements.[8] Moreover the magnitude of this effect appears to be about the same size for tungsten as for the lighter elements. Specifically, the manganese-55 resonance in solutions of $Mn(CO)_5^+$ is 2600 ppm above that of potassium permanganate solution.[9]

TABLE I

NMR DATA FOR TUNGSTEN AND PLATINUM COMPLEXES AT ROOM TEMPERATURE

Compound	δ(P),[a] ppm	J(P–M), Hz	δ(M),[b] ppm
cis-$(CO)_4W((C_4H_9)_3P)_2$	+10.0	224	+1965
trans-$(CO)_4W((C_4H_9)_3P)_2$	+2.6	270	+2021
cis-$((C_4H_9)_3P)_2PtCl_2$[c]	−1.4	3508	+4450
trans-$((C_4H_9)_3P)_2PtCl_2$	−4.9	2380	+3930

[a] δ(^{31}P) relative to 85% H_3PO_4. [b] δ(^{183}W) relative to WF_6(l) and δ(^{195}Pt) relative to H_2PtCl_6(soln). [c] Taken from ref 3.

It is also interesting to note the tungsten-183 nmr shift difference between the cis and trans isomers of the carbonyl–phosphine complex studied. Previous attempts to observe manganese[9] or cobalt[10] nmr isomer shift differences in their analogous carbonyl complexes have been unsuccessful; in view of our results this is probably because of the much larger line widths associated with the spectra of those nuclei. For purposes of comparison with the present study the platinum-195 nmr data for *cis*- and *trans*-$((C_4H_9)_3P)_2PtCl_2$[3] have been included in Table I. In that complex the platinum resonance of the trans isomer was found 520 ppm to lower field than that of the cis isomer. In fact, as mentioned, this is a general trend which has been observed for all the metal halide complexes so far studied. (The isomer shift difference was as small as 40 ppm for the compound $((CH_3)_2Se)_2PtCl_2$.[4]) However, in the present study the tungsten resonance of the trans isomer of $(CO)_4W((C_4H_9)_3P)_2$ is found to *higher* field than that of the cis isomer, opposite to that in the halide complexes.

It is perhaps surprising that the trends in the central atom chemical shifts reported in Table I appear to parallel those in the metal–phosphorus coupling constants. Thus in the platinum halide complexes the metal–phosphorus coupling is always larger in the cis isomer than in the trans isomer while just the opposite is true for the tungsten–carbonyl complexes. The trends in the coupling constant data have already been interpreted[6] as being consistent with the π-bonding model in the complexes. Whether there is a significant relation between the observed trends in the coupling constants and those in the central atom shifts might possibly be resolved by calculations. However, this study gives further evidence of the sensitivity of the metal atom shifts to the differences in chemical bonding between various types of metal complexes.

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[7] For a description of the method see T. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, **91**, 3378 (1969).

[8] T. H. Brown and P. J. Green, *Phys. Lett. A*, **31**, 148 (1970).

[9] W. J. Miles, B. B. Garrett, and R. J. Clark, *Inorg. Chem.*, **8**, 2817 (1969).

[10] E. A. C. Lucken, K. Noack, and D. F. William, *J. Chem. Soc. A*, 148 (1967).

Correspondence

Geometrical Configuration of the Product Obtained from Ammonia Photoaquation of Chloropentaamminechromium(III) Ion

Sir:

The photochemical behavior of mixed-ligand chromium(III) complexes has been extensively investigated in recent years.[1] The main features which emerge from the body of the available results are as follows: (i) different photoreactions may occur simultaneously (*e.g.*, photoaquation reactions involving different ligands); (ii) the predominant photoreaction is not necessarily the one which occurs thermally; (iii) the photochemical behavior may be spectrospecific (*i.e.*, the type of photoreaction and the quantum yield may be wavelength dependent). In order to systematize and predict the photochemical behavior of these complexes, two *empirical* rules have been given by Adamson.[2–4] They

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[1] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970.

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

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

[4] A. W. Adamson, *Coord. Chem. Rev.*, **3**, 169 (1968).

are as follows. (I) Consider the six ligands to lie at the ends of three mutually perpendicular axes: that axis having the weakest average crystal field will be the one labilized. (II) If the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates.

In the paper[2] where these rules were first proposed, it was considered that they implied stereochemical consequences. In subsequent papers,[3–5] however, Adamson claimed that isomer prediction was not contained in his rules. Thus, as a typical example of application of these rules he usually quoted the case of the $Cr(NH_3)_5X^{2+}$ complexes (X = Cl, NCS), where the dominant photoreaction mode is ammonia aquation (eq 2)

$$Cr(NH_3)_5X^{2+} + H_2O \begin{cases} \xrightarrow{h\nu} Cr(NH_3)_5H_2O^{3+} + X^- & (1) \\ \xrightarrow{h\nu} Cr(NH_3)_4(H_2O)X^{2+} + NH_3 & (2) \end{cases}$$

It should be noted, however, that the fact that the predominantly released ligand is ammonia does *not* prove by itself that the above rules are obeyed. In fact, if the ammonia released in process 2 comes out from a position cis to the X ligand, it is clear that the photochemical behavior of the $Cr(NH_3)_5X^{2+}$ complexes does not conform to the rules since the labilized axis is the NH_3–NH_3 axis, whereas the axis having weakest cyrstal field is the NH_3–X one. It follows that, contrary to the recent interpretation given by their author,[3–5] Adamson's *empirical* rules must imply stereochemical consequences; otherwise, they would in fact be devoid of any significance since they could not be based on or tested by any experiment. Therefore, one can generally conclude that the validity of these empirical rules must be judged on the basis of (i) the determination of the quantum yields for the different aquation modes and (ii) the isomeric characterization of the reaction products. Unfortunately, for most of the complexes (Table III in ref 2) which were considered for the formulation of these rules, only one reaction mode was investigated and the geometrical configuration of the photolysis product was not well established.

As far as $Cr(NH_3)_5Cl^{2+}$ is concerned, Wasgestian and Schläfer[6] reported some spectral evidence in favor of a cis configuration for the product of process 2. At the time, however, only the spectrum of *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ was available since the trans isomer was yet unknown. Thus, their result might have left some reasonable doubt.[4,5] Since *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ has now been prepared and its spectrum made available,[7] we decided to determine definitely the geometrical configuration of the product obtained from NH_3 aquation of $Cr(NH_3)_5Cl^{2+}$ (process 2). From previous investigations, it was known that, for this complex, process 2 has a quantum yield about 50 times higher than process 1 when irradiation is performed with visible light (ligand field bands),[6,8] whereas the two photoreactions have almost the same quantum yield upon uv irradiation.[9] In our experiments, acid (0.1 *M*) solutions of 5×10^{-2} *M* $Cr(NH_3)_5Cl^{2+}$ were irradiated using a high-intensity beam of visible light obtained from an incandescent lamp filtered with a borosilicate glass and a $CuSO_4$ solution. In order to minimize simultaneous thermal reactions, the irradiation periods were very short (about 5 min) and the reaction cell (which was a 1-cm spectrophotometric cell) was maintained at 8° in a thermostated cell holder. To prevent the occurrence of secondary photochemical reactions, only a small percent of the reactant was photolyzed. After suitable periods of irradiation, the reaction cell was brought to the spectrophotometer (Turner Spectro 210) and the changes in absorbance caused by process 2 (which, in our experimental conditions, is practically the only process which occurs in the system) were recorded by the differential spectrophotometric method in the range 350–600 nm, using a sample of nonirradiated solution as reference. The curves obtained are shown in Figure 1A.

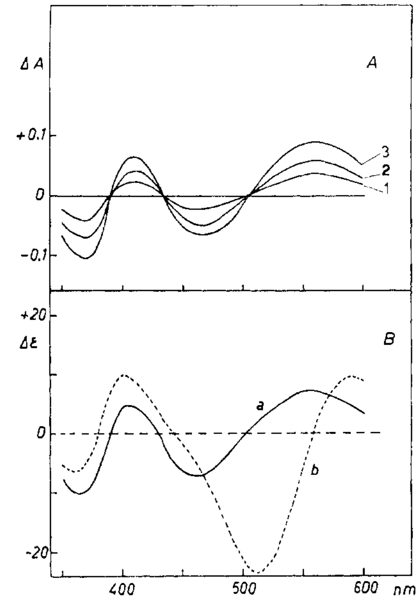

Figure 1.—A. Experimental curves obtained by differential spectrophotometric measurements on irradiated $Cr(NH_3)_5Cl^{2+}$ solutions; 1, 2, and 3 refer to 1.30, 3, and 5 min of irradiation, respectively. B. Spectral changes expected for the transformation of $Cr(NH_3)_5Cl^{2+}$ into *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ (curve a) or *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ (curve b).

The comparison between these curves and those expected for the formation of *cis*- or *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ (curves a and b, respectively, in Figure 1B) clearly shows that the actual product is the cis isomer. We have also verified that no postphotochemical effect was present in our solutions. Moreover, since it is known[7a,d] that *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ does not undergo rapid trans → cis isomerization, the possibility that the cis isomer is obtained as a result of the thermal

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

(6) H. F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem.* (*Frankfurt am Main*), **57**, 282 (1968).

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(8) L. Moggi, F. Bolletta, and V. Balzani, *Ric. Sci.*, **36**, 1228 (1966).

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isomerization of a primary trans product can be ruled out. Therefore, one must conclude that *the photochemical behavior of* $Cr(NH_3)_5Cl^{2+}$ *does not conform to Adamson's empirical rules.* We also wish to mention that in recent papers dealing with $Cr(NH_3)_5NCS^{2+}$ [5] and $Cr(NH_3)_5Br^{2+}$ [10] some indirect evidence concerning the geometric characterization of photoproducts has been reported. In the case of $Cr(NH_3)_5NCS^{2+}$, the product seems to have a trans configuration as is predicted by the rules, whereas for $Cr(NH_3)_5Br^{2+}$, the product seems to have a cis configuration, which is in disagreement with the rules.

In our opinion, the only empirical conclusion that can be drawn from the available results[1] on the mixed-ligand Cr(III) complexes is that the cationic complexes preferentially release neutral ligands. A reason for this may be the relative importance of geminate recombination processes similar to that described for $Pt(dien)Br^+$.[11]

Acknowledgment.—The authors are indebted to Professor V. Carassiti for his interest in this work.

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Nitro- and Nitritotetraammineamidoplatinum(IV) Complex Ions

Sir:

The NO_2^- group is a typical ambidentate ligand. The linkage isomers $Co(NH_3)_5(ONO)^{2+}$ and $Co(NH_3)_5(NO_2)^{2+}$ have been known for a long time.[1] More recently, the preparations of the nitrito isomers $M(NH_3)_5(ONO)^{n+}$ (where M = Rh(III), Ir(III), and Pt(IV)) have been reported and their rates of linkage isomerization investigated.[2,3]

We have attempted to prepare the two linkage isomers of Pt(IV) with the aim of studying their photochemical behavior. As far as the *nitrito* isomer is concerned, we followed the method described in ref 3, based on the nitrosation of $Pt(NH_3)_5(H_2O)^{4+}$ with $NaNO_2$ and HCl in aqueous solution at 0°.[4] Such a procedure should lead[3] to $[Pt(NH_3)_5(ONO)]Cl_3$. We obtained a crystalline compound whose ir and uv spectra were in qualitative agreement with those previously reported.[3] Moreover, the ir spectrum of a solid sample of the compound changed with time as reported in ref 3 (*i.e.*, as expected for the nitrito → nitro isomerization), and the uv spectrum of its aqueous solutions also changed as reported in ref 3b (such variations were also assigned[3] to the linkage isomerization; in fact, they are mainly due to some decomposition reaction[6]). The elemental analysis of three samples obtained from distinct preparations showed that the compound was not isolated as a pure salt. The values obtained, in fact, varied within broad limits. *Anal.* Calcd for $[Pt(NH_3)_5(ONO)]Cl_3$: Pt, 45.1; Cl, 24.6; N, 19.4; H, 3.49. Found: Pt, 46–48; Cl, 18–22; N, 18–19; H, 2.9–3.3. Attempts to purify the compound were unsuccessful, presumably because of its thermal reactivity. Additional determinations were carried out on aqueous solutions of one of the samples. The results obtained were as follows (those expected for $[Pt(NH_3)_5(ONO)]Cl_3$ are given in parentheses): Cl^-, 17.6% (24.6%); molar conductivity (10^{-3} *M* solution) $\sim$280 $ohm^{-1}\ cm^2\ mol^{-1}$ ($\sim$400 $ohm^{-1}\ cm^2\ mol^{-1}$ [7]); cationic charge[8] about +2 (+3). These results seem to indicate that the (impure) nitrito compound is a ternary electrolyte formed by a complex cation having electric charge +2 and two Cl^- anions.

According to Basolo and Hammaker,[3] the *nitro* isomer can be obtained by the thermal isomerization of the solid nitrito form. A sample of this compound was then stored at 50° in the dark until both its ir and uv spectra (the latter recorded after dissolution in water) did not change any more. The presence of isosbestic points in the uv spectra confirmed that only one product was formed. The appearance in the ir spectra of bands at 1330 and 825 cm^{-1} (characteristic of the $Pt-NO_2$ isomer[3]) and the disappearance of the band at 995 cm^{-1} (characteristic of the Pt–ONO bond[3]) indicated that a complete isomerization had occurred. The aqueous solutions of the nitro isomer were quite stable, so that it was possible to purify this compound by repeated recrystallizations. *Anal.* Calcd for $[Pt(NH_3)_5(NO_2)]Cl_3$: Pt, 45.11; Cl, 24.57; N, 19.42; H, 3.49. Found: Pt, 48.84; Cl, 17.72; N, 21.05; H, 3.37. The complex charge[8] was found to be +2.1 (calcd +3); the molar conductivity of the purified compound (10^{-3} *M* solution) was 246 $ohm^{-1}\ cm^2\ mol^{-1}$ (calcd $\sim$400 $ohm^{-1}\ cm^2\ mol^{-1}$ [7]). It clearly appears that the $[Pt(NH_3)_5(NO_2)]Cl_3$ formulation[3] is not compatible with the experimental results. The electric charge +2 of the complex cation and the molar conductivity (which

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 291.

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[4] $Pt(NH_3)_5(H_2O)^{4+}$ was obtained as the chloride salt from $PtCl_6^{2-}$, through the $Pt(NH_3)_5Cl^{3+}$ intermediate.[5]

[5] L. A. Tschugajeff, *Z. Anorg. Allg. Chem.*, **137**, 20 (1924).

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[7] A. A. Grinberg, "An Introduction to the Chemistry of Complex Compounds," Pergamon Press, Oxford, 1962.

[8] For this determination, an aqueous solution of the complex was percolated through a cation exchanger in H^+ form (Amberlite IR 120) and the H^+ ions so obtained were titrated potentiometrically.