At concentrations greater than 7×10^{-3} M in carbon disulfide, new signals appear in the EPR spectrum of $((TPP)Fe)_2N$ at $g = 2.12$ and 2.04 (Figure 2). The $g = 2.01$ signal is more intense relative to the 2.15 signal than in the spectrum recorded on lower concentration samples. Also, a broad shoulder is observed on the low-field side of the $g = 2.15$ signal. The spectrum obtained for the new species by subtracting the powder pattern of the species observed at low concentrations (with the assumption that the $g = 2.15$ signal is entirely due to the latter species) is shown in Figure 3. The resulting powder pattern is similar to that expected for a simple rhombic ($g = 2.12$, $g = 2.04$, and $g = 2.01$) system, except for the broad shoulder near $g \approx 2.20$. These new signals which are observed at high concentrations are similar to (although not identical with) those reported in our preliminary EPR study of $((TPP)Fe)_2N$.[1,13] The details of the appearance of the EPR spectrum of $((TPP)Fe)_2N$ at high cncentrations in carbon disulfide are quite sensitive to the exact concentration and rate of cooling. Some solute precipitation and aggregation are apparent upon freezing the nearly saturated solutions. In all of the preparations at high concentration, a signal is observed at $g = 4.14$. This signal is characteristic of a triplet species and suggests that the new signals which appear in the EPR spectrum are due to $((TPP)Fe)_2N$ molecules which form aggregates in which first-order magnetic interactions occur between two of the $S = {}^1/_2$ spin centers.

We have attempted to determine the separation and relative orientation of the interacting molecules in the aggregate unit by performing computer simulations of the triplet EPR spectrum using the theoretical procedures developed by Smith and Pilbrow[14-18] to describe two coupled $S = {}^1/_2$ spin centers. Unfortunately, the separation and relative orientation for the two spin centers cannot be determined unambiguously. The computer simulations do show, however, that the $\Delta m_s = 2$ transition of the triplet species can only be calculated at the observed value of $g = 4.14$ if the **g** tensor of *each* of the interacting molecules is rhombic with the values $g = 2.12$, $g = 2.04$, and $g = 2.01$ (Figure 3). Interactions between two spin centers with axially symmetric **g** tensors ($g_\perp = 2.15$ and $g_\parallel = 2.01$) or between one molecule with the axially symmetric **g** tensor and another with the rhombic tensor result in calculated $\Delta m_s = 2$ transitions at $g = 4.27$ and $g = 4.21$, respectively.

The lowering of the symmetry of the **g** tensor from axial to rhombic which occurs in the interacting $((TPP)Fe)_2N$ molecules suggests that there is a weak electrostatic interaction between the molecules in the oligomeric unit, in addition to the magnetic dipole–dipole coupling which results in the triplet EPR signal. Although our computer simulations of the triplet spectrum do not allow the unambiguous determination of the relative orientation of the two molecules, certain geometries would seem to be more consistent with the rhombicity in the **g** tensor. For example, the interactions between the phenyl groups on neighboring molecules situated side-by-side or side-by-side and rotated 90° with respect to one another could result in a slight distortion of the Fe–N–Fe linkage from linearity. Such a distortion would break the degeneracy of the e_1 molecular orbitals[7] and mix d_{xz} (d_{yz}) character into the a_1 (d_{z^2}) orbital which contains the unpaired electron, resulting in a rhombic **g** tensor. A separation between the bridging nitrogen atoms on adjacent molecules in a side-by-side structure of ~9 Å would be close enough for substantial steric interactions to occur.[4] A simple stacked structure would seem to be less likely since this structure would not maintain the symmetry between the halves of the unit were the constituents to have a rhombic **g** tensor. The fact that simple monomeric tetraphenylporphyrins *do not* form dimeric species in solution also suggests that a stacked structure is unlikely.[17-19] Presumably, the bulky phenyl groups prevent the face-to-face approach of the porphyrin macrocycles. Thus, the structural features which are unique to the $((TPP)Fe)_2N$ unit must be the dominant factor in the interaction rather than features which are common to both simple monomeric and dimeric tetraphenylporphyrins.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Cottrell Research Grants Program of the Research Corp., and the Committee on Research, University of California, Riverside, CA, for support of this research. We thank Professor J. R. Pilbrow for providing the triplet EPR simulation program and Mr. Craig D. Martin for aid with the program. We also thank Professor M. F. Rettig and Professor J. R. Pilbrow for helpful discussions. We are grateful to Professor L. A. Bottomley for communicating his results to us prior to publication.

Registry No. $((TPP)Fe)_2N$, 59114-43-1.

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(12) Dickinson, L. C.; Chien, J. C. W. *J. Am. Chem. Soc.* **1971**, *93*, 5036–5040.

(13) The concentration of $((TPP)Fe)_2N$ is given as 0.1 mg/mL in the caption of Figure 2 of ref 1. This value is in error and should read 10 mg/mL.

(14) Dunhill, R. H.; Pilbrow, J. R.; Smith, T. D. *J. Chem. Phys.* **1966**, *45*, 1474–1481.

(15) Boas, J. F.; Dunhill, R. H.; Pilbrow, J. R.; Srivastava, R. C.; Smith, T. D. *J. Chem. Soc. A* **1969**, 94–108.

(16) Price, J. H.; Pilbrow, J. R.; Murray, K. S.; Smith, T. D. *J. Chem. Soc. A* **1970**, 968–976.

(17) Boyd, P. D. W.; Smith, T. D.; Price, J. H.; Pilbrow, J. R. *J. Chem. Phys.* **1972**, *56*, 1253–1263.

(18) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1974**, *13*, 173–278.

(19) (a) White, W. I. "The Porphyrins"; Dolphin, D. E., Ed.; Academic Press: New York, 1978; Vol. V, pp 303–339. (b) Scheer, H.; Katz, J. J. "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 399–524.

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A Reinvestigation of the Kinetics of the $Co(CN)_5OH_2^{2-}$–N_3^- Reaction

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The earliest[1] kinetic measurements of the reactions of $Co(CN)_5OH_2^{2-}$ with N_3^- or SCN^- yielded pseudo-first-order rate constants, k_{obsd}, that varied with the anion concentration, $[X^-]$, according to eq 1. At 40.0 °C and ionic strength 1.0 M

$$k_{obsd} = k_1[X^-]/((k_2/k_3) + [X^-]) \qquad (1)$$

($NaClO_4$), values of k_1 and k_2/k_3 were 1.4×10^{-3} s^{-1} and 1.7 M, respectively, for N_3^- (pH 6.4) and 2.0×10^{-3} s^{-1} and 3.9 M, respectively, for SCN^- (pH 3.4).[2] The functional dependence of k_{obsd} with respect to $[X^-]$ and the reasonable agreement between the values of k_1 for the azide and thiocyanate systems were interpreted on the basis of an S_N1 mechanism for the reactions under consideration.[1]

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(1) Haim, A.; Wilmarth, W. K. *Inorg. Chem.* **1962**, *1*, 573.

(2) The values of k_1 and k_2/k_3 given in the present paper differ from those given in ref 1. The values reported in ref 1 had been obtained by a graphical procedure. The values reported in the present paper were obtained by nonlinear least-squares calculation.

More recently,[3] in connection with some photosubstitution studies of $Co(CN)_5OH_2^{2-}$, the thermal reaction with N_3^- was briefly studied. The measurements, carried out at 25 °C, pH 8, and ionic strength 1.0 M, yielded pseudo-first-order rate constants that exhibited the functional dependence of eq 1 with $k_1 = 3.5 \times 10^{-4}$ s^{-1} and $k_2/k_3 = 3.0$ M.[3]

Very recently,[4] the reactions of $Co(CN)_5OH_2^{2-}$ with N_3^- and SCN^- were studied in detail. These studies yielded a functional dependence of k_{obsd} upon $[SCN^-]$ given by eq 1 with $k_1 = 2.3 \times 10^{-3}$ s^{-1} and $k_2/k_3 = 3.7$ M. However, a first-order dependence of k_{obsd} upon $[N_3^-]$ was obtained, $k_{obsd} = k[N_3^-]$, with $k = (6.62 \pm 0.13) \times 10^{-4}$ M^{-1} s^{-1} at 40.0 °C, ionic strength 1.0 M, and pH 6.4 (0.01 M phosphate). Since the mechanistic interpretation of the original data[1] depends *critically* on a less than a first-order dependence with respect to $[N_3^-]$, new kinetic measurements of the $Co(CN)_5OH_2^{2-}$–N_3^- reaction have been carried out and are reported herein.

Experimental Section

Materials. Sodium perchlorate (G. F. Smith) and sodium azide (Fisher) were recrystallized twice from water. The house-distilled water was deionized and then distilled in a modified (all-glass) Corning Model AG1B apparatus. $K_3[Co(CN)_5Cl]$ was prepared by reaction of $[Co(NH_3)_5Cl]Cl_2$ with the stoichiometric amount of potassium cyanide. Aquation of $Co(CN)_5Cl^{3-}$ yielded a solution of $Co(CN)_5OH_2^{2-}$ with a molar absorbance of 279 M^{-1} cm^{-1} at 380 nm. $K_6[Co_2O_2(CN)_{10}]\cdot H_2O$ was prepared as described.[5] Aquation of $Co_2O_2(CN)_{10}^{6-}$ in the presence of the theoretical amount of HCl followed by decomposition of the H_2O_2 produced by heating at 50 °C for ~3 h[1] yielded a solution of $Co(CN)_5OH_2^{2-}$ with a molar absorbance of 260 M^{-1} cm^{-1} at 380 nm.

Kinetic Measurements. Solutions containing the desired amounts of pH 6.86 phosphate buffer, sodium perchlorate, and sodium azide were placed in a constant-temperature bath at 40.0 °C. After temperature equilibration, the desired volume of a solution of $Co(CN)_5OH_2^{2-}$ at 40.0 °C was added. The resulting solution, which was 0.020 M in total phosphate, ~8 × 10^{-4} M in $Co(CN)_5OH_2^{2-}$, 0.2–0.9 M in NaN_3, and had enough sodium perchlorate to maintain a 1.00 M ionic strength, was transferred rapidly to a 1-cm cell in the thermostated (40.0 °C) cell compartment of a Cary 118 spectrophotometer. A continuous recording of the absorbance vs. time at 380 nm was obtained for a period of ~15–20 half-lives. The analogue absorbance vs. time data were digitized with a 9864A Hewlett-Packard digitizer and then processed in a 9820 Hewlett-Packard calculator by one or both of two procedures. One was a linear least-squares procedure that utilized a fixed A_∞ value to obtain k_{obsd} from the function $\ln (A_t - A_\infty) = \ln (A_0 - A_\infty) - k_{obsd}t$. The other procedure floated A_∞ so that the A_t vs. t data gave the best fit to the $\ln (A_t - A_\infty) = \ln (A_0 - A_\infty) - k_{obsd}t$ equation, and calculated the least-squares value of k_{obsd}.

Results and Discussion

In the first set of measurements the $Co(CN)_5OH_2^{2-}$ solution was prepared by aquation of $Co(CN)_5Cl^{3-}$. Each individual kinetic run obeyed good first-order kinetics, e.g., plots of $\ln (A_t - A_\infty)$ vs. t, with A_∞ measured after 8–10 half-lives were linear for at least 3 half-lives. For each run, the absorbance after about 8 half-lives changed only very slowly. For example, with $[N_3^-] = 0.774$ M, the absorbances after 10 000 s (~$8t_{1/2}$), 13 000 s (~$10t_{1/2}$), and 23 000 s (~$17t_{1/2}$) were 0.580, 0.581, and 0.583, respectively. Moreover, the value of A_∞ which gave the best linear fit of $\ln (A_t - A_\infty)$ vs. t was 0.580. Values of k_{obsd} obtained by fixing A_∞ at the absorbance value after 8–10 half-lives (these fixed A_∞ values agreed within 0.002 absorbance units with the values obtained by floating A_∞) are listed in Table I and plotted in Figure 1 (filled circles). It will be seen that k_{obsd} varies lineary with $[N_3^-]$. A linear least-squares treatment of the k_{obsd} vs. $[N_3^-]$ data gave a slope of (6.69 ± 0.14) × 10^{-4} M^{-1} s^{-1} if the intercept was allowed to float (intercept was (4.6 ± 9.6) × 10^{-6} s^{-1}) and a slope of (6.76 ± 0.08) × 10^{-4} M^{-1} s^{-1} if the intercept was fixed at 0. The results agree well with those of Burnett and Gilfillan[4] as can be seen by comparing the filled circles (present work) and the filled squares[4] in Figure 1 and also by comparing the reported[4] second-order rate constant (6.62 ± 0.13) × 10^{-4} M^{-1} s^{-1} with the value obtaned in the present work (6.76 ± 0.18) × 10^{-4} M^{-1} s^{-1} (fixed 0 intercept). Since the original[1] measurements (Figure 1, open squares) did not exhibit a first-order dependence with respect to $[N_3^-]$, a second set of measurements was carried out in an attempt to elucidate possible reasons for the discrepancy between the original and the present measurements. In this set, $Co(CN)_5OH_2^{2-}$ solutions were prepared, as was done in the original work,[1] by acid aquation of $Co_2O_2(CN)_{10}^{6-}$ followed by heating the solution at 50 °C for ~3 h to decompose the hydrogen peroxide produced. For each run in this set, the absorbance continued increasing after 8–10 half-lives. For example, with $[N_3^-] = 0.854$ M, the absorbances at 10 000 s (~$7t_{1/2}$), 15 000 (~$11t_{1/2}$), and 25 000 s (~$18t_{1/2}$) were 0.572, 0.580, and 0.582, respectively. Moreover, treatment of the A_t vs. t data with the program that floats A_∞ gave a value of A_∞ of 0.569. With $[N_3^-] = 0.221$, the absorbances at 38 000 s (~$8t_{1/2}$) and 78 000 s (~$16t_{1/2}$) were 0.535 and 0.545, respectively, while the floated value of A_∞ was 0.525. Moreover, tailing in the absorbance vs. time traces was clearly discernible after about 4 half-lives. Evidently, the solutions of $Co(CN)_5OH_2^{2-}$ prepared from $Co_2O_2(CN)_{10}^{6-}$ contain a slowly reacting component, pre-

Table I. Pseudo-First-Order Rate Constants for the Reaction of $Co(CN)_5OH_2^{2-}$ with N_3^- [a]

$[N_3^-]$, M	10^4k_{obsd},[b] s^{-1}	$[N_3^-]$, M	10^4k_{obsd},[c] s^{-1}
0.227	1.50	0.221	1.50
0.379	2.69	0.403	2.53
0.566	3.96	0.616	3.75
0.700	4.83	0.714	4.24
0.774	5.19	0.854	4.95
0.797	5.19	0.903	5.01
0.904	6.16		
0.909	6.17		

[a] At 40.0 °C, 0.020 M phosphate buffer pH 6.86, ionic strength 1.00 M (sodium perchlorate), $[Co(CN)_5OH_2^{2-}] \approx 8 \times 10^{-4}$ M.
[b] $Co(CN)_5OH_2^{2-}$ prepared by aquation of $Co(CN)_5Cl^{3-}$.
[c] $Co(CN)_5OH_2^{2-}$ prepared by acid hydrolysis of $Co_2Co_2(CN)_{10}^{6-}$ with the stoichiometric amount of HCl followed by heating at 50 °C for 3 h.

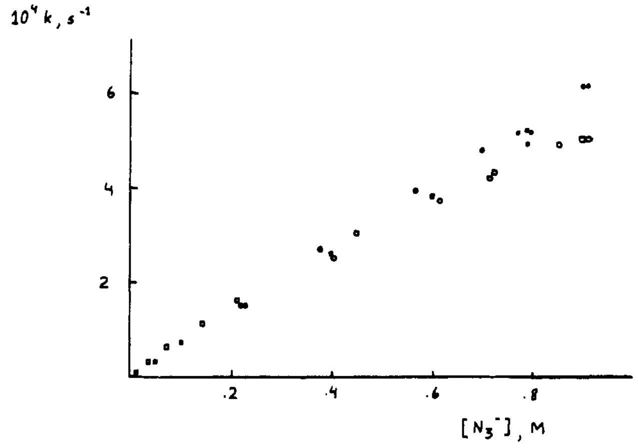

Figure 1. Observed rate constants at 40.0 °C and ionic strength 1.00 M vs. azide ion concentration: (closed circles) present work with $Co(CN)_5OH_2^{2-}$ prepared from $Co(CN)_5Cl^{3-}$; (closed squares) work from ref 4; (open circles) present work with $Co(CN)_5OH_2^{2-}$ prepared from $Co_2O_2(CN)_{10}^{6-}$; (open squares) work from ref 1.

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(3) Viaene, L; D'Olieslager, J.; De Jaegere, S. *Bull. Soc. Chim. Belg.* **1976**, *85*, 89.
(4) Burnett, M. G.; Gilfillan, M. W. *J. Chem. Soc., Dalton Trans.* **1981**, 1578.
(5) Haim, A.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1961**, *83*, 509.

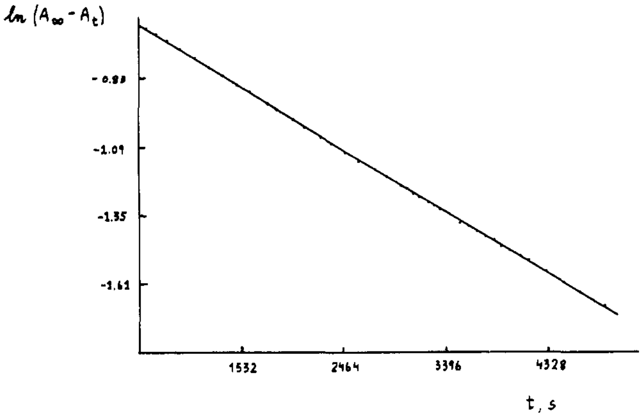

Figure 2. ln ($A_\infty - A_t$) vs. time plot for the $Co(CN)_5OH_2^{2-}$–N_3^- reaction at 40.0 °C, [N_3^-] = 0.403 M, pH 6.86, $Co(CN)_5OH_2^{2-}$ prepared from $Co_2O_2(CN)_{10}^{6-}$.

sumably the polymeric pentacyanocobaltate(III) produced on heating concentrated solutions of the monomer.[5,6] The lower molar absorbance of $Co(CN)_5OH_2^{2-}$ solutions prepared from $Co_2O_2(CN)_{10}^{6-}$ as compared to $Co(CN)_5OH_2^{2-}$ solutions prepared from $Co(CN)_5Cl^{3-}$ is indicative of the presence of the polymeric species.[5] The tailing noted above would not have been observed in the earlier[1] work (if indeed such tailing obtained) because a manual spectrophotometer and a point-sampling technique were utilized: five to six samples were withdrawn during the first 2 half-lives, the "infinity" absorbance was measured after 8–10 half-lives, and the slopes of the ln ($A_\infty - A_t$) vs. t plots were estimated by a graphic procedure. In fact, if the present measurements are processed by a similar procedure, namely, least-squares fitting of ln ($A_\infty - A_t$) vs. t data during 2 half-lives utilizing a fixed A_∞ value measured after 8–10 half-lives, excellent first-order plots are obtained (Figure 2). The slopes of these plots give k_{obsd} values (listed in column 4 of Table I) in agreement with those reported earlier.[1] (Compare the open circles, present work, with the open squares, earlier work, in Figure 1.)

Although the earlier results[1] can be reproduced if the same preparations and methods for treating the data are followed, the present data obtained with samples of $Co(CN)_5OH_2^{2-}$ prepared from $Co(CN)_5Cl^{3-}$ and the new results[4] obtained with $Co(CN)_5OH_2^{2-}$ prepared from $Co(CN)_6^{3-}$ almost certainly represent the intrinsic $Co(CN)_5OH_2^{2-}$–N_3^- reaction. Therefore, it must be concluded, as Burnett and Gilfillan[4] did, that the reaction is first order in azide. Presumably, the deviations from first-order behavior in azide observed in the earlier work[1] and in the present work with samples prepared from $Co_2O_2(CN)_{10}^{6-}$ are associated with the presence of the polymeric pentacyanocobaltate(III) species in the reacting solutions. However, there are some unanswered questions. Even with samples of $Co(CN)_5OH_2^{2-}$ prepared by photolysis of $Co(CN)_6^{3-}$, a procedure that appears to produce pure samples,[7-10] both first-order[4] and less than first-order[3] kinetics with respect to azide ion have been reported. Moreover, the reaction of $Co(CN)_5OH_2^{2-}$ with SCN^- studied with samples prepared from either $Co_2O_2(CN)_{10}^{6-}$[1] or from $Co(CN)_6^{3-}$[4] exhibits in both cases the functional dependence of eq 1.[11] Evidently, additional work is necessary. However, since the functional dependence given by eq 1 for the $Co(CN)_5OH_2^{2-}$–N_3^- reaction was of *essence* in the assignment of an S_N1 mechanism to substitution reactions of pentacyanocobaltate(III) complexes,[1] with the finding of a first-order reaction with respect to N_3^-, the question of the mechanism of these reactions must be regarded as unsettled by the kinetic measurements. On the basis of measurements of volumes of activation[12] and of linear free energy considerations,[4] it seems clear that a dissociative mechanism obtains, but whether a genuine, long-lived pentacoordinate intermediate is present in the spontaneous substitution reactions remains an open question. Intermediates are apparently present in the assisted[13,14] substitution reactions of $Co(CN)_5N_3^{3-}$ (by H^+ and by NO^+), but preliminary measurements of competition ratios suggest different intermediates for different reactions. Still different intermediates appear to be formed in the photochemical reactions of $Co(CN)_6^{3-}$[7,15] and $Co(CN)_5OH_2^{2-}$.[5,7] In this context, it is noteworthy that a common pentacoordinate intermediate has been excluded in the spontaneous aquations of pentaamminecobalt(III) complexes[16] and that the question of a common intermediate in their assisted aquations is highly controversial.[17-19]

Registry No. $Co(CN)_5OH_2^{2-}$, 14842-83-2; N_3^-, 14343-69-2.

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(6) Similar polymerization effects and tailing in the absorbance vs. time traces are observed with aged solutions of $Fe(CN)_5OH_2^{3-}$: Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 2080. Jwo, J. J.; Haim, A. *J. Am. Chem. Soc.* **1976**, *98*, 1172.

(7) Adamson, A. W.; Chiang, A.; Zinato, E. *J. Am. Chem. Soc.* **1969**, *91*, 5467.

(8) Moggi, L.; Bolletta, F.; Balzani, V.; Scandola, F. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2589.

(9) Wrighton, M.; Bredesen, D. *Inorg. Chem.* **1973**, *12*, 1707.

(10) However, note that molar absorbances 301 and 260 M^{-1} cm^{-1} at 380 nm are reported for $Co(CN)_5OH_2^{2-}$ prepared by photolysis of $Co(CN)_6^{3-}$: ref 4. Nishazawa, M.; Ford, P. C. *Inorg. Chem.* **1981**, *20*, 294.

(11) For thiocyanate, there exists the additional complication associated with the formation of N- and S-bonded linkage isomers and their possible interconversion during reaction.

(12) Palmer, D. A.; Kelm, H. *Z. Anorg. Allg. Chem.* **1979**, *450*, 50.

(13) Haim, A.; Wilmarth, W. K. *Inorg. Chem.* **1962**, 1, 583.

(14) Haim, A.; Grassi, R.; Wilmarth, W. K. *Adv. Chem. Ser.* **1965**, *No. 49*, 31.

(15) Wrighton, M.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 5254.

(16) Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M.; Jackson, W. G. *Inorg. Chem.* **1981**, *20*, 1647.

(17) Buckingham, D. A.; Edwards, J. D.; Lewis, T. W.; McLaughlin, G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 892.

(18) Reynolds, W. L.; Hafezi, S.; Kessler, A.; Holly, S. *Inorg. Chem.* **1979**, *18*, 2860.

(19) Jackson, W. G.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 1001.

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Dinuclear, Metal–Metal-Bonded Platinum(III) Compounds. 1. Preparation and Structure of $K_2[Pt_2(SO_4)_4(OSMe_2)_2]\cdot 4H_2O$

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In recent years it has become evident that there is a class of dinuclear compounds of platinum(III) containing metal–metal bonds comparable to those of rhodium(II),[1] although it is not yet clear whether this class of Pt^{III}_2 species will be as extensive as the rhodium group. Thus far only a few have been identified conclusively by X-ray crystallography. These are $K_2[Pt_2(SO_4)_4(H_2O)_2]$[2] (**1**), $[Pt_2(O_2CCF_3)_2(CH_3)_4(p\text{-}CH_3C_5H_4N)_2]$[3] (**2**), $[(H_2O)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2$-

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(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982; Chapter 8.

(2) Muraveiskaya, G. S.; Kukina, G. A.; Orlova, V. S.; Evstaf'eva, O. N.; Porai-Koshits, M. A. *Dokl Akad. Nauk SSSR* **1976**, *226*, 76.

(3) Schagen, J. D.; Overbeek, A. R.; Schenk, H. *Inorg. Chem.* **1978**, *17*, 1938.