its application to clusters in general is summarized here.

(a) The Simple Soluble Problem—a Set of Fragments. (i) The cluster is divided up into separated fragments that are frozen in the geometry they possess in the equilibrium geometry of the cluster. (ii) The number of electrons is held fixed. (iii) The fragments are brought together by rigid motions that preserve the point-group symmetry of the equilibrium geometry of the final cluster. Then perturbation theory suggests that *weakly interacting isolobal fragments* will indeed have qualitatively similar interactions and energy level diagrams; the symmetry of the ground electronic state and the numbers of occupied and unoccupied levels (or the relative position of the HOMO–LUMO gap) are not altered by the interaction.

(b) The True Problem—the Cluster in Its Equilibrium Geometry. As the fragments are brought together, we expect to reach a region where strong interfragment interactions take place. By exploiting features (i), (ii), and (iii) of the soluble problem (section 5a) that are conserved, we may derive a qualitative understanding of the cluster at, or near, its equilibrium geometry. The results of such arguments are Wade's rules,[8–10] which describe the number of bonding and antibonding *molecular orbitals* in the cluster, and *the likely position of the HOMO–LUMO gap*. These rules may be justified by symmetry-based arguments such as those of Stone,[13,14] which, however, do *not* tell us the details of the atomic orbital composition of the cluster MO's. The success of Stone's model can be understood when it is appreciated that the overall *near-spherical symmetry* of most clusters discussed in these terms is a powerful constraint on the distribution of energy levels (as between bonding and antibonding) as the fragments come together. Implicit in this isolobal argument is the *assumption* that the interfragment interactions leave (i), (ii), and (iii) basically unaltered or, in other words, that the geometric and electronic symmetry adopted by the cluster at equilibrium is determined by the initial weak interaction of the separated isolobal fragments; this is the principle that underlies the use of isolobal mappings in synthetic studies.[32] The *details* of the electronic structure of main-group-element and transition-metal cluster compounds is a quite separate issue that should not be mixed up with the isolobal argument and must be determined by recourse to the methods of theoretical chemistry.

6. Conclusions

Two principal ideas required for an account of the electronic structure of transition-metal cluster compounds have been developed in detail in these two papers: (i) The metal d electrons play a crucial role in the bonding between transition-metal atoms in low oxidation states at separation distances comparable to those found in the bulk metals.

(ii) The d band of a transition-metal cluster is significantly affected by its ligand polyhedron when cluster compound formation occurs, and may be further modified in the compound's subsequent chemistry.

This second conclusion is actually in agreement with earlier (extended Hückel) accounts of cluster carbonyls[11,15] to the extent that the participation of a limited number of cluster d-band levels in cluster–ligand bonding was correctly identified (see especially Lauher's comments on $M_3(CO)_{12}$ and $M_4(CO)_{12}$ clusters[15]). Since the frontier orbitals of a metal cluster include *all* the low-energy cluster MO's of s- and p-orbital parentage, the extended Hückel model offers no explanation for the metal–metal bonding in the cluster. However by retaining the parts of these EH discussions that refer to cluster ligand bonding (which is largely controlled by the overall near-spherical symmetry of the cluster[13–15]), and making use of recent results from transition-metal physics, one can give a consistent account of both cluster–ligand *and* metal–metal bonding in transition-metal cluster compounds. It is expected that the account given here can be usefully applied to transition-metal cluster chemistry; it is already known to be consistent with the physical properties of these materials.[17,23,31,34–37]

Acknowledgment. It is a pleasure to acknowledge helpful discussions with Prof. K. Wade and Dr. A. M. Woolley.

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Kinetics and Mechanisms of the Reduction of *trans*-Dihalogenotetracyanoplatinate(IV) Complexes by Inorganic Anions[†1]

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Received December 17, 1984

The stoichiometries and kinetics of the reduction of *trans*-$Pt(CN)_4X_2^{2-}$ (X = Br, Cl) by SCN^-, $S_2O_3^{2-}$, CN^-, and SO_3^{2-} in aqueous solution have been examined at 25 °C, $\mu = 0.10$ M, pH 2–8. These reactions are described in terms of a mechanism that involves an X^+ transfer from platinum complex to the reducing anion. $Pt(CN)_4^{2-}$ is the platinum product in all the reactions studied. Reductions of *trans*-$Pt(CN)_4X_2^{2-}$ by SCN^- and of *trans*-$Pt(CN)_4Cl_2^{2-}$ by $S_2O_6^{2-}$ are first order in Pt(IV) complex, first order in reducing anion, and zero order in H^+. Reductions of *trans*-$Pt(CN)_4X_2^{2-}$ by CN^- and SO_3^{2-} are first order in Pt(IV) complex, first order in reducing anion, and inverse first order in H^+. Rate ratios of k_{Br}/k_{Cl} for the reduction of *trans*-$Pt(CN)_4X_2^{2-}$ by SCN^-, I^-, CN^-, and SO_3^{2-} were found to be nearly constant. The implication of the constant ratio is discussed.

Introduction

The interest in inner-sphere electron-transfer mechanisms for Pt(II)-assisted substitution on Pt(IV) complexes[2] has prompted our study of the reduction of Pt(IV) complexes by several inorganic substrates. We have reported that the reduction of *trans*-$Pt(CN)_4Br(OH)^{2-}$ and $Pt(CN)_4Br(H_2O)^-$ by inorganic anions proceeds via an inner-sphere Br^+-transfer mechanism.[3] The trans ligand, i.e. OH^- or H_2O, has a profound influence on the reaction rate. In this paper we report the results of studies of the reduction of *trans*-$Pt(CN)_4X_2^{2-}$ (X = Br, Cl) by SCN^-, $S_2O_3^{2-}$, SO_3^{2-}, and CN^-. The purpose is to extend our understanding of the reductive-elimination reactions of Pt(IV) complexes.

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(1) Taken, in part, from: Fanchiang, Y.-T. Ph.D. Thesis, University of Southern California, 1976.

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Table I. Moles of Pt(IV) Reduced per Mole of Reducing Agent

	SCN^-	$S_2O_3^{2-}$	CN^-	SO_3^{2-}
$Pt(CN)_4Br_2^{2-}$	3.0	0.53	1.0	0.96
$Pt(CN)_4Cl_2^{2-}$	3.1	0.53		1.0

Experimental Section

Materials. In this report all of the Pt(IV) complexes that are discussed are trans isomers. Therefore, the designation of trans in the prefix of the Pt(IV) complex will be omitted. $Na_2Pt(CN)_4 \cdot 3H_2O$ was obtained from Goldsmith Chemical & Metal Corp. and was recrystallized from aqueous solution. Complexes of $Na_2Pt(CN)_4Br_2$ and $Na_2Pt(CN)_4Cl_2$ were synthesized according to the methods in the literature.[4-6] All other chemicals except for the $NaClO_4$ were commercially available reagent grade and were used as received. All experiments involving SO_3^{2-} were performed under an atmosphere of N_2.

Stoichiometries and Reaction Products. Stoichiometries of reactions of the Pt(IV) complexes with SCN^-, $S_2O_3^{2-}$, and SO_3^{2-} were examined spectrophotometrically with methods described in ref 3. The stoichiometry of the reaction of $Pt(CN)_4Br_2^{2-}$ with CN^- was studied with an iodometric titration of the BrCN generated by using a 10-fold excess of NaCN over the Pt(IV) complex.[7]

The platinum product was identified by comparing its UV–vis spectrum with that of an authentic sample of $Pt(CN)_4^{2-}$. The quantity of $S_4O_6^{2-}$ formed in the reduction of Pt(IV) complex by $S_2O_3^{2-}$ was determined with a spectrophotometric method described by Kelly et al.[8]

Kinetic Measurements. All kinetic measurements were made at 255 nm (absorbance maximum of $Pt(CN)_4^{2-}$) or 342 nm (absorbance maximum of $Pt(CN)_4Br_2^{2-}$) with a large excess of reducing anion over Pt(IV) complex in order to provide the pseudo-first-order conditions. A few measurements with a large excess of Pt(IV) complex over the reducing anion were also carried out in order to assure the first-order dependence on Pt(IV) complex. Specific rates were measured with a procedure described in ref 3. All reactions were studied at 25 ± 0.1 °C and 0.10 M ionic strength (maintained with $NaClO_4$ or NaX). The pH was controlled in the range 2–8 by using $HClO_4$ or an appropriate buffer. Reproducibility of the data was generally better than 6%.

Results and Discussion

Under the conditions of the kinetic studies both $Pt(CN)_4Br_2^{2-}$ and $Pt(CN)_4Cl_2^{2-}$ are quantitatively reduced to $Pt(CN)_4^{2-}$ by SCN^-, $S_2O_3^{2-}$, CN^-, and SO_3^{2-}. The moles of Pt(IV) reduced per mole of reducing anion are listed in Table I for all of the anions.

The reduction of $Pt(CN)_4Br_2^{2-}$ by CN^- produces BrCN. This was determined by an iodometric titration. The yield (2 min after mixing the reactants, pH 5.6) was 99% based on the amounts of Pt(IV) used. Note should be made that, under the experimental conditions, the Pt(IV) complexes were completely reduced to Pt(II). Accordingly, we formulated the reaction as

$$Pt(CN)_4Br_2^{2-} + CN^- \rightarrow Pt(CN)_4^{2-} + BrCN + Br^- \quad (1)$$

We were not able to measure the consumption ratio between $Pt(CN)_4Cl_2^{2-}$ and CN^- because of the secondary reaction between $Pt(CN)_4^{2-}$ and ClCN, which presumably produces $Pt(CN)_5Cl^{2-}$.

The oxidation of SO_3^{2-} results in the formation of SO_4^{2-}. This is based on the 1:1 consumption ratio and the complete reduction of Pt(IV) to Pt(II) by an excess of SO_3^{2-}. Accordingly, we formulate the reactions as

$$Pt(CN)_4X_2^{2-} + SO_3^{2-} + H_2O \rightarrow Pt(CN)_4^{2-} + SO_4^{2-} + 2H^+ + 2X^- \quad (2)$$

The oxidation of $S_2O_3^{2-}$ results in a quantitative formation of $S_4O_6^{2-}$. On the basis of the reaction products and results of the mole ratio determinations, we formulate the reactions as

$$Pt(CN)_4X_2^{2-} + 2S_2O_3^{2-} \rightarrow Pt(CN)_4^{2-} + S_4O_6^{2-} + 2X^- \quad (3)$$

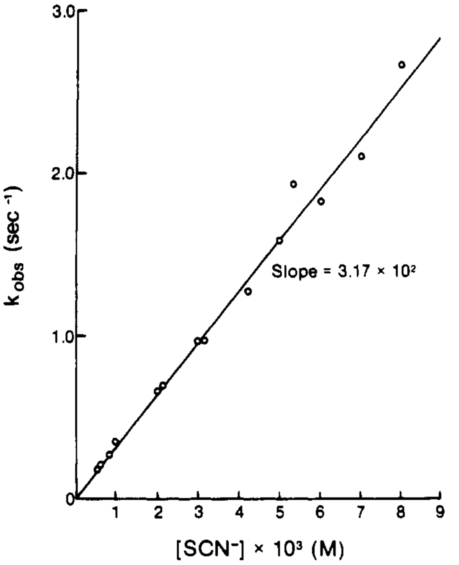

Figure 1. Kinetic data of the reduction of $Pt(CN)_4Br_2^{2-}$ by SCN^- ($[Pt(IV)] = (2.0–4.0) \times 10^{-5}$ M; pH 2 ($HClO_4$); $\mu = 0.10$ M; 25 °C).

The reduction of the Pt(IV) complexes by SCN^- results in the formation of SO_4^{2-} which was detected by the precipitation of $BaSO_4$ on addition of $BaCl_2$ to the final reaction solution. On the basis of the mole ratio $[Pt(IV)]/[SCN^-]$ of 3.0, the detection of SO_4^{2-}, and previous studies on the reduction of $Pt(CN)_4Br(OH)^{2-}/Pt(CN)_4Br(H_2O)^-$ by SCN^-,[3] we formulate the reactions as

$$3Pt(CN)_4X_2^{2-} + SCN^- + 4H_2O \rightarrow 3Pt(CN)_4^{2-} + SO_4^{2-} + HCN + 7H^+ + 6X^- \quad (4)$$

No attempt to identify the HCN formed in the SCN^- oxidation was made in the present study. However, both SO_4^{2-} and HCN are known to be products of oxidation of SCN^- by other complexes.[9]

Kinetic Measurements and Reaction Mechanisms. All kinetic data are tabulated and are available in the supplementary material.

In all cases, the reduction of $Pt(CN)_4X_2^{2-}$ by SCN^-, $S_2O_3^{2-}$, CN^-, and SO_3^{2-} are first order in Pt(IV) and, with the exception of the $S_2O_3^{2-}$ reaction with $Pt(CN)_4Br_2^{2-}$, first order in reducing anion according to

$$-\frac{d[Pt(IV)]}{dt} = \frac{d[Pt(II)]}{dt} = k_0[\text{substrate}][Pt(IV)] \quad (5)$$

In the studies of the reduction of $Pt(CN)_4Br(OH)^{2-}/Pt(CN)_4Br(H_2O)^-$ by SCN^-, $S_2O_3^{2-}$, SO_3^{2-}, CN^-, and I^-,[3] we have presented results that support a mechanism involving Br^+ transfer to the reducing anion by both the hydroxo and aquo complexes. On the basis of the stoichiometries and kinetic behavior, we adopted a similar mechanism for the reduction of $Pt(CN)_4X_2^{2-}$. The detection of BrCN for the reduction of $Pt(CN)_4Br_2^{2-}$ by CN^- lends strong support for the X^+-transfer mechanism. In addition, $BrSCN$[10] and $BrS_2O_3^-$[11] are known species, although relatively unstable.

(a) SCN^- Reaction. Values of k_0 for the reactions with SCN^- are independent of pH. A typical set of results of kinetic measurements is shown in Figure 1. The mechanism is formulated as

$$Pt(CN)_4X_2^{2-} + SCN^- \xrightarrow{k} Pt(CN)_4^{2-} + XSCN + X^- \quad (6)$$

$$2Pt(CN)_4X_2^{2-} + XSCN + 4H_2O \xrightarrow{\text{rapid}} 2Pt(CN)_4^{2-} + SO_4^{2-} + HCN + 5X^- + 7H^+ \quad (7)$$

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Table II. Rate Constants (in $M^{-1}\ s^{-1}$) for the Reduction of $Pt(CN)_4X_2^{2-}$ by Inorganic Anions[a]

	SCN^-	$S_2O_3^{2-}$	I^{-b}	CN^-	SO_3^{2-}
$Pt(CN)_4Br_2^{2-}$	$(1.1 \pm 0.10) \times 10^2$		8.9×10^4	$(3.6 \pm 0.30) \times 10^5$	$(1.8 \pm 0.090) \times 10^8$
$Pt(CN)_4Cl_2^{2-}$	$(3.1 \pm 0.090) \times 10^{-1}$	$(8.5 \pm 0.25) \times 10^3$	2×10^2	ca. 10^3	$(4.3 \pm 0.42) \times 10^5$
k_{Br}/k_{Cl}	3.6×10^2		4.5×10^2	ca. 4×10^2	4.2×10^2

[a] Conditions: μ = 0.10 M; 25 °C. [b] At 20.9–22 °C, μ = 0.07 M; taken from ref 5.

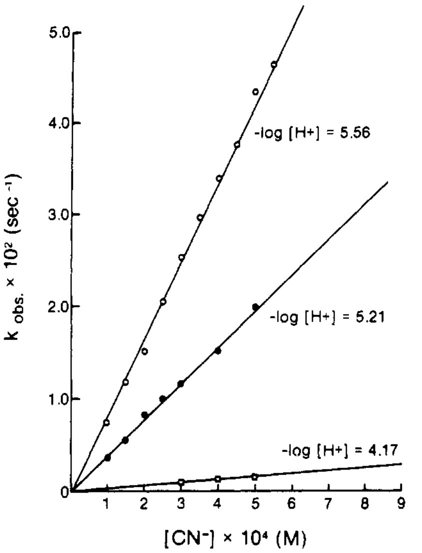

Figure 2. Kinetic data of the reduction of $Pt(CN)_4Br_2^{2-}$ by CN^- ([Pt(IV)] = 1.8×10^{-5} M; μ = 0.10 M; 25 °C).

(b) $S_2O_3^{2-}$ Reaction. Values of k_0 for the reactions of $Pt(CN)_4Cl_2^{2-}$ with $S_2O_3^{2-}$ are also independent of pH. The mechanism is formulated as

$$Pt(CN)_4Cl_2^{2-} + S_2O_3^{2-} \xrightarrow{k} Pt(CN)_4^{2-} + ClS_2O_3^- + Cl^- \quad (8)$$

$$ClS_2O_3^- + S_2O_3^{2-} \xrightarrow{\text{rapid}} S_4O_6^{2-} + Cl^- \quad (9)$$

The kinetic behavior for the reaction of $Pt(CN)_4Br_2^{2-}$ with $S_2O_3^{2-}$ is ambiguous, and we were not able to derive a rate expression for it.

(c) CN^- Reaction. Values of the k_0 for the reactions with CN^- are inverse first order in H^+. Plots of k_{obsd} vs. $[CN^-]$ at various pHs for the reactions of $Pt(CN)_4Br_2^{2-}$ are shown in Figure 2. Rate measurements for the reactions of $Pt(CN)_4Cl_2^{2-}$ are less accurate because of the interference by the reaction between $Pt(CN)_4^{2-}$ and ClCN. The mechanism is formulated as

$$HCN \overset{K_a}{\rightleftharpoons} CN^- + H^+ \quad (10)$$

$$Pt(CN)_4X_2^{2-} + CN^- \xrightarrow{k} Pt(CN)_4^{2-} + XCN + X^- \quad (11)$$

(d) SO_3^{2-} Reaction. Values of k_0 for the reactions with SO_3^{2-} are also inverse first order in H^+. The mechanism is formulated as

$$HSO_3^- \overset{K_a}{\rightleftharpoons} SO_3^{2-} + H^+ \quad (12)$$

$$Pt(CN)_4X_2^{2-} + SO_3^{2-} \xrightarrow{k} Pt(CN)_4^{2-} + XSO_3^- + X^- \quad (13)$$

$$XSO_3^- + H_2O \xrightarrow{\text{rapid}} SO_4^{2-} + X^- + 2H^+ \quad (14)$$

Reactions with SCN^- or $S_2O_3^{2-}$ lead to the simple rate law (5). Since the reactions were monitored at the consumption of Pt(IV) or the generation of Pt(II) complex, and because there was a stoichiometry of 3:1 for the reactions with SCN^-, $k_0 = 3k$ for SCN^-. Reactions with CN^- or SO_3^{2-} lead to the rate expression

$$\frac{d[Pt(CN)_4^{2-}]}{dt} = \frac{kK_a[\text{substrate}][Pt(IV)]}{K_a + [H^+]} \quad (15)$$

The acid dissociation constants, pK_a's, for HCN and HSO_3^- have been estimated to be 6.17×10^{-10}[12] and 6.20×10^{-8} M,[13] respectively. Therefore, in the pH range of this study rate law 15 is simplified to rate law 16 with $k_0 = kK_a/[H^+]$. Values of

$$\frac{d[Pt(CN)_4^{2-}]}{dt} = \frac{kK_a[\text{substrate}][Pt(IV)]}{[H^+]} \quad (16)$$

k (in $M^{-1}\ s^{-1}$) for all substrates are listed in Table II. Rate constants for the reduction of $Pt(CN)_4Br_2^{2-}$ and $Pt(CN)_4Cl_2^{2-}$ by I^- (20.9 °C) were taken from an independent work of Poe et al.[5] The reaction rates were found to be unaffected by the addition of $Pt(CN)_4^{2-}$ or the substitution of $NaClO_4$ with NaX.

The distinguishing feature of Table II is that relative effects on the reaction rates of different platinum(IV) complexes, i.e. $Pt(CN)_4Br_2^{2-}$ and $Pt(CN)_4Cl_2^{2-}$, are independent of the reducing anions. It is worth noting that the kinetic studies of one of the reducing anions, I^-, were carried out independently from another laboratory.[5] A similar result has been reported by Peloso et al. in which the relative effects on the reaction rates of different reducing anions are shown to be independent of the platinum complexes.[14] On the basis of this observation, they concluded that bond making between the reducing agents [SCN^-, I^-, $SeCN^-$, and $S_2O_3^{2-}$) and the platinum(IV) complexes (*trans*-PtL_2X_4 complexes, where L = pyridine, piperidine, methyl- and ethylamine, dimethyl and diethyl sulfides and X = Cl, Br) was small. We have pointed out[3] that this conclusion is not necessarily correct because the independence of the platinum complexes may merely reflect that the contribution of the bond making to the activation energy is similar in all the reactions studied.

For the reductive-elimination reaction of Pt(IV) complexes, it is useful to consider as states of the reacting systems (1) the "ground state" of uncorrelated reactants, (2) a "precursor complex" in which the reactants have been assembled in a solvent cage but are otherwise noninteracting, (3) a move of the trans ligand away from the oxidant and, simultaneously, formation of a bond between the bridging ligand and the reductant, and (4) breaking of the bonds between platinum and the leaving ligand and between platinum and bridging ligand and formation of Pt(II) product. In light of the nearly constant ratios of k_{Br}/k_{Cl} for the series of reductants presented in this study, and a similar result for *trans*-PtL_2X_4 complexes,[14] the "intrinsic" barrier for the $Pt(CN)_4X_2^{2-}$ or PtL_2X_4 complexes to reach the transition state in state 3, i.e. the reorganization energy of the reacting species along the reaction coordinates, may be viewed as constant.

Acknowledgment. We wish to thank Dr. James E. Byrd for his help throughout this research.

Registry No. *trans*-$Pt(CN)_4Cl_2^{2-}$, 20756-57-4; *trans*-$Pt(CN)_4Br_2^{2-}$, 20756-58-5; SCN^-, 302-04-5; $S_2O_3^{2-}$, 14383-50-7; CN^-, 57-12-5; SO_3^{2-}, 14265-45-3.

Supplementary Material Available: Kinetic data for the reductions of $Pt(CN)_4Br_2^{2-}$ by SCN^- (Table I), $Pt(CN)_4Cl_2^{2-}$ by SCN^- (Table II), $Pt(CN)_4Cl_2^{2-}$ by $S_2O_3^{2-}$ (Table III), $Pt(CN)_4Br_2^{2-}$ by SO_3^{2-} (Table IV), $Pt(CN)_4Cl_2^{2-}$ by SO_3^{2-} (Table V), and $Pt(CN)_4Br_2^{2-}$ by CN^- (Table VI) (7 pages). Ordering information is given on any current masthead page.

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