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]

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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) ~280 ohm^{-1} cm^2 mol^{-1} (~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 ~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

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

(2) F. Basolo and G. S. Hammaker, *J. Amer. Chem. Soc.*, **82**, 1001 (1960).

(3) (a) F. Basolo and G. S. Hammaker, *Inorg. Chem.*, **1**, 1 (1962); (b) G. S. Hammaker, Ph.D. Dissertation, Northwestern University, Evanston, Ill., 1961.

(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).

(6) V. Balzani, N. Sabbatini, and V. Carassiti in "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, Amsterdam, 1968, p 80.

(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.

corresponds to that of a ternary electrolyte[7]) indicate that, besides the NO_2^- anion, another anion must be present in the first coordination sphere of platinum. However, the mild conditions used in the preparation of the parent nitrito isomer from $[Pt(NH_3)_5(H_2O)]Cl_4$ should prevent NH_3 substitution. Moreover, the elemental analysis shows that NH_3 substitution by NO_2^- or Cl^- (which were the only anions available in the reaction medium) did not occur. Therefore, the only reasonable hypothesis is that our compound contains an amido group (presumably, trans to the NO_2^- group), *i.e.*, that its formulation is $[Pt(NH_3)_4(NH_2)(NO_2)]Cl_2$. The per cent composition calculated for this formula gives 49.26% Pt, 17.89% Cl, 21.20% N, and 3.56% H. These values are in good agreement with those experimentally found (see above). The complex cation maintains the above formulation also in solution. In fact, if a proton associates to the NH_2^- ligand, the molar conductivity should correspond to that expected for a quaternary electrolyte, contrary to what we have found; moreover, the aqueous solutions of the complex should result strongly basic, whereas they are practically neutral.

The acid–base equilibria of other complexes of the $Pt(NH_3)_5X^{3+}$ type have already been investigated.[9] For example, it has been found that the pK_a values of $Pt(NH_3)_5Cl^{3+}$, $Pt(NH_3)_5Br^{3+}$, and $Pt(NH_3)_5OH^{3+}$ are 8.4, 8.3, and 9.5, respectively. It is also known[10] that the electronic absorption bands of the amido forms are displaced toward longer wavelengths in comparison with the bands of the ammine complexes. Therefore, we have carried out potentiometric titrations and spectrophotometric measurements in solutions of various acidities for establishing the pH range in which the nitro- and nitritotetraammineamidoplatinum(IV) complexes exist.

As far as the *nitro* isomer is concerned, the titration of a 10^{-2} *M* solution (which was near the solubility limit of the complex) with standard acid and base proved to be reversible and did not show any acid–base equilibrium below pH 9 (at higher pH values, the progressive acid dissociation of the other NH_3 ligands occurred). Moreover, the absorption spectrum of the complex did not undergo any change in the pH range from 9 to 0 and even in concentrated H_2SO_4. Thus, one must conclude that the pentaamminenitro complex, $Pt(NH_3)_5(NO_2)^{3+}$, is such a strong acid that it cannot exist in aqueous solutions.

As far as the *nitrito* isomer is concerned (which, as previously mentioned, cannot be obtained as a pure salt), no acid–base equilibrium was found between pH 4 and 9. Moreover, the spectra of freshly prepared solutions at pH 4 and 9 were practically identical. Unfortunately, at pH lower than 4 the complex undergoes isomerization and decomposition reactions, so that its acid–base behavior cannot be investigated at any lower acid level. Thus, from the available data, it can be only concluded that the pK_a of the pentaamminenitrito form is lower than 4. This result is a rather surprising one, considering the much higher pK_a values of the other $Pt(NH_3)_5X^{3+}$ complexes (see above), but it is consistent with the fact that the nitrito complex is isolated in its tetraammineamido form from acid solutions.

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

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Carboranes and Boranes; Polyhedra and Polyhedral Fragments

Sir:

Because the *nido*-boranes B_6H_{10} and $B_{10}H_{14}$ and the *arachno*-boranes B_4H_{10} and B_5H_{11} were discovered and structurally characterized as icosahedral fragments before the *closo*-carboranes were discovered, a dominant thesis during the evolution of boron chemistry has been the characterization of borane structures as icosahedral fragments. B_5H_9 has been the only exception. The more recently discovered species B_6H_{12}, B_8H_{14}, and two isomers of B_9H_{15}, all presumably icosahedral fragment structures, would also appear to augment and confirm the icosahedral fragment thesis. If the reverse had been true, that is, had the *closo*-carboranes been discovered first, then possibly the entire series of *closo*-carborane polyhedral structures would have been accepted as a set of standard structures for subsequent comparison. We believe the tacit acceptance of the icosahedral fragment thesis was somewhat unfortunate because, as we will illustrate below, it is demonstrable that all of the known borane and carborane structures can more clearly be derived from the *closo*-carborane series of polyhedral structures in a simplistic fashion with few if any exceptions (Figure 1). Even if our preferred "polyhedral-series" thesis is found to have no theoretical basis and is simply the unlikely result of quite a number of coincidences, it should at least serve as a convenient memory aid in the teaching of this subject. Additionally, the polyhedral-series thesis predicts a different set of nonicosahedral structures for yet to be discovered *nido*-carboranes and, we believe, rationalizes the lack of stability for such hypothetical species as B_7H_{11}, B_9H_{13}, and perhaps B_7H_{13}.