Solution Equilibria of Tetrakis(ethyisocyanide)platinum(II) with Tetracyanoplatinate(II): Equilibria and Thermodynamics of the Formation of Di-, Tri-, and Tetraplatinum Species

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In aqueous solution, the tetrakis(ethylisocyanide)platinum(II) cation, $Pt(CNC_2H_5)_4{}^{2+}$, reacts with tetracyanoplatinate(II), $Pt(CN)_4{}^{2-}$, to form four multinuclear species. These species are the diplatinum(II) compound $[Pt(CNC_2H_5)_4{}^{2+}][Pt(CN)_4{}^{2-}]$, two triplatinum compounds, $[Pt(CNC_2H_5)_4{}^{2+}]_2[Pt(CN)_4{}^{2-}]^{2+}$ and $[Pt(CNC_2H_5)_4{}^{2+}][Pt(CN)_4{}^{2-}]_2{}^{2-}$, and the tetraplatinum species $[Pt(CNC_2H_5)_4{}^{2+}]_2[Pt(CN)_4{}^{2-}]_2$. The interactions leading to the stability of these species are not simply ionic. The interactions result in major differences in the electronic absorption spectra, and the oligomers are not disrupted by the addition of other salts. The formation constant for each of the oligomers was determined at several temperatures, and the enthalpies and entropies of formation were measured. Species with even numbers of platinum ions have more negative stepwise enthalpies of formation than do the species with odd numbers of platinum ions. Entropies of formation are negative as well; however, the values are significantly more positive for the species with odd numbers of platinum ions than for those with an even number. These thermodynamic trends can be rationalized by recognizing that the species with even numbers of platinum ions are dipolar and organize the solvent better than the species with odd numbers of platinum ions, which are not dipolar. Thus, the more negative enthalpies of formation of the species with even numbers of platinum ions are a consequence of better solvation than species with odd numbers of platinum ions. Accordingly, the entropies of formation of the species with even numbers of platinum ions are more negative because they organize solvent to a greater extent. Exclusive of solvent effects, the anion−cation interaction is about 30 kJ/mol.

Introduction

Various salts of the tetracyanoplatinate(II) anion display different colors in the solid state depending on the nature of the countercation and the number of water molecules per formula unit. Structural analysis reveals that the crystalline forms of all the alkali and alkaline earth salts consist of stacks of the square planar anion such that the Pt(II) ions are above one another in continuous chains.[1,2] The color is correlated with the Pt−Pt separation.[3] The Pt−Pt separations vary from 3.1 to 3.7 Å, and the maximum for the absorption band ranges from 600 to 283 nm. Complexes with Pt−Pt separations greater than 3.5 Å are nearly colorless. Analogous observations have been reported for the double salts exemplified by Magnus's green salt, $[Pt(NH_3)_4]^{2+}[PtCl_4]^{2-}$.[4,5] The nature of the band leading to the green color has been the subject of considerable interest.[6−10]

Nearly all studies of these double salt interactions have been carried out in the solid state perhaps because of the very low solubility of most of the Magnus type salts.[11,12] However, Isci and Mason have reported the electronic spectroscopic analysis of the interaction of $[Pt(CNC_2H_5)_4]^{2+}$ with $[Pt(CN)_4]^{2-}$ in acetonitrile solution.[6−8] A single band is observed in the visible region and assigned to the dinuclear complex $[Pt(CNC_2H_5)_4]^{2+}$-$[Pt(CN)_4]^{2-}$. The formation constant of the complex and extinction coefficient of the band in the visible region were reported.

Isoelectronic rhodium(I) isocyanides behave similarly to the platinum(II) double salts. They polymerize, forming complexes as large as octamers. Polymerization is accompanied by spectral changes analogous to those observed in the Pt(II) cases and is indicative of covalent bond formation.[13,14] The monomers are cationic, and yet their interaction is strong enough to overcome the Coulombic repulsion.

Experimental Section

Starting Materials. KCN (Baker), potassium tetrachloroplatinate(II) (Johnson Mathey), and triethyloxoniumtetrafluoroborate (Aldrich) were used as received. All solvent water was deionized and distilled. The $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$ was prepared from $K_2Pt(CN)_4$ as previously reported.[15] The $[Pt(CNC_2H_5)_4][BF_4]_2$ was prepared from $K_2Pt(CN)_4$ and triethyloxonium tetrafluoroborate as previously reported.[16]

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(1) Williams, J. M.; Underhill, A. E.; Watkins, D. M.; Carneriro, K. *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; pp 119−154.
(2) Cox, E. G.; Pinkard, F. W.; Wardlaw, W.; Preston, G. H. *J. Chem. Soc. (London)* **1932**, 2527.
(3) Yamada, S. *Bull. Chem. Soc. Jpn.* **1951**, *4*, 1251.
(4) Buss, C. E.; Anderson, C. E.; Pomije, M. K.; Lutz, C. M.; Britton, D.; Mann, K. R. *J. Am. Chem. Soc.* **1998**, *120*, 7783.
(5) Cradwick, M. E.; Hall, D.; Phllips, R. K. *Acta Crystallogr.* **1971**, *B27*, 480.
(6) Isci, H.; Mason, W. R. *Inorg. Chem.* **1974**, *13*, 1175.
(7) Isci, H.; Mason, W. R. *Inorg. Chem.* **1975**, *14*, 905.
(8) Isci, H.; Mason, W. R. *Inorg. Chem.* **1975**, *14*, 913.
(9) Martin, D. S.; Hunter, L. D.; Kroening, R.; Coley, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 5433.
(10) Martin, D. S.; Robbins, G. A.; Rush, R. M. *Inorg. Chem.* **1980**, *19*, 1705.
(11) Exstrom, C. L.; Sowa, J. R.; Daws, C. A.; Janzen, D.; Mann, K. R. *Chem. Mater.* **1995**, *7*, 15.
(12) Nagel, C. C. U.S. Patent 4,826,774, May 2, 1989.
(13) Mann, K. R.; Gordon, J. G.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553.
(14) Lewis, N. R.; Mann, K. R.; Gordon, J. G.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461.
(15) Mason, W. R.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5721.
(16) Treichel, P. M.; Knebel, W. J.; Hess, P. W. *J. Am. Chem. Soc.* **1971**, *93*, 5424.

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Preparation of Potassium Tetracyanoplatinate(II) Trihydrate. An amount of 1.0 g of $K_2Pt(Cl)_4$ (2.4 mmol) was dissolved in 200 mL of water. To this was added 4 equiv (9.6 mmol) of KCN in small portions over 15 min. Within an hour the initially red solution became colorless. It was filtered, and the solvent was removed in vacuo. The resulting solid was dissolved in a minimum volume of water at 70 °C and placed in an ice bath. The yellow needlelike crystals that formed were filtered and washed with cold water. The $K_2Pt(CN)_4$ that was formed was recrystallized three times.

Preparation of the Double Salt $[Pt(CNC_2H_5)_4][Pt(CN)_4]_2$. Equal molar solutions (0.1 M) of $[Pt(CNC_2H_5)_4][BF_4]_2$ and $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$ were prepared in separate vessels with dry dichloromethane as the solvent. When they were mixed, a bright-green solid precipitated. The solid was filtered off and stored under argon at 0 °C. The yield was 90%.

Solutions Studied by Continuous Variations.[17] Equal molar solutions of the $[Pt(CNC_2H_5)_4][BF_4]_2$ and $K_2Pt(CN)_4$ were prepared in separate volumetric flasks. The $[Pt(CNC_2H_5)_4^{2+}$ and $Pt(CN)_4^{2-}$ solutions were then mixed in different ratios keeping the total platinum concentration the same in all the solutions. Solutions of $Pt(CNC_2H_5)_4^{2+}$ are unstable in water and begin to decompose within one-half hour at the highest temperatures studied. All equilibria data were taken within one-half hour, and measurements of solutions from the beginning of a series of experiments were repeated to ensure that significant decomposition had not occurred.

UV-Visible Spectroscopy and the Determination of Equilibrium Constants. Measurements were made with a HP 8453 diode array spectrophotometer. Spectra were taken in 1.0, 0.1, and 0.01 cm quartz cells with deionized and distilled water as the solvent. Temperature was controlled with a Neslab RTE-110 constant temperature bath. Measurements were made at a solution pH of 5.5. The general procedure for determining the equilibrium constants was as follows. First, the principal electronic absorption bands were determined by varying the concentrations of the reactants over several orders of magnitude. Subsequently, the stoichiometries of each of the species were determined by the method of continuous variations. Where possible, extinction coefficients were measured. With these data in hand, the equilibrium constants were calculated using the Hyperquad suite of programs developed by Gans and described in his papers.[18] This program determines the equilibrium constants from absorption data by a least-squares approach given the formulas of the species involved.

Labeling of Oligomers. In this paper, the oligomers are referred to according to their stoichiometry and following IUPAC rules of cation first followed by the anion. For example, the trinuclear species $[Pt(CNC_2H_5)_4]_2[Pt(CN)_4]^{2+}$ is labeled 2:1.

Results

Evidence for Oligomer Formation from Absorption Spectra. $Pt(CNC_2H_5)_4^{2+}$ and $Pt(CN)_4^{2-}$ have rather similar electronic absorption spectra. No bands are observed at wavelengths longer than 280 nm. When an aqueous solution is prepared in which each ion is ca. 1.0×10^{-5} M, a band is observed at 319 nm. At concentrations above 1.0×10^{-4} M a band is observed at 363 nm as well. As the concentration is raised toward 1.0×10^{-2} M, the 363 nm band appears to shift and broaden and its maximum reaches 455 nm at the solubility limit. Identical spectra are observed when the total concentration of the double salt complex, $[Pt(CNC_2H_5)_4^{2+}][Pt(CN)_4^{2-}]$, is varied in solution. These facts are consistent with the formation of three or more oligomers of the two ions. Figure 1 is the absorption spectrum of a solution that is 5.0×10^{-4} M in the double salt. The maximum of the lowest energy band is at 390 nm. This is compared to 363 nm when the total concentration is 1.0×10^{-4} M and 420 nm at 1.0×10^{-3} M in double salt.

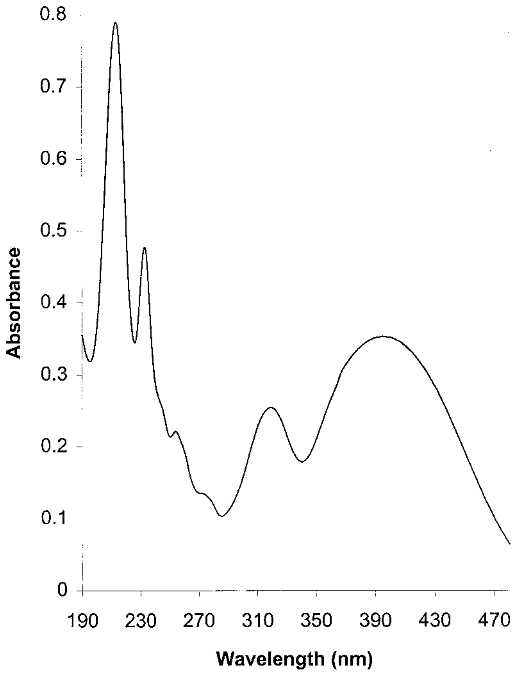

Figure 1. Electronic absorption spectrum of a 5×10^{-4} M solution of the double salt in water showing multiple absorption bands in the visible region.

The stoichiometry of the various species in solution was determined by the continuous variations (CV) method.[17] CV experiments at a total concentration of 1.0×10^{-5} M show that the 319 nm absorbance arises from a complex with 1:1 stoichiometry and has the formula $[Pt(CNC_2H_5)_4^{2+}][Pt(CN)_4^{2-}]$. At 1.0×10^{-4} M total concentration, the 363 nm band is prominent. Its intensity maximizes at a 2:1 ratio of cation to anion. The band does not shift position when the ratio of anion to cation is varied at a total concentration of 1.0×10^{-4} M. The formula for the compound giving rise to this band is therefore $[Pt(CNC_2H_5)_4^{2+}]_2[Pt(CN)_4^{2-}]^{2+}$. At 1.0×10^{-3} M total concentration a single band is observed with a maximum at 420 nm. The CV method shows that the band is optimized at a cation-to-anion ratio of 1:1. The likely formula for the species giving rise to this band is $[Pt(CNC_2H_5)_4^{2+}]_2[Pt(CN)_4^{2-}]_2$.

In the concentration range 1.0×10^{-3} to 5.0×10^{-3} M the lowest energy band maximizes at 420 nm. Above 5.0×10^{-3} M the band shifts progressively to 450 nm. At these concentrations oligomers with more than four platinum ions form. The data reported in this paper were restricted to total platinum concentrations less than 5.0×10^{-3} M where the largest species are tetranuclear.

The CV method gave clear and definite proof for three oligomers. However, in the initial analysis, no distinct band was detected corresponding to the 1:2 complex $[Pt(CNC_2H_5)_4^{2+}][Pt(CN)_4^{2-}]_2^{2-}$. In the total concentration range of 1.0×10^{-5} to 1.0×10^{-4} M, the 2:2 complex does not form significantly and the mononuclear species have no absorptions at wavelengths longer than 300 nm. If the only species present were the 1:1 and 2:1 complexes, an isosbestic point is anticipated between 319 and 363 nm. None is observed, indicating that a 1:2 complex formed but it either had a substantially smaller formation constant or smaller extinction coefficients than the 2:1 species. Ultimately the equilibrium analysis (vide infra) showed that the 1:2 complex has a maximum at 350 nm, but in most spectra the band appears as a broadening of the more intense 363 nm band. Upon retrospective examination, we found that in a narrow

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(17) Ingle, J. D.; Crouch, S. R. *Spectrochemical Analysis*; Prentice Hall: Englewood Cliffs, NJ, 1988; p 386.

(18) Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, *43*, 1739.

concentration range at high ratios of cyanide to isocyanide a distinct band is observed at 350 nm.

Equilibrium Model Selection. When the stoichiometries of the products of the equilibria were identified, the following equilibrium constants were sought:

$$\mathrm{Pt(CNC_2H_5)_4}^{2+} + \mathrm{Pt(CN)_4}^{2-} \rightleftharpoons [\mathrm{Pt(CNC_2H_5)_4}^{2+}][\mathrm{Pt(CN)_4}^{2-}] \qquad K_1$$

$$[\mathrm{Pt(CNC_2H_5)_4}^{2+}][\mathrm{Pt(CN)_4}^{2-}] + \mathrm{Pt(CNC_2H_5)_4}^{2+} \rightleftharpoons [\mathrm{Pt(CNC_2H_5)_4}^{2+}]_2[\mathrm{Pt(CN)_4}^{2-}]^{2+} \qquad K_2$$

$$[\mathrm{Pt(CNC_2H_5)_4}^{2+}][\mathrm{Pt(CN)_4}^{2-}] + \mathrm{Pt(CN)_4}^{2-} \rightleftharpoons [\mathrm{Pt(CNC_2H_5)_4}^{2+}][\mathrm{Pt(CN)_4}^{2-}]_2^{\,2-} \qquad K_3$$

$$[\mathrm{Pt(CNC_2H_5)_4}^{2+}]_2[\mathrm{Pt(CN)_4}^{2-}]^{2+} + \mathrm{Pt(CN)_4}^{2-} \rightleftharpoons [\mathrm{Pt(CNC_2H_5)_4}^{2+}]_2[\mathrm{Pt(CN)_4}^{2-}]_2 \qquad K_4$$

K_1 was determined directly at low concentrations (10^{-5} M) in a regime where the other species do not form. A plot of $C/A^{1/2}$ versus $A^{1/2}$ gives a slope of ϵ^{-1} where C is concentration and A is absorbance. Substituting Beer's law into the equilibrium expression gives

$$K = \frac{A/\epsilon}{(C - A/\epsilon)^2}$$

Isci and Mason[6] used this method to determine the equilibrium constant for the dimer of the double salt in acetonitrile solution.

The remaining equilibria overlap and were most easily evaluated using the computer program Hyperquad.[17] This program fits equilibrium constants to electronic absorption data for systems in chemical equilibrium by a least-squares method. To achieve convergence in the iterations, approximate values of extinction coefficients must be supplied. For the 2:1 complex, these were determined at 1.0×10^{-4} M assuming no formation of the 2:2 complex. Ultimately, all the equilibrium constants and extinction coefficients were refined simultaneously. The values obtained for the 1:1 complex were not significantly different from those determined directly at low concentrations. Convergence could be obtained without including the 1:2 complex, but a statistically better fit was achieved by including it. The standard deviation of the equilibrium constants without the 1:2 complex included was never better than 25% of the equilibrium constants determined. The equilibrium model was tested by attempting to include formation constants for the penta- and hexanuclear species. No statistically significant equilibrium constants could be determined for penta- and hexanuclear species at the concentrations studied. In the initial analysis, equilibrium constants and molar extinction coefficients were evaluated simultaneously for each of the different temperatures studied. Values for the extinction coefficients at four different temperatures agreed well with each other. In the concluding refinement of the equilibrium constants, extinction coefficients were held fixed at the averages of their values for all of the temperatures. The absorptivites of the parent complexes were all held constant throughout the refinement because they are known from independent measurement.

The equilibrium constants that were determined by this method appear in Table 1. Included in Table 1 is the molar extinction coefficient for each oligomer at its absorption maximum. The absorptivities tabulated are averages from the refinements at the different temperatures.

Table 1. Stepwise Formation Constants for the Oligomerization of the Double Salt $[\mathrm{Pt(CNC_2H_5)_4}^{2+}][\mathrm{Pt(CN)_4}^{2-}]$ in Water[a]

	oligomer	K (22 °C)	K (17 °C)	K (12 °C)	K (7 °C)	$\epsilon_{\max}$
K_1	1:1	5.1×10^4	6.8×10^4	8.5×10^4	1.1×10^5	$15000_{319\ \mathrm{nm}}$
K_2	2:1	9.5×10^2	1.2×10^3	1.3×10^3	1.6×10^3	$57000_{363\ \mathrm{nm}}$
K_3	1:2	8.1×10^2	9.7×10^2	1.1×10^3	1.3×10^3	$21000_{350\ \mathrm{nm}}$
K_4	2:2	3.0×10^5	2.5×10^5	1.7×10^5	1.3×10^5	$35000_{420\ \mathrm{nm}}$

[a] The constants were refined using the hyperquad suite of programs. The units are M^{-1}. Values are accurate to better than $\pm 0.3\ \mathrm{M}^{-1}$.

Table 2. Thermodynamic Parameters for the Stepwise Formation Constants for the Oligomerization of the Double Salt $[\mathrm{Pt(CNC_2H_5)_4}][\mathrm{Pt(CN)_4}]$ in Water[a]

stepwise constant	$\Delta H°$, kJ/mol	$\Delta G°$, kJ/mol	$\Delta S°$, J/(mol K)
K_1	−35	−27	−30
K_2	−22.	−17	−18.
K_3	−21	−16	−15
K_4	−40	−29	−36

[a] Enthalpies are accurate to better than ±1 kJ/mol. Entropies are accurate to better than ±3 J/(mol K).

Thermodynamic Studies of the Formation of the Oligomers. Values of $\Delta H°$ were determined from Van't Hoff plots for which correlation coefficients were better than 0.99. $\Delta S°$ was determined from $\Delta H°$ and the value of the equilibrium constant. The thermodynamic results from the stepwise equilibrium constants at the four temperatures appear in Table 2.

Discussion

An issue of considerable interest is the nature of the interaction between cation and anion in these double salt complexes. As discussed in the Introduction, it has long been recognized that the appearance of new bands in the electronic absorption spectrum of related compounds indicates that the interaction involves important changes in the orbitals of anion and cation in addition to Coulombic attraction between the ions.

Initially, the equilibrium constants in this system were measured without an inert electrolyte to maintain ionic strength. This was done to prevent potential complications from additional ion−ion interactions beyond those of the platinum anion and cation. Subsequently, measurements were made with a 100-fold excess of $\mathrm{KNO_3}$, $\mathrm{Al_2(SO_4)_3}$, or $\mathrm{(NH_4)H_2PO_4}$. At these concentrations, equilibria were not significantly shifted. This is further evidence that the covalence of each double salt is quite substantial and not readily disrupted by salts. Yet another indication of the covalent nature of bonding is that the double salt containing the tertiary butylisocyanide, $[\mathrm{Pt(CNC_4H_9)_4}][\mathrm{Pt(CN)_4}]$, was reported by Isci and Mason to have a larger formation constant than the corresponding ethylisocyanide species in acetonitrile solutions.[6] Evidently, the electron-donating properties of the tertiary butyl group strengthens the metal−metal interaction more than enough to compensate for the steric repulsions they exert on the anion. In the case of the rhodium(I) isocyanides, the fact that polymerization overcomes Coulombic repulsion is further evidence of covalence.[13,14]

It should also be pointed out that in other related systems, bonding interactions through the ligands have been discussed;[19,20] however, this probably plays no role in the system reported herein.

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(19) Connick, W. B.; Marsh, R. E.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1997**, *36*, 913.

(20) Miller, J. S. *Inorg. Chem.* **1976**, *15*, 2357.

A striking feature of the thermodynamic data in Table 2 is that the enthalpies and entropies of formation of the 1:1 and 2:2 complexes are quite similar. Likewise, the enthalpies and entropies of formation of the 2:1 and 1:2 are quite similar to each other but are significantly less negative than the values for the 1:1 and 2:2 species. A plausible explanation for the less negative enthalpies of formation for 1:2 and 2:1 complexes comes from the recognition that these species are not dipolar while the 1:1 and 2:2 complexes are very strongly dipolar. Dipolar molecules interact much more strongly with a polar solvent like water, organizing it extensively. Thus, the formation of 1:1 and 2:2 complexes not only entail direct covalent and ionic interactions between platinum complexes but they also involve the formation of stronger bonding to the solvent than is possible for the 1:2 or 2:1 complexes. The less negative entropies of formation for the 1:2 and 2:1 complexes are reflections of the same phenomenon. These species organize the water more poorly than the 1:1 and 2:2 complexes.

Considered in this light, the data offer an estimate of the strength of the anion−cation interaction in these systems. Evidently, the 1:1 and 2:2 complexes are solvated to a comparable extent on a per platinum atom basis. Likewise the 2:1 and 1:2 complexes are solvated comparably. Therefore, by averaging the formation constants of the species, one may arrive at an estimate of the anion−cation interaction of about 30 kJ/mol. The data at hand do not speak to how this figure is distributed between ionic and covalent terms.

An additional feature of this system is that 1:2 complex is a less conspicuous participant in the equilibria than is the 2:1 complex, based on the electronic absorption spectroscopy. As the data indicate, this is mainly the result of a smaller molar extinction coefficient for the 1:2 complex. The enthalpy of formation of the 1:2 complex is, however, somewhat less negative than that for the 2:1 complex, and it is worth noting that its lowest energy electronic absorption band is to higher energy than the band for the 2:1 complex, consistent with a weaker interaction between cationic and anionic portions of the 1:2 complex.

Finally, it is interesting to consider the nature of the bonding between anion and cation. The highest occupied orbital in both cation and anion is the $5d_{z^2}$ platinum orbital, and both orbitals contain an electron pair. At first glance, it is not obvious how a covalent bond can be formed. Some time ago, Krogmann offered an explanation based on molecular orbital considerations.[21] Filled $5d_{z^2}$ orbitals of adjacent platinum ions interact to form bonding and antibonding levels of A_{1g} and A_{2u} symmetry, respectively. Normally, this would not lead to a net bonding interaction; however, the empty $6p_z$ orbitals form molecular orbitals with the same symmetry as the $5d_{z^2}$ orbitals and repel them, leading to net stability.[7,15] This is illustrated on the left-hand side of Figure 2. It is worth noting that one can arrive at an equivalent explanation for the net stabilization through simple electron pair bonding considerations. Hybridization of the $5d_{z^2}$ orbitals with the $6p_z$ orbitals followed by molecular orbital formation between the hybrids can result in exactly the same energy acheived by symmetry repulsion considerations. This is illustrated on the right-hand side of Figure 2.

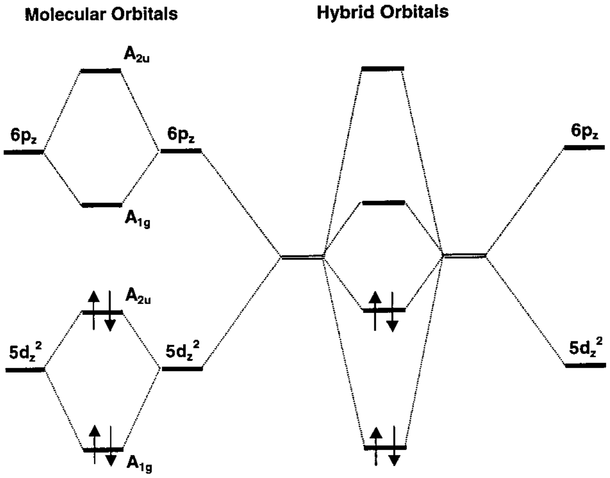

Figure 2. Stabilization of the double salt $[Pt(CNC_2H_5)_4][Pt(CN)_4]$ through symmetry repulsion of molecular obitals based on platinum $5d_{z^2}$ and $6p_z$ orbitals (left-hand side) and from electron pair bonds formed with $5d_{z^2}-6p_z$ hybrid orbitals (right-hand side).

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Supporting Information Available: Tables listing absorbance and concentration data for the various temperatures studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] Krogmann, K. *Angew. Chem., Int. Ed. Engl.* **1969**, *1*, 35.