As shown in this paper, six-coordinate σ-bonded complexes are also formed upon the addition of NO to (P)Fe(R) and a summary of potentials for oxidation and reduction of (OEP)Fe(C_6H_5)(NO) and (TPP)Fe(C_6H_5)(NO) is given in Table VI. This table is organized according to the type of electrode reaction and, for the case of (P)Fe(C_6H_5)(NO), all of the electrode reactions are identified on the basis of an Fe(II) oxidation state for the starting neutral complex. This is consistent with the spectroscopic characterization given in this manuscript.

In summary, the data in Table VI indicate the dramatic effect of the NO group, which stabilizes the Fe(II) oxidation state of (P)Fe(C_6H_5)(NO). This is most evident from the potentials for the Fe(III)/Fe(II) electrode reaction. There is more than a 1.5-V absolute difference in potentials between the electrooxidation and electroreduction of (OEP)Fe(C_6H_5)(NO) and (OEP)Fe(C_6H_5) or between (TPP)Fe(C_6H_5)(NO) and (TPP)Fe(C_6H_5) in the same solvent and supporting electrolyte mixtures. These potential differences are extremely large and indicate that the effect of an NO molecule in stabilizing the iron(II) oxidation state is much greater than that of the σ-bonded phenyl group, which produces an Fe(III) species.

Acknowledgment. The support of the National Institutes of Health (K.M.K., Grant No. GM25172) is gratefully acknowledged.

Registry No. **1a**, 97704-85-3; **1b**, 97704-86-4; **1c**, 89672-72-0; **1d**, 97704-87-5; **1e**, 89672-73-1; **1f**, 97704-88-6; **2a**, 89672-68-4; **2b**, 97704-89-7; **2c**, 89672-69-5; **2d**, 89672-70-8; **2e**, 89672-71-9; **2f**, 97704-90-0; (OEP)Fe(CH_3), 79197-83-4; (OEP)Fe(n-C_4H_9), 79198-01-9; (OEP)Fe(C_6H_5), 83614-06-6; (OEP)Fe(C_6H_4Me-p), 83614-08-8; (OEP)Fe(C_6H_4OMe-p), 83614-07-7; (OEP)Fe(C_6F_4H), 96482-32-5; (TPP)Fe(CH_3), 79197-95-8; (TPP)Fe(n-C_4H_9), 79198-00-8; (TPP)Fe(C_6H_5), 70936-44-6; (TPP)Fe(C_6H_4Me-p), 87621-56-5; (TPP)Fe(C_6H_4OMe-p), 89673-27-8; (TPP)Fe(C_6F_4H), 96482-33-6; NO, 10102-43-9.

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[40] The most negative potential ever measured for reduction of a six-coordinate Fe(III) porphyrin is that for reduction of the negatively charged $[(TPP)Fe(F_2)]^-$. This complex has $E_{pc} = -1.10$ V in Me_2SO.[41]

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and Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 31400 Toulouse, France

Unusual Paramagnetic Platinum Complexes. An ESR Study of Platinum Blues

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The well-resolved ESR powder spectra of blue platinum complexes prepared from 1-methylhydantoin and 5-methyl-2-pyrrolidinone offer the possibility of probing various structural models. A good agreement between the experimental and the calculated spectra is obtained by assuming that the hyperfine structure is attributed to the coupling of an unpaired electron with four ^{195}Pt nuclei involved in a tetrameric structure.

Introduction

In recent years, a great interest has been raised in a particular area of platinum chemistry, i.e. compounds having a metallic chain and displaying anisotropic properties.[1] This interest has been mainly focused on complexes in which the formal oxidation state of the metal is nonintegral. Partial removal of d_{z^2} electrons (z taken along the mean Pt chain) from the metallic atoms upon oxidation allows substantially improved d_{z^2} orbital overlap and, through a shortening of metal-metal separation, an increased metal-metal interaction. This results in metallic or semimetallic behavior. Independently of the electrical properties of these complexes, which potentially lend themselves to future technologies, a variety of cooperative or localized magnetic properties may be observed. This is seemingly the case for the so-called "platinum blues" for which ESR signals have been reported by Lippert[2] in 1977 and further related by others in more recent works.[3-5] However, these magnetic properties have not been extensively studied, since the main interest paid to these complexes originates from their potential antitumor activity.[6]

The structure of one of these products, the *cis*-diammineplatinum α-pyridone blue, has been fully characterized,[3,7] and comparative studies strongly suggest that all the known amidato blue species are mixed-valent, metal-metal-bonded, and ligand-bridged polymers. Moreover, they exhibit an ESR signal in contrast to the diamagnetic behavior of Pt(II) and Pt(IV) compounds,[4] and therefore, they should be viewed as original materials that may display cooperative properties in connection with electronic delocalization over a number of platinum atoms. However, as the ^{195}Pt hyperfine structure observed with this compound is very poorly resolved, these spectra could never be used to establish definitively the number of platinum atoms involved in these blue complexes. At this stage it may be underlined that ESR signals may also be observed in irradiated platinum complexes[8] but more interestingly in some platinum mixed-valence compounds such as partially oxidized tetracyanoplatinate salts (KCP family), which have been extensively studied.[9,10]

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[1] See, for example: (a) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247-263 and references therein. (b) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1-45. (c) Reis, A. H., Jr.; Peterson, S. W. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 560-579. (d) Miller, J. S. *Ibid.* **1978**, **313**, 25-59.

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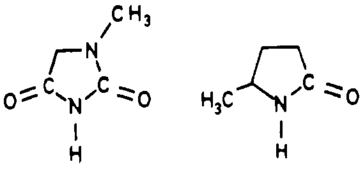

1 2

Figure 1. Ligands (**1**) 1-methylhydantoin and (**2**) 5-methyl-2-pyrrolidinone.

The present paper is devoted to an analysis of the ESR spectra of two blue complexes obtained from $[Pt(NH_3)_2(H_2O)_2]^{2+}$ and, respectively, 1-methylhydantoin and 5-methyl-2-pyrrolidinone (cf. Figure 1). Exceptionally well-resolved hyperfine structures are observed in both cases. A simulation process has been written in order to find a set of hyperfine constants that may be consistent with the experimental spectra and to determine the most probable number of platinum atoms that participate in the molecular structure. The ability for the complexes to retain their structure in solution is also discussed.

Experimental Section

Synthesis and Characterization. The blue complex (A) derived from 1-methylhydantoin is obtained by oxidation of bis(μ-1-methylhydantoinato-*N,O*)bis(*cis*-diammineplatinum(II)) dinitrate, which has been previously described.[11] In a typical experiment, 1.01 mmol of the yellow precursor were dissolved in 300 mL of H_2O_2 (15%). The pH was adjusted to 1.0 with NO_3H (1 N). The solution immediately turned green-blue and was allowed to stand for 1 h at room temperature. An amorphous green-blue powder (A) was obtained by adding a large excess of acetone to the reaction mixture. Water solutions of (A) are unstable and are converted to yellow diamagnetic solutions within a few hours. Solid samples are more stable, but a loss of color and paramagnetism is also observed with time (several days). This unstability prevents a reliable determination of the elemental composition. However, it is noteworthy that all the samples are characterized by a platinum-to-ligand ratio virtually equal to unity. No attempt has been made to characterize further the decomposition products. The visible spectrum of a freshly prepared sample shows a broad transition at 700 nm.

The methylpyrrolidinone blue product (B) was obtained from an aqueous solution of (2) and *cis*-dichlorodiammineplatinum(II) hydrolysis products. The ligand (10 mg, 10^{-4} M) was dissolved in water (2 mL) and was added to an aqueous solution of platinum hydrolysis products (200 μL, 1.25 10^{-4} M). The mixture was incubated at 37 °C in the dark. After incubation for 1 day, the solution turned blue. The ESR spectrum was obtained directly on the frozen mother solution.

The synthesis of the platinum 1-carboxycyclohexane-2-carboxamide blue has been described previously.[12]

ESR Measurements. The ESR spectra were recorded on a Bruker ER 200 D spectrometer (X-band, 100 kHz field modulation) at 77 K. The klystron frequency was measured by using a Hewlett-Packard transfer oscillator and a Racal frequency meter. The magnetic field was calibrated with an NMR marker. All ESR spectra were recorded on frozen aqueous solutions, directly on the mother solution, and on the powdered sample over a wide range of temperature.

ESR Simulation. The spectra were calculated by using the effective spin Hamiltonian

$$\mathcal{H} = \beta HS\mathbf{g}\mathbf{h} + \beta_n HI g_n \mathbf{h} + \sum_i S\mathbf{T}_i I_i$$

where $\mathbf{h}$ is the unit vector along the magnetic field direction and $\mathbf{T}_i$ are the hyperfine interaction tensors. The nuclear Zeeman tensor was assumed to be isotropic. β, β_n, g, g_n, S, and I have their usual meaning.

A polyoriented sample ESR spectrum was simulated[13] by generating 120 000 random orientations of the magnetic field and by summing the corresponding 120 000 absorption spectra. The final spectrum was obtained by performing a convolution (Gaussian line shape) of each transition line, adding all the contributions, and calculating the first derivative of the spectrum. Due to the presence of several platinum isotopes, many isotopic distributions have to be taken into consideration (vide infra) so that the simulation process becomes highly time consuming. Consequently, we were compelled to use a second-order perturbation.

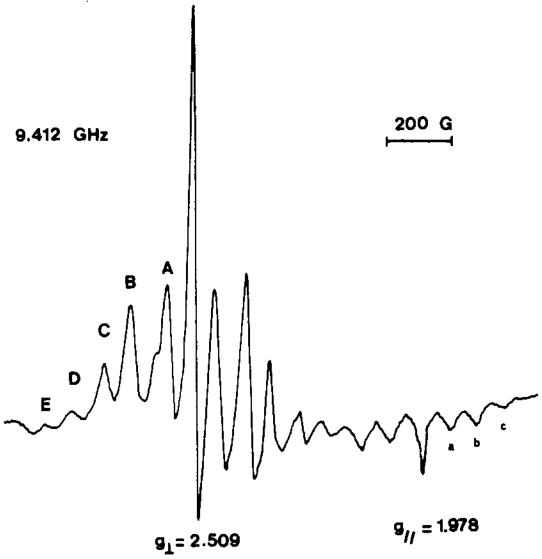

Figure 2. ESR spectrum obtained with a solid sample of *cis*-diammineplatinum 1-methylhydantoin blue.

Results and Discussion

Most of the known blue complexes show ESR signals that have been obtained with powder or frozen solution samples. The large anisotropy of the **g** tensor and the fact that $g_\perp > g_\parallel$ allow a description in terms of a d_{z^2} hole state (z along the mean Pt chain) with an admixture of lower lying d_{xz}, d_{yz} states due to spin–orbit coupling. The spectral pattern is quite often restricted to two broad signals, but in some instances additional hyperfine structures are clearly discernible. They have not yet been fully explained, but they are generally related to delocalization of the spin over several platinum atoms.

In contrast to previously reported spectra, the powder spectra of blue complexes obtained from 1-methylhydantoin and methylpyrrolidinone display an hyperfine structure that is not only extensive but also well resolved. The spectrum obtained with the former ligand is shown in Figure 2. Thus, these complexes offer the opportunity of testing the validity of various models.

Whereas it is clear that the two experimental spectra (Figure 2, Figure 5) correspond to an axial symmetry of the **g** tensors, it is more difficult to analyze the hyperfine structure. We have thus tried to simulate these spectra by assuming that the ^{195}Pt hyperfine tensors also have an axial symmetry and that their principal axes are aligned along the **g** eigenvectors.

As previously mentioned, the blue complexes are generally viewed as oligomers. In this instance, the first problem in analyzing their ESR spectra rests on the choice of the size of the oligomer. As a first hypothesis, we have considered a model containing a single platinum atom[14] and tried to simulate the experimental spectra by assuming hyperfine interaction with ^{195}Pt and ^{14}N nuclei of the ligands. No satisfying simulation could be obtained.

As a second hypothesis, we have supposed that the unpaired electron is delocalized on only two platinum atoms. This structure has been previously suggested by Neubacher et al.[5] Such a model would be consistent with the structure of the yellow complex that is a direct precursor of the 1-methylhydantoin blue since this structure may be described in terms of "dimer of dimer". The resulting spectrum is the sum of four subspectra[15] Pt_1–Pt_2, $^{195}Pt_1$–Pt_2, Pt_1–$^{195}Pt_2$, and $^{195}Pt_1$–$^{195}Pt_2$, which contribute in the

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(15) The ^{195}Pt isotope has a spin different from zero ($I = {}^1/_2$, natural abundance 33.7%), the others are spinless.

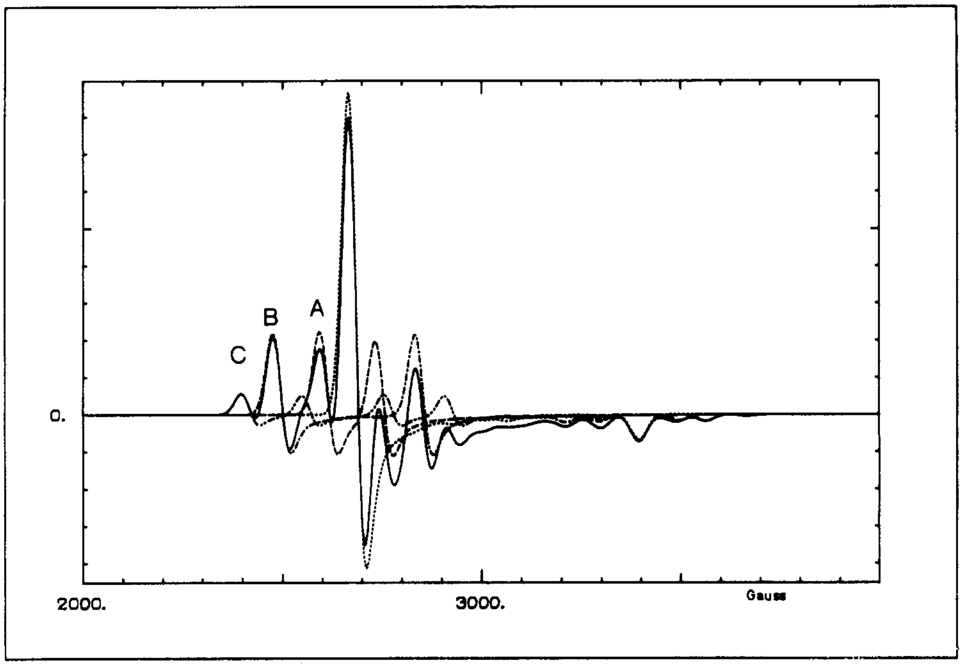

Figure 3. Simulation of the ESR spectrum of 1-methylhydantoin platinum blue following the second hypothesis (electron delocalized over two different platinum centers in a dimeric molecule): dashed lines, weighted contribution of each Pt_1–Pt_2 subspectrum; solid line, resultant spectrum.

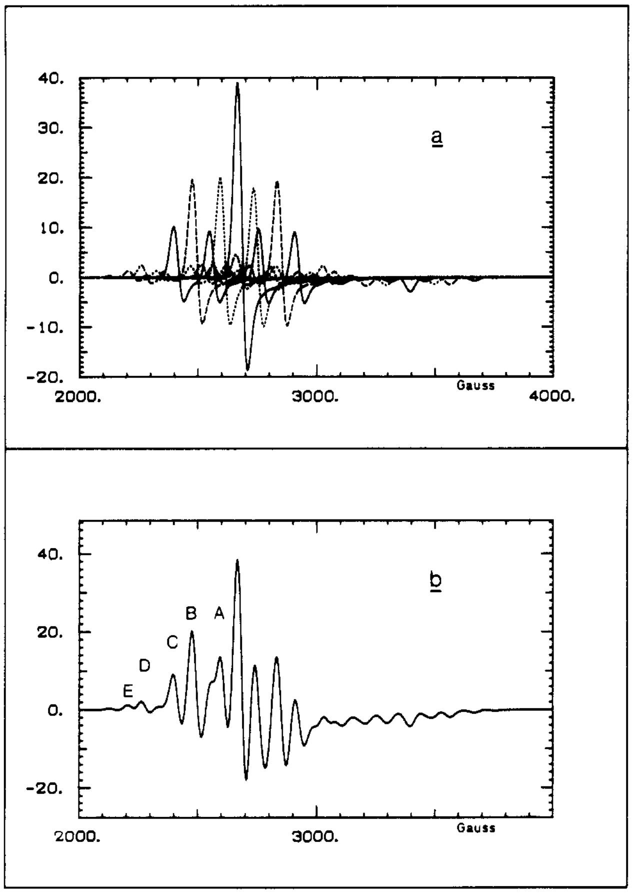

Figure 4. Simulation of the ESR spectrum of 1-methylhydantoin platinum blue following the third hypothesis (electron delocalized over two pairs of different platinum atoms in a tetrameric structure): (a) weighted contribution of each Pt_o–Pt_i–Pt_i–Pt_o subspectrum; (b) resultant spectra.

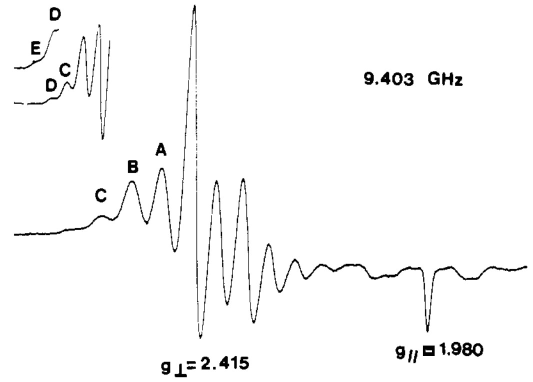

Figure 5. ESR spectrum of a frozen aqueous solution of *cis*-diammineplatinum 5-methyl-2-pyrrolidinone blue (77 K).

proportion 43.95, 22.34, 22.34, and 11.35%, respectively. The simulated spectrum are shown in Figure 3 and imply that the two platinum atoms are not equivalent ($A_{1\perp} \simeq 1250$ MHz, $A_{2\perp} = 500$ MHz, $A_{1\parallel} \sim 980$ MHz, and $A_{2\parallel} \simeq 560$ MHz).

As third hypothesis, we have assumed that platinum blues have a tetrameric structure for which two pairs (outer and inner platinum centers) are present. This led us to calculate the nine subspectra (Figure 4a) that correspond to the various isotopic distributions (e.g., Pt_o–Pt_i–Pt_i–Pt_o, $^{195}Pt_o$–Pt_i–Pt_i–Pt_o, Pt_o–$^{195}Pt_i$–Pt_i–Pt_o, $^{195}Pt_o$–$^{195}Pt_i$–Pt_i–Pt_o,···, and $^{195}Pt_o$–$^{195}Pt_i$–$^{195}Pt_i$–$^{195}Pt_o$) and to weigh their contributions according to the natural abundance of ^{195}Pt. The simulated resulting spectrum that gives the best fitting with the experimental spectrum corresponds to the following parameters: $g_\perp = 2.509$, $g_\parallel = 1.978$, $A_{1\perp} = 502$ MHz, $A_{1\parallel} = 556$ MHz, $A_{2\perp} = 1253$ Hz, and $A_{2\parallel} = 980$ MHz, as shown in Figure 4. This spectrum displays all the lines of its experimental counterpart. In particular the external low-intensity lines (D, E) are present, while they were absent on the simulated spectrum shown in Figure 3. From the subspectra, we can attribute these relevant lines to the isotopic distributions that contain three and four ^{195}Pt.

In spite of an overall agreement between the calculated and the experimental spectra, some deviations in the intensity distributions are perceptible. They are probably due to the use of constant line width in the simulation while the occurrence of an anisotropic m_I-dependent line width has been recognized in several paramagnetic platinum compounds.[8,10] Moreover, resonance field positions obtained by second-order perturbation treatment is not altogether satisfying, particularly when such an anisotropic system exhibiting several hyperfine couplings is implied.

Finally, powder spectra of the blue complexes derived from 1-methylhydantoin and 5-methyl-2-pyrrolidinone are suitably explained in terms of a simple model involving (i) delocalization of one hole over a four-platinum chain, (ii) lack of magnetic interaction between the tetrameric units, and (iii) two pairs of platinum (outer and inner) whose hyperfine constants require appreciably different spin densities.

Points i and ii are in agreement with the X-ray structural determination of the α-pyridone blue. They further imply that the mean oxidation state of the platinum atoms is 2.25 in both complexes. This value is in agreement with those usually cited in the literature,[7] though higher values have been mentioned (e.g. 3.3 for the phthalimide blue[16]). Yet, values above 2.5 would imply that more than one odd electron would be actually present in the molecular unit, in contradiction with points i and ii. Static susceptibility measurements are generally used to provide information on the number of odd electrons through consideration of the related magnetic moments. However, the high spin–orbit coupling evidenced by ESR can cause metal ions of the third transition series to have magnetic moments that cannot be easily interpreted in terms of number of unpaired electrons.[17] Furthermore, structural data are prerequisite to interpret suitably these data.[12]

Our analysis includes inequivalence between the outer and the inner platinum atoms since two sets of A values are required (point iii). Reference to the structures of α-pyridone blue and the yellow precursor of 1-methylhydantoin blue points to a possible connection with the surrounding of the platinum atoms. A head-to-head disposition of the ligands would result in two different metal environments, i.e. N_2N_2 and N_2O_2. Nevertheless, the large difference between the two sets of hyperfine constants would reasonably reflect a nonuniform unpaired spin distribution[18] along the platinum chain. This inequivalence, which here is a necessary condition for a good fit between simulated and experimental spectra, is in total accordance with the very recent result obtained from polarized spectroscopy and Xα calculations.[19] These calculations point to a substantial difference in the s component of the hybrid atomic orbitals related to the inner and outer Pt atoms. Due to the dependence of the hyperfine coupling constant on this s character,[20] it is very likely that the difference between the two sets of hyperfine constants reflects not only a nonuniform unpaired spin distribution but also a larger s-orbital component on the inner Pt atoms to which the greater coupling constants may be attributed.[21]

This result is important in regard to the electronic structure of these blue species since other spectroscopies fail to give a nonambiguous answer to this problem. This is the case when Hush's theory[22] is used to calculate the extent of delocalization from the visible spectroscopy data. First of all, this theory is merely restricted to dinuclear complexes. Then, the optical density, which is a significant parameter in Hush's formulation, is not an intrinsic characteristic of blue species because of its dependence on the "history" of the sample (duration, temperature, pH, etc. of the reaction).

X-ray photoelectron spectroscopy (XPS), which allows a determination of the inner-shell electron-binding energies, is known to discriminate between the different oxidation states of an element. To our knowledge, XPS study of platinum blues is restricted to three examples.[7,23,24] In two cases,[23,24] two signals have been observed and attributed to the simultaneous occurrence of platinum(II) and platinum(IV). Moreover, for one of these complexes, the intensity ratio of the two signals agrees well with the average value of the oxidation state deduced from redox titration. However, it may be underlined that the spectrum of the structurally characterized α-pyridone blue shows one signal.[7] From these data, it is tempting to conclude that in the former cases there are inequivalent and "trapped-valence" sites and in the latter case there is a complete delocalization. However, several remarks permit us to shade this conclusion. First of all, it has been evidenced that radiation damage may occur and cause either a reduction of platinum(IV) or an oxidation of platinum(II). However, Hush has shown that, if the photoionized state of mixed-valence compounds is close to the ground state, the valence electron may be more or less localized in the excited state. In this instance, the photoionized state may be very nearly localized and two peaks observed for complexes with the delocalized ground state, with the peak separation very close to that expected for "trapped-valence" compounds.

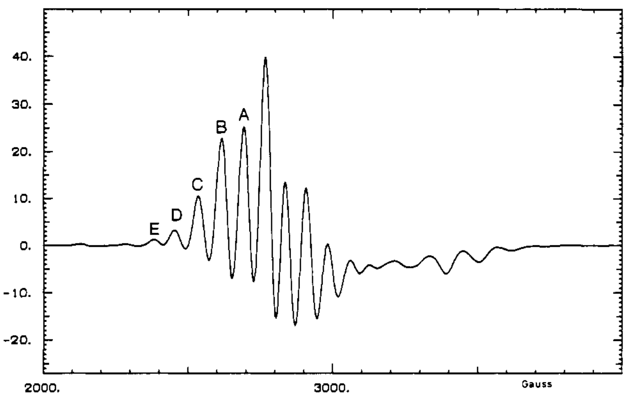

Figure 6. Simulation of the ESR spectrum of an aqueous frozen solution of 5-methyl-2-pyrrolidinone blue (77 K).

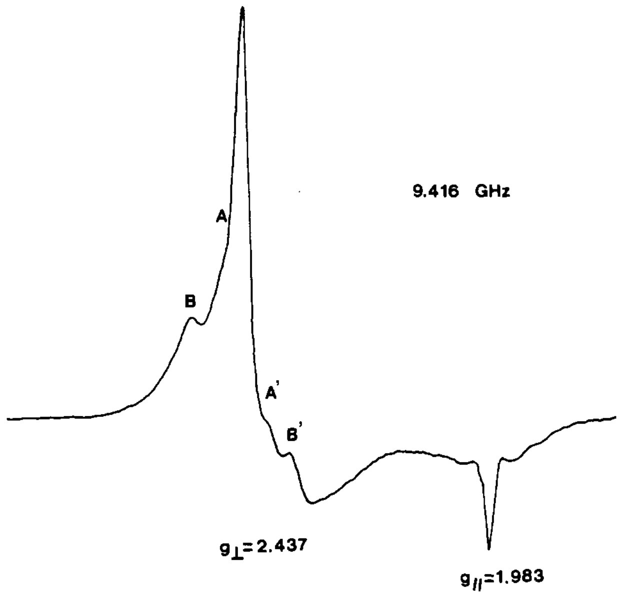

Figure 7. Powder ESR spectrum of 1-carboxycyclohexane-2-carboxamide blue.

At this stage of the discussion it is tempting to look for an enlargement of the analysis. Frozen-solution spectra of two blue compounds prepared from 5-methyl-2-pyrrolidinone and nonsubstituted hydantoin were obtained. In Figure 5, we show the spectrum obtained with B. A similar spectrum has been shown by Lippert[2] with δ-valerolactam as ligand. The overall pattern

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(16) Allen Chang, C.; Marcotte, R. B.; Patterson, H. H. *Inorg. Chem.* **1981**, *20*, 1632–1636.

(17) The relation between the value of the magnetic moment and the number of odd electrons is not straightforward. In this respect an intriging problem is offered by the interpretation of the 6.93 μ_B per platinum atom value attributed by Lerner (Lerner, E. I. Ph.D Thesis, Columbia University, NY, 1977) for a uracil blue.

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is strongly reminiscent of the spectrum of the powdered sample in Figure 2. More particularly, observation of the C, D, and E lines supports an analysis in terms of a tetrameric structure at least. The best fit of the experimental spectrum is obtained with the following set of parameters: $g_{\perp} = 2.415$, $g_{\parallel} = 1.980$, $A_{1\perp} = 480$ MHz, $A_{1\parallel} = 557$ MHz, $A_{2\perp} = 980$ MHz, and $A_{2\parallel} = 731$ MHz (Figure 6). It may be emphasized that this type of spectrum is characteristic of most of the blue complexes obtained from lactams or pyrimidines, which, therefore, may retain an oligomeric structure in solution. A somewhat different type of spectrum characterizes the blue complexes prepared from ligands involving a C(O)–NH_2 group. A typical spectrum is represented in Figure 6. These spectra display a too limited number of broad and ill-resolved hyperfine lines to probe simulation models. The poor quality of the spectra may be tentatively attributed to a broadening of the lines due to unresolved hyperfine interactions with ^1H nuclei of the ligand.

Finally, the less ambiguous data regarding the structure of amorphous blue complexes are likely afforded by ESR spectroscopy. This emphasized the need for a suitable analysis of the related spectra. It is of interest to note that, in many cases, this can be achieved by using a relatively simple model, which may be directly compared with the structure of Lippard's blue.[3,7,18]

Registry No. $[Pt(NH_3)_2(H_2O)_2]^{2+}$, 20115-64-4; bis($\mu$-1-methylhydantoinato-*N*,*O*)bis(*cis*-diammineplatinum(II)) dinitrate, 83710-06-9; *cis*-dichlorodiammineplatinum(II), 15663-27-1.

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A Competitive NMR Technique for Measurements of Metal Ion–Macrocyclic Polyether Complexation Constants in Solutions

ROGER D. BOSS and ALEXANDER I. POPOV*

Received December 28, 1984

An NMR technique has been developed for the determination of formation constants of metal ion complexes that uses competition of two metal cations for a given ligand. The technique is applicable in a wide variety of media, but it is particularly useful for reactions in aprotic solvents. This technique allows measurement of complexes of metal ions whose nuclear properties make precise NMR measurements very difficult, if not impossible. It also allows measurements of formation constants that are too large to be measured by the conventional NMR technique involving a single cation. The feasibility of this technique is first illustrated by measurements of formation constants determined previously by other techniques. Results are also given for a series of 18-crown-6 complexes with a variety of cations, including a paramagnetic cation, Ni^{2+}, in dimethylformamide solutions with formation constant values varying from $\log K_f < 1.23$ to $\log K_f = 4.21$. The precision of the determination is limited by the precision of the known formation constant used in the competitive reaction and by the precision of the chemical shift measurements.

Introduction

Practically every physicochemical technique known to chemists has been used, at one time or another, for the measurements of equilibrium constants in solutions. The vast majority of such measurements have been carried out in aqueous solutions, where electrochemical techniques are particularly effective. On the other hand, in nonaqueous solutions, and particularly in aprotic solvents, electrochemical techniques are often not effective due to difficulties of finding reversible electrodes in these media. In such cases spectroscopic techniques must be used; however, lack of sensitivity often precludes measurements of large equilibrium constants (e.g., $>10^5$).

This problem is particularly troublesome in the NMR studies of complexation reactions of macrocyclic ligands (crown ethers and cryptates) with a variety of cations in aprotic media. In many cases formation constants can be determined from the variation of the chemical shift of the studied cation with the ligand:cation mole ratio.[1,2] The accuracy of the method depends on the chemical shift range of the nucleus and on the accuracy with which the resonances can be measured (difficult with broad lines); under the best conditions, the upper limit of K_f is only somewhat larger than 10^4. Of course, the difficulties are exacerbated when the cationic nuclei have low receptivities or when they are paramagnetic.

Cox, Schneider, and their co-workers[3-6] have developed a competitive potentiometric technique for the determination of large formation constants of macrocyclic complexes. They use a silver/silver ion electrode, which behaves reversibly in a number of aprotic solvents, to probe the competition between the Ag^+ cation and the studied cation for a given ligand. When the K_f of the silver complex is known, that of the other complex can be obtained. This method works particularly well for systems where the Ag^+ ion forms fairly stable complexes ($K > 10^4$), as in the case of the cryptates. The usefulness of the technique, of course, is limited to solvents where the Ag/Ag^+ electrode behaves reversibly and where other cations, which may be present, and the counterions, do not influence the electrode potential.

It seemed to us that the competition method of Cox and Schneider could be applied to the NMR measurements where it would be largely indepedent of the solvent and where, depending on circumstances, various cations with suitable NMR properties could be used as probes for nuclei with less satisfactory properties, such as high quadrupole moment, high Steinheimer antishielding factor, low natural abundance, and/or paramagnetism. Such a technique could significantly expand the use of NMR spectroscopy for studies of reactions in solutions.

Some years ago Zink and co-workers[7] reported the use of thallium-205 NMR measurements for the determination of *relative* formation constants of the Tl^+ ion and of another cation M^+. This technique is useful for the determination of the selectivity order but it is limited to the systems where the ligand:metal cation ratio is such that the ligand is totally in the complexed form, which may not be true for some systems. It is also not applicable to cases where complexes with stoichiometries other than 1:1 are also formed.

More recently, Reid and Rabenstein[8,9] have used the proton NMR of mercaptoacetic acid, as a function of pH, to monitor

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