

Figure 4. Calculated 270.13-MHz proton spectrum of  $^{11}\text{B}_2\text{H}_6$ . (See Table I for parameters.)

Table I. Optimum  $J$  Coupling Values (Hz) for Calculated  $\text{B}_2\text{H}_6$   $^1\text{H}$  and  $^{11}\text{B}$  Spectra

$J(^{11}\text{B}-^{11}\text{B})$	$\pm 3.8 \pm 0.5^{*a,b}$	$ J(\text{H}_t-\text{H}_t) $	$7.45 \pm 0.5^{*a,c}$
$ J(^{11}\text{B}-\text{H}_b) $	$46.3 \pm 0.5^{*a}$	$J(\text{H}_t-\text{H}_t)$ (cis or trans)	$\pm 14.8 \pm 1.0^d$
$J(^{11}\text{B}-\text{H}_t)$	$+133.5 \pm 1.0$	$J(\text{H}_t-\text{H}_t)$ (trans or cis)	$\pm 4.5 \pm 1.0^d$
$J(^{11}\text{B}-\text{H}_t)$	$+4.0 \pm 1.0$	$ J(\text{H}_t-\text{H}_t)$ (gem)	$4.5 \pm 1.0$

<sup>a</sup> Key:  $\text{H}_t$ , terminal proton;  $\text{H}_b$ , bridge proton; \*, directly measured. <sup>b</sup> The sign of  $J(\text{B}-\text{B})$  can be either negative or positive; it has the same sign as  $J(\text{H}-\text{H})$ (cis and trans). <sup>c</sup> Reversing the sign of  $J(\text{H}_t-\text{H}_t)$  has no effect on the calculated spectrum. <sup>d</sup> Same comment as footnote b.

### Calculated Spectra

SPINNAKER (spin polarization intensities of numerous Nuclei analyzed by key eigenvector rotations), a modified version of the UEANMRII NMR simulation program,<sup>7-9</sup> was used to calculate the  $^{11}\text{B}$  and  $^1\text{H}$  spectra. SPINNAKER is capable of calculating spectra for systems containing nuclei with spins greater than  $1/2$  and makes use of symmetry. The present version can accommodate up to seven spins of any spin quantum number or up to seven groups of equivalent spin  $1/2$  nuclei (e.g., a  $\text{CH}_3$  group is treated as a single group spin with a group spin quantum number of  $3/2$ ). All the calculations here were done with an IBM S-9000 computer. Source programs are available on request.

Most often, iterative calculations are used to achieve an optimum fit between computed and experimental spectra. An iterative procedure was not possible in the case of diborane, however, because its proton and boron spectra consist of several thousand transitions, all of which were not resolved. Several trial sets of coupling constants were used in the computations until an optimum fit to the experimental spectrum was achieved. Only those coupling constants for which a direct measurement was not possible were varied. The directly observed parameters were  $J(\text{H}_b\text{H}_t) = 7.45$  Hz,  $J(\text{B}-\text{B}) = 3.8$  Hz,  $J(\text{BH}_b) = 46.3$  Hz, and  $|J(\text{BH}_t) + J(\text{BH}_t)| = 137.5$  Hz. Unless  $J(^{11}\text{B}-^{11}\text{B}) > 0$ , no combination of the other coupling constants produced a calculated proton spectrum that came even close to matching the observed spectrum. Furthermore, if the value of  $J(\text{B}-\text{B})$  was changed by more than  $\pm 0.5$  Hz from its directly measured value of 3.8 Hz, no reasonable fit could be obtained.

The closest fit of calculated to experimental proton and boron-11 spectra was obtained with the  $J(\text{H}_t-\text{H}_t)$ (cis and trans) and  $J(\text{B}-\text{B})$  having the same relative signs. In particular, the fine structure near the three main middle peaks in the calculated  $^{11}\text{B}$  spectrum clearly fits the experimental spectrum best when the relative signs of the three couplings were identical.  $J(\text{H}-\text{H})$ (geminal) had the greatest influence on these same features, yet it had no effect on other parts of the calculated  $^{11}\text{B}$  spectrum.

Figures 4 and 5 show the calculated fully coupled  $^{11}\text{B}$  and  $^1\text{H}$  spectra that gave the closest fit to the experimental spectra. Minor discrepancies remain that are due to error in the three, less critical cis, trans, and geminal proton-proton couplings. Table I sum-

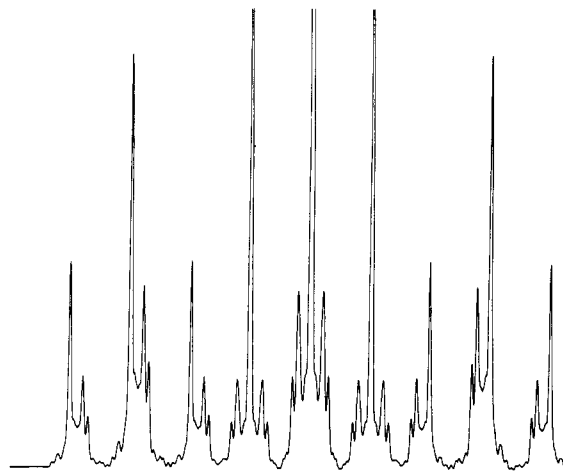


Figure 5. Calculated 86.7-MHz boron-11 spectrum of  $^{11}\text{B}_2\text{H}_6$ . (See Table I for parameters.)

marizes the chemical shift and coupling parameters that correspond to the best fit, calculated spectra.

The experimental and calculated results reported here agree well with some of those reported earlier.<sup>1,2</sup> The present results are not, however, in such good agreement with those reported in ref 4. Odom and co-workers<sup>4</sup> obtain an upper limit of the  $^{11}\text{B}-^{11}\text{B}$  spin coupling constant of  $1.1 \pm 0.2$  Hz, on the basis of a series of elegant multiple-resonance experiments. We can only speculate on the difference between our values and theirs. In our view, the most plausible explanation is the greatly improved sensitivity, resolution, and dispersion of modern high-field FT NMR instruments compared to those used by Odom over 12 years ago (in 1972).

### Conclusions

Because of its small size and simplicity, diborane is an attractive model compound for a variety of theoretical studies, including calculations of the proton and boron-11 chemical shifts and coupling constants. The present studies provide clear experimental results that unequivocally demonstrate that for diborane  $J(\text{B}-\text{B}) > 0$ . The results presented here provide reasonably precise values for most of the NMR parameters and can be used as experimental bench marks for future theoretical work.

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Registry No.  $\text{B}_2\text{H}_6$ , 19287-45-7;  $^{10}\text{B}$ , 14798-12-0.

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### Kinetic and Equilibrium Study of the Monomer-Dimer Reaction of [Tetrakis(*p*-(trimethylammonio)phenyl)porphinato]silver(III) in Aqueous Medium

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The aggregation of porphyrins and porphyrin-like molecules has been the subject of several recent reports.<sup>1-4</sup> Not only do

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these molecules aggregate in water due in part to their hydrophobicity and to their near planarity but their metal complexes, which may be neutral, yet coordinatively unsaturated, have been found to aggregate in nonpolar solvents in such a manner as to satisfy the coordination of the central metal ion.<sup>3</sup>

In order to solubilize these synthetic porphyrins in water several ionic functional groups may be substituted into the peripheral positions. If poorly solvated, these porphyrins with negatively charged functional groups tend to aggregate appreciably.<sup>4-6</sup> Further, water-soluble metalloporphyrins that have a central metal ion that will form a stable square-planar complex tend to aggregate in a way to minimize their hydrophobic repulsion.<sup>7</sup> In other instances such properties of the metal ion as chelation also aid aggregate formation.

Tetrakis(*N*-methylpyridinium-4-yl)porphyrin, a peripherally positively charged synthetic porphyrin, and its metal complexes have been found to be nonaggregating by *T*-jump studies.<sup>6</sup> A similar positively charged porphyrin, tetrakis(*p*-(trimethylammonio)phenyl)porphyrin also does not aggregate, although some of its metal derivatives, particularly Cu(II), Ni(II), and Ag(II) complexes, do.<sup>8</sup>

Trivalent silver, being isoelectronic with Pd(II), is expected to form stable square-planar complexes. We have studied and characterized the equilibrium and kinetics of the dimerization of [tetrakis(*p*-(trimethylammonio)phenyl)porphinato]silver(III) (AgTAPP).

### Experimental Section

Sodium nitrate (Allied Chemical, B & A quality), *N*-(2-hydroxyethyl)piperazine-*N*-2-ethanesulfonic acid (HEPES) (United States Biochemical), potassium peroxydisulfate (Allied Chemical), and other common chemicals were used as received. [Tetrakis(*p*-(trimethylammonio)phenyl)porphinato]silver(II) perchlorate (Ag<sup>II</sup>TAPP) was synthesized as described by Okoh.<sup>9</sup> One gram of the perchlorate salt of Ag<sup>II</sup>TAPP was dissolved in 400 mL of hot distilled water and passed through a column of anion-exchange resin (Rexyn 202, Fisher) in the acetate form. The effluent solution was evaporated to 100 mL, 0.1 g sodium acetate was added, and the solution was brought to a boil. Potassium peroxydisulfate (0.1 g) was then added. Five minutes after the addition, a drop of the porphyrin solution was withdrawn, diluted to 5 mL with 0.1 M HNO<sub>3</sub>, and tested for completeness of oxidation by recording the spectrum. If there was any dication form of the porphyrin in the solution as indicated by the absorption in the 650–700-nm region, a further 0.1-g sample of peroxydisulfate was added. One such addition was found to be sufficient. To this AgTAPP solution was added saturated NaClO<sub>4</sub> solution dropwise with stirring until precipitation of the AgTAPP perchlorate was complete. The precipitate was filtered, washed with small portions of ice-cold water, and dried in vacuo. (Caution! Perchlorate salts of organic compounds are known to be explosive!). Anal. Calcd for C<sub>56</sub>H<sub>74</sub>N<sub>8</sub>Cl<sub>5</sub>O<sub>27</sub>Ag (mol wt 1576): C, 42.6; H, 4.7; N, 7.1. Found: C, 42.5; H, 3.8; N, 7.4. Analyses were performed by MicAnal.

The kinetics of the monomer–dimer equilibrium were studied at 420 nm on a temperature-jump apparatus that has been described previously.<sup>10</sup> Known concentrations of AgTAPP were made by weight, the pH was adjusted to 7.0 with HEPES buffer (0.01 M), and the salt concentration was fixed at 0.05 M. This salt concentration allowed a sufficiently short heating time constant for the Joule heating and at the same time did not shift the equilibrium to an extreme in favor of the dimer.

A Beckman Acta CIII spectrophotometer with thermostated sample compartment and a Radiometer Model PHM 64 pH meter were used for

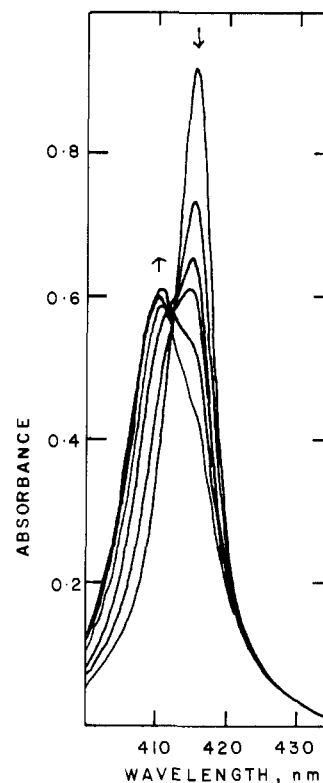


Figure 1. Variation of the spectrum (Soret region only) of AgTAPP with the increase in NaNO<sub>3</sub> concentration. (Arrows point the direction of change of absorption with the increasing nitrate concentration.)

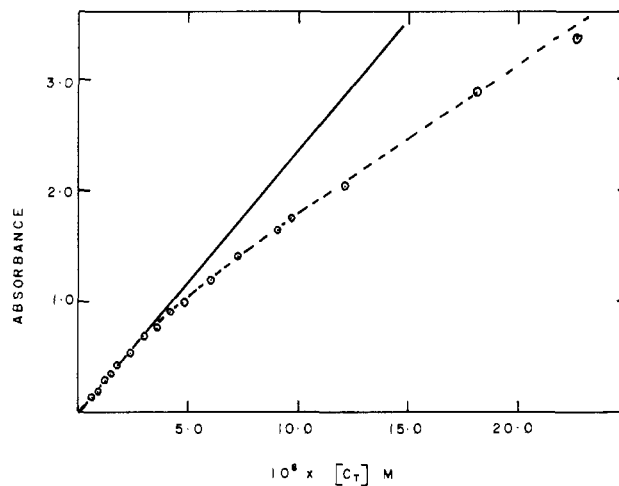


Figure 2. Plot of absorbance at 420 nm vs. concentration of AgTAPP.

Beer's law and equilibrium studies.

### Results and Discussion

Earlier studies established that addition of inert electrolytes to the solution of some porphyrins promoted aggregation.<sup>6,7</sup> To determine the optimum inert salt concentration, spectrophotometric titrations were carried out. The AgTAPP concentration was kept constant, but the NaNO<sub>3</sub> concentration was varied. The resulting spectra are shown in Figure 1. From a plot of the absorbance at 420 and 410 nm vs. NaNO<sub>3</sub> concentration, it was found that salt concentrations greater than 0.15 M shifted the equilibrium completely in favor of the dimer. An optimum salt concentration of 0.05 M was then chosen for this study.

Several porphyrin solutions in the concentration range  $6.0 \times 10^{-7}$  to  $2.4 \times 10^{-5}$  M were made from the stock solution and their spectra in the Soret region recorded at 25 °C. Absorbances of these solutions at 420 and 410 nm were plotted vs. porphyrin concentration. Figure 2 shows a plot of the results obtained at 420 nm. The concentration range to be used in the kinetic studies

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**Table I.** Experimental Reciprocal Relaxation Times and Their Concentration Dependence<sup>a</sup>

$C_{Ag^{III}}$ , M $\times 10^6$	$1/\tau$ , s <sup>-1</sup> $\times 10^{-3}$	$C_{Ag^{III}}$ , M $\times 10^6$	$1/\tau$ , s <sup>-1</sup> $\times 10^{-3}$
$t = 10^\circ\text{C}$			
4.83	1.61	10.87	2.20
6.04	1.59	12.08	2.21
7.25	1.89	13.29	2.53
8.46	1.82	14.49	2.49
$t = 20^\circ\text{C}$			
1.18	1.68	7.08	3.25
3.54	2.32	9.44	3.54
4.72	2.78	10.87	3.76
6.04	2.91	14.49	4.22

<sup>a</sup> Conditions: pH 7.0; 0.05 M NaNO<sub>3</sub>; 420 nm.

**Table II.** Kinetic and Thermodynamic Results of the Relaxation Experiments

	10 °C	20 °C
$k_1$ , M <sup>-1</sup> s <sup>-1</sup>	$(9.33 \pm 0.02) \times 10^7$	$(1.04 \pm 0.03) \times 10^8$
$k_{-1}$ , s <sup>-1</sup>	$(5.51 \pm 0.09) \times 10^2$	$(1.36 \pm 0.07) \times 10^3$
$K$ , M <sup>-1</sup>	$1.69 \times 10^5$	$7.65 \times 10^4$

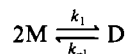
$\Delta H_1^\ddagger = 1.2$  kcal;  $\Delta S_1^\ddagger = -17.7$  eu  
 $\Delta H_{-1}^\ddagger = 14.3$  kcal;  $\Delta S_{-1}^\ddagger = +4.5$  eu  
 $\Delta H = -13.0$  kcal (-13.4 kcal)<sup>a</sup>;  $\Delta S = -22.0$  eu (-21.7 eu)<sup>a</sup>

<sup>a</sup> Computed from equilibrium data.

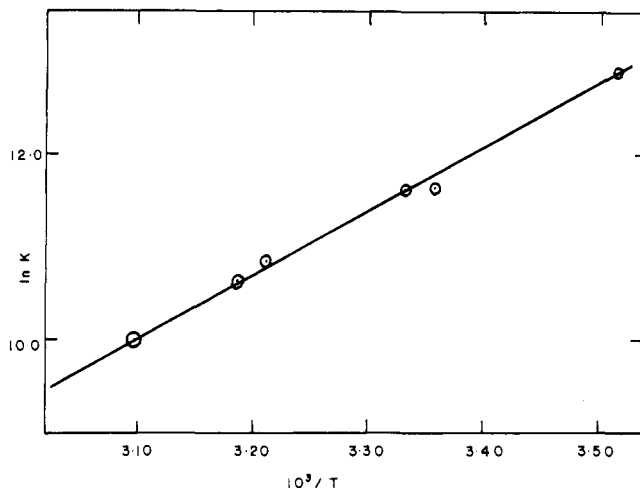
was determined from the nonlinear portions of these curves, where Beer's law is not obeyed. In this region, both monomer and dimer are present. From the linear region and by extrapolation of the nonlinear portions of the curves to the region of high porphyrin concentration, where the dimer is the exclusive species, the extinction coefficients of the monomer ( $\epsilon_M^\lambda$ ) and the dimer ( $\epsilon_D^\lambda$ ) were evaluated to be  $2.5 \times 10^5$ ,  $1.8 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup> at 420 nm and  $1.0 \times 10^5$ ,  $4.5 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup> at 410 nm, respectively. With these extinction coefficients and the absorbances in the nonlinear portion, the equilibrium constant,  $K_D$ , was computed to be  $1.2 \times 10^5$  M<sup>-1</sup> from the relationship  $K_D = (A_{420}\epsilon_M^{410} - A_{410}\epsilon_M^{420})(\epsilon_M^{410}\epsilon_D^{420} - \epsilon_M^{420}\epsilon_D^{410}) / (A_{410}\epsilon_D^{420} - A_{420}\epsilon_D^{410})^2$ , where  $A_{420}$  and  $A_{410}$  refer to absorbances at 420 and 410 nm, respectively. Four porphyrin solutions,  $(8-18) \times 10^{-5}$  M, were prepared and equilibrated at six different temperatures and their spectra recorded. Following the procedure outlined above, the equilibrium constants for these solutions were computed at these temperatures. A plot of  $\ln K$  vs.  $1/T$  was found to be linear (Figure 3), and the slope,  $\Delta H$ , for the equilibrium was computed to be -13.4 kcal. The extinction coefficients and equilibrium constant at 420 nm and 25 °C were also calculated by computer using a method described previously.<sup>11</sup> The results of the graphical and computer values were in excellent agreement. (See Table II.)

The kinetics were performed at two temperatures. The thermostat was adjusted such that the temperatures of the solution after the perturbation, the kinetic temperature, was either 10 or 20 °C. The exponentially changing relaxation signal was taken from the photomultiplier of the  $T$ -jump apparatus and digitized on a 12-Bit Aminco/DASAR. The data were then analyzed by using nonlinear least-squares fitting programs. Table I shows the experimental results. Eight concentrations of porphyrin were studied kinetically at each of the two temperatures. Four runs were averaged at each of these concentrations. The agreement of the reciprocal relaxation times was generally 5-10%.

For a monomer-dimer equilibrium



$k_1$  and  $k_{-1}$  are the forward and reverse rate constants and  $K = k_1/k_{-1}$ . The relaxation times are related to concentration by the

**Figure 3.** Plot of  $\ln K$  vs.  $1/T$  for the monomer-dimer equilibrium of AgTAPP.

equation<sup>6</sup>  $1/\tau^2 = 8k_1k_{-1}(C_T) + k_{-1}^2$  where  $C_T$  is the total concentration of the silver porphyrin. Table II shows the values of  $k_1$ ,  $k_{-1}$ , and  $K$  obtained at the two temperatures. In addition, the activation parameters and standard enthalpy and entropy have been estimated from the limited temperatures studied.

Using eq 90 of ref<sup>12</sup> and a diffusion coefficient of  $5 \times 10^{-6}$  cm<sup>2</sup>/s along with a value of  $5 \times 10^{-8}$  cm for  $a$ , the distance of closest approach, one obtains a value of approximately 1.0 for the diffusion-controlled rate constant for a pair of 5+ ions. Although AgTAPP has a charge of 5+, it is apparent that this charge is at least partially reduced since the experimentally determined association rate constant,  $k_1$ , is several orders of magnitude faster than a diffusion-controlled approach of two species of this charge type. If it is assumed that the association process is an uncomplicated diffusion-controlled reaction, then a calculation employing the experimentally obtained rate constant,  $k_1$ , and the same set of parameters as above, except the charge, yields a charge of 2+ on the monomeric porphyrins.

This charge reduction can be accomplished in at least two ways. Simple ion pairing of AgTAPP<sup>5+</sup> with available anions could be responsible, or a particular geometrical arrangement of the 5+ ions such that electrostatic repulsion is minimized through a skewing of the porphyrin rings is possible.<sup>3,13</sup> Extensive ordering of the rings into their final dimeric positions, with perhaps solvent participation, would suggest a two-step mechanism. Our findings do not support such a mechanism. We plan to investigate this and possible anion involvement in the near future.

Both  $k_1$  and  $k_{-1}$  determined for this silver(III) porphyrin compare favorably with such constants for other metalloporphyrins.<sup>7</sup> [Tetrakis(*N*-methylpyridin-4-yl)porphyrinato]nickel(II) has been shown to exist in solution in a square-planar form in equilibrium with an axially solvated form.<sup>14</sup> Unlike that complex, this silver(III) porphyrin, being only square planar, resembles the isoelectronic palladium(II) porphyrins more closely in its aggregation behavior. To our knowledge, this is the only silver(III) complex that has been shown to aggregate in solution.

In the meso-substituted synthetic porphyrins, the plane of the aromatic ring (phenyl, substituted phenyl, pyridyl) is known to be perpendicular to the plane of the porphyrin<sup>15</sup> (though in solution a certain extent of free rotation has been shown),<sup>16</sup> offering a steric hindrance to stacking. Since the charge density of positive ions is usually greater compared to similar negatively charged ions, an electrostatic repulsion to stacking exists in peripherally positively

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charged porphyrins. In agreement with this argument, no synthetic peripherally positively charged porphyrin has been found to aggregate in aqueous solution, to date. The only other peripherally positively charged porphyrin that has been shown to aggregate is a modified protoporphyrin<sup>17,18</sup> (with only hydrogens at meso positions) that contained ethylenediammonium side chains attached to the vinyl groups. There is a recent fluorescence, nonkinetic study<sup>19</sup> that suggests the stacking of the free base of tetrakis(*N*-methylpyridin-4-yl)porphyrin in water. The lack of quantitative information makes it difficult to compare with our results.

In spite of such steric as well as electrostatic factors, the fact that our silver(III) porphyrin aggregates in solution seems to indicate that its hydrophobicity, when compared to that of the free base, enhanced by the square-planar complex formation (which precludes solvation at the axial positions) is an important factor in aggregation, regardless of the type of charge at the peripheral positions. Furthermore, this dimerization of metalloporphyrins could be used as a guide in determining the coordination geometry of the central metal ion in solution as to whether it is square planar or not.

Registry No. [AgTAPP](ClO<sub>4</sub>)<sub>5</sub>, 96129-06-5.

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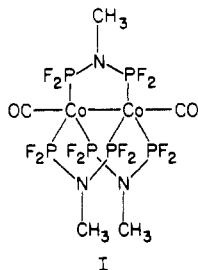
Contribution from the Laboratoire de Spectrochimie du Solide (LA 302), Université Paris VI, 75230 Paris Cedex 05, France, Department of Chemistry, University of Georgia, Athens, Georgia 30602, and Institut de Recherches sur la Catalyse, 69626 Villeurbanne Cedex, France

### Spectroscopic Properties of a Mixed-Valence Binuclear Cobalt Complex: [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Co<sub>2</sub>(CO)<sub>2</sub><sup>-</sup>

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In recent years (alkylamino)bis(difluorophosphines) have been used as novel bidentate ligands for stabilizing low metal oxidation state and metal-metal bonded systems.<sup>1</sup> The binuclear cobalt derivative [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Co<sub>2</sub>(CO)<sub>2</sub> was obtained by the reaction of the bidentate fluorophosphine CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> with Co<sub>2</sub>(CO)<sub>8</sub> at room temperature and atmospheric pressure.<sup>2,3</sup> X-ray diffraction studies on this complex reveal the presence of three CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> ligands bridging the Co-Co bond, with each cobalt atom having an approximately trigonal-bipyramidal environment (I).



This binuclear cobalt compound (I) is quite interesting because of the high stability of its [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Co<sub>2</sub> structural unit

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toward redox reactions. For example, this binuclear unit remains intact upon reaction with bromine to give a tetrabromide, [C-H<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Co<sub>2</sub>Br<sub>4</sub>.<sup>4</sup> Moreover, electrochemical studies on this complex indicate reversible one- and two-electron reductions giving a green radical anion, [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Co<sub>2</sub>(CO)<sub>2</sub><sup>-</sup>, and a pale yellow dianion, [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Co<sub>2</sub>(CO)<sub>2</sub><sup>2-</sup>, respectively.<sup>5</sup> Structural studies have not yet been performed on either the radical anion or the dianion owing to the difficulty of separating pure crystalline products from the supporting electrolyte. Nevertheless, the [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Co<sub>2</sub> structural unit seems to be preserved in these reduction products. Thus the two reduction steps are perfectly reversible, not only electrochemically but also chemically. The spectroscopic study described in this paper confirms this assumption. In addition, the radical anion is of special interest in being an unusual mixed-valence d<sup>9</sup>-d<sup>10</sup> cobalt dimer.

Other radical anions of dicobalt carbonyl derivatives have been reported in the literature. Thus Co<sub>2</sub>(CO)<sub>6</sub>(ER<sub>3</sub>)<sub>2</sub><sup>-6-8</sup> [ER<sub>3</sub> = (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>P, (CH<sub>3</sub>O)<sub>3</sub>P, and (*i*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>As] are generated by irradiation of a frozen solution of Co<sub>2</sub>(CO)<sub>6</sub>(ER<sub>3</sub>)<sub>2</sub> at 77 K. In addition, Co<sub>2</sub>(CO)<sub>6</sub>(RC<sub>2</sub>R')<sup>7</sup> can be produced by electrolysis in situ inside the ESR cavity usually at -60 °C. Both techniques lead to radicals having short lifetimes, which are therefore difficult to study by spectroscopic methods. An advantage of the radical anion [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Co<sub>2</sub>(CO)<sub>2</sub><sup>-</sup> is its stability in an inert atmosphere at room temperature. This property allowed us to undertake a complete ESR study from 4 to 300 K and also to record its optical spectrum.

This paper presents the ESR and optical spectra of the mixed-valence complex [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Co<sub>2</sub>(CO)<sub>2</sub><sup>-</sup>. A detailed study of these experimental data show a strong electronic interaction between the two cobalt units so that this complex belongs to class III according to the classification of mixed-valence compounds of Robin and Day.<sup>9</sup>

### Experimental Section

The complex [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Co<sub>2</sub>(CO)<sub>2</sub> was prepared according to the previously described procedure.<sup>3</sup> Its electrochemical one-electron reduction was carried out under an argon atmosphere at -0.7 V vs. SCE. A mercury working electrode and an aluminum auxiliary electrode were used. Before use, the supporting electrolyte, [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][PF<sub>6</sub>], was dehydrated by melting under vacuum. The solvent used, tetrahydrofuran, was freshly distilled over sodium benzophenone ketyl under an argon atmosphere.

The X-band ESR spectra were recorded on a Bruker 220D spectrometer supplied with a variable-temperature accessory in the range 4-293 K. For the Q-band, a Varian E09 spectrometer was used. The optical spectra were recorded from 10 000 to 40 000 cm<sup>-1</sup> on a UV-visible Beckman 5240 spectrophotometer. All ESR tubes and optical cells were filled under argon by using Schlenk techniques.

For analyses of the ESR spectra, a simulation program REPELEC<sup>10</sup> was used, based on a second-order perturbation solution<sup>11</sup> of the spin Hamiltonian. For all simulations, the estimated errors are ±0.005 for the *g* values and ±1 G for the hyperfine parameters.

### Results

(A) ESR. The room-temperature ESR spectrum of the radical anion [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>Co<sub>2</sub>(CO)<sub>2</sub><sup>-</sup> in tetrahydrofuran solution is shown in Figure 1a. This spectrum exhibits approximately 60 well-resolved lines centered around *g* = 2.025. Its relative com-

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