110. $[M(bpy)_3]$ (M = Fe, Ru, Os): New Crystalline Materials from the Reductive Electrocrystallization of $[M(bpy)_3](PF_6)_2$

by **Eduardo Pérez-Cordero**, **Rosanna Buigas**, **Nancy Brady**, and **Luis Echegoyen***
Department of Chemistry, University of Miami, Coral Gables, FL 33124, USA
and **Claudia Arana** and **Jean-Marie Lehn**
Laboratoire de Chimie Supramoléculaire, Université Louis Pasteur, 4, rue Blaise Pascal, F-67000 Strasbourg

(1.III.94)

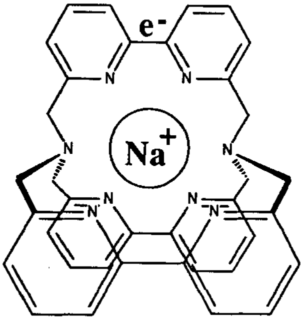
Reductive electrocrystallization at a constant current density (11.0–11.5 μA/cm^2) of millimolar solutions of $[M(bpy)_3](PF_6)_2$, where M = Fe, Ru, or Os, and bpy = 2,2′-bipyridine in acetonitrile containing 0.1M Bu_4NPF_6 results in the formation of dark crystals on the Pt cathode. The crystals grow as long, thin, and shiny needles having a hexagonal cross section of 0.1–0.5 mm in diameter. Combustion microanalyses results are consistent with the composition for $[Fe(bpy)_3]$, $[Ru(bpy)_3]$, and $[Os(bpy)_3]$. In addition, the chromophores are conserved, as confirmed by recording both the electronic and the ^{1}H-NMR spectra after reoxidation of the electrocrystals in humid air. The spectra are identical to those for authentic samples of $[Fe(bpy)_3]^{2+}$, $[Ru(bpy)_3]^{2+}$, and $[Os(bpy)_3]^{2+}$. A ratio of 2.0 ± 0.1 e$^-$/molecule is observed upon completion of the controlled potential electrolysis of a solution of $[M(bpy)_3]^{2+}$, which results in the precipitation of a dark solid and the almost complete fading of the color of the original solution. Unexpectedly, the crystals do not exhibit an ESR signal. These data indicate the formation of novel materials, crystalline $[Fe(bpy)_3]$, $[Ru(bpy)_3]$, and $[Os(bpy)_3]$.

---

1. Introduction. – A recent article began by stating that 'tris(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, has evolved from a quite esoteric complex ion of a rare platinum metal into an immensely popular, almost magic compound' [1]. We present here evidence of new crystalline materials derived from this molecule and the related species $[Fe(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ which gives further support for this statement. Despite the multiple electrochemical [2] and photochemical [3] studies that have been performed with $[Ru(bpy)_3]^{2+}$ for over two decades, there was no indication that these novel crystalline materials had been previously communicated.

Part of the impetus behind the present work stemmed from our recent success in preparing the first crystalline CRYPTATIUM in 1991; a neutral, expanded-atom type species, structure **1**, formed by the reductive electrocrystallization of sodium tris(2,2′-bipyridyl)cryptate [4a]. The overall interest in the electrochemical properties of similar macrobicycles, macrocycles, and even of carbon clusters was directed by the possibility of manipulating and transforming them into novel materials with unique properties [4b].

The reduced complex **1** can be represented as $[Na^+ \subset (bipy)_3]$, where $(bipy)_3$ stands for the tris(2,2′-bipyridyl) cryptand, not for three isolated bpy groups. The X-ray structure of this CRYPTATIUM was solved and indicated that the extra unpaired electron that was added to the system upon electrocrystallization was localized in one of the three bipy units of the cryptand [4a].



1

On the other hand, non-cryptand but bipy-containing neutral species, [M(bpy)$_3$], where M=Fe, Os, and Ru, were first prepared and reported as early as 1964 [5]. The first published report appeared in 1966 for the system [Fe(bpy)$_3$] [6]. This material was prepared *via* the reaction of solid anhydrous $FeCl_3$ with a slight excess of $Na^+(bpy)^-$ [6]. The product was described as a 'black precipitate' and was characterized by the electronic spectrum of the material after decomposition in moist air. The spectrum corresponded to that of $[Fe(bpy)_3]^{2+}$, which was prepared independently [6].

Since then, many others have reported similar neutral species in the series [M(bpy)$_3$] [7–9]. Particularly noteworthy is the description of the formation of [Fe(bpy)$_3$] as 'black crystals' on the surface of a Hg electrode upon electrolysis of a solution containing $[Fe(bpy)_3]^{2+}$ [7]. This appears to be the only report where reference is made to the crystalline nature of one of these neutral complexes. However, there was no apparent attempt to characterize these 'black crystals'.

Subsequent characterization of these materials continued in the 1980's. The work of *DeArmond* and coworkers is noteworthy and particularly relevant, since they conducted extensive electrochemical and ESR studies of the different reduced states of a variety of these bipy-based complexes [8] [9]. Solid [M(bpy)$_3$] species prepared *via* electrochemical reduction exhibited, in all cases, ESR spectra indicative of paramagnetism. Solid [Os(bpy)$_3$] exhibited an ESR spectrum that was identical to that for the species in solution [8]. This was not the case for the corresponding Fe and Ru complexes, a situation explained on the basis of the energy difference between the $L\pi^*$ and the $d\sigma^*$ orbitals, which is largest for the Os complex. This reasoning correctly explained why solid [Os(bpy)$_3$] had the two extra electrons in ligand-localized orbitals, while the corresponding [Ru(bpy)$_3$] and [Fe(bpy)$_3$] showed substantial electron localization in the metal centers. However, none of these solid materials was reported as being crystalline. All controlled potential electrolyses products were characterized as powders. Interestingly, the [Fe(bpy)$_3$], [Ru(bpy)$_3$], and [Os(bpy)$_3$] solid samples generated in the present work, either by controlled current electrocrystallization or by controlled potential electrolysis, are ESR silent, *vide infra*.

Our interest in preparing crystalline [Ru(bpy)$_3$] thus arose from three independent observations: *1*) our recent success in electrocrystallizing **1**, *2*) the potential conceptual and structural similarity between **1** and the family of compounds [M(bpy)$_3$] (M = Fe, Ru, Os), and *3*) the very tenuous evidence, limited to a passing remark in the literature [7], suggesting that crystalline [Fe(bpy)$_3$] had been observed.

2. Results and Discussion. – When a 1 mM solution of $[Fe(bpy)_3]^{2+}$, $[Ru(bpy)_3]^{2+}$, or $[Os(bpy)_3]^{2+}$ (as their hexafluorophosphate salts) in MeCN containing 0.1M Bu_4NPF_6 is electrolyzed at constant current, dark crystals are formed and deposited on the Pt cathode (see *Fig. 1*). Electrocrystallization experiments were conducted at room temperature after evacuating the reagents in the special H-cell [4] to a pressure of 10^{-5} Torr prior to the solvent transfer. The crystals produced are long, thin, and shiny, as can be appreciated from *Fig. 1*. The morphology of the crystals is a function of the current density applied. Those shown in *Fig. 1* were grown at a constant current density of 11.0 μA/cm². The growth pattern is somewhat reminiscent of the way TMTSF- and other TTF-like systems grow upon oxidative electrocrystallization [10], suggesting that these may also be conducting. The crystals are very brittle and have so far eluded characterization by X-ray crystallography and conductivity¹).

Fig. 1. *$[Ru(bpy)_3]$ grown by reductive electrocrystallization on a Pt wire cathode* (0.7 mm in diameter) *from a solution that was 1mM $[Ru(bpy)_3](PF_6)_2$ in MeCN and contained 0.1M Bu_4NPF_6*. The current density used was 11.0 μA/cm². The photograph was taken after removing the electrode from the solution and placing it in a *Schlenk* tube under purified Ar.

Several techniques have been used to characterize these crystals. Combustion microanalyses were supposedly conducted under an inert atmosphere, since the samples were supplied sealed under vacuum to *Atlantic Microlab, Inc.* The results were: Calc. for $[Os(bpy)_3]$: C 54.53, N 12.73, H 3.66; found: C 53.50, N 12.67, H 3.96. Calc. for $[Ru(bpy)_3]$: C 63.15, N 14.74, H 4.24; found: C 62.04, N 14.45, H 4.42. Calc. for $[Fe(bpy)_3]$: C 68.68, N 16.03, H 4.61; found: (1st analysis) C 64.71, N 13.70, H 5.45; (2nd analysis) C 63.39, N 14.47, H 5.02. The agreement is not good, but the materials are very reactive and probably partially decompose in the atmosphere in the process of being analyzed.

Since the crystalline solids could potentially react with the atmosphere during their handling, thus forming the species $[M(bpy)_3](OH)_2$, several mixtures containing

---

¹) These measurements are being conducted in collaboration with Mr. *Michael Wagner* and Prof. *James L. Dye* from Michigan State University, and Prof. *Simon Bott* from the University of North Texas.

$m[M(bpy)_3] + n[M(bpy)_3](OH)_2$, $m + n = 1$, were considered: Calc. for $0.65[Os(bpy)_3] + 0.35[Os(bpy)_3](OH)_2$: C 53.57, N 12.50, H 3.70. Calc. for $0.70[Ru(bpy)_3] + 0.30[Ru(bpy)_3](OH)_2$: C 62.04, N 14.48, H 4.27. Both of these cases are close to the experimental results. *Birch* reductions were also considered as possible decomposition pathways, producing sample mixtures of the form $m[M(bpy)_3] + n[M(bpy)_2\text{-}(H_2bpy)](OH)_2$: Calc. for $0.65[Os(bpy)_3] + 0.35[Os(bpy)_2(H_2bpy)](OH)_2$: C 53.51, N 12.49, H 3.80. Calc. for $0.70[Ru(bpy)_3] + 0.30[Ru(bpy)_2(H_2bpy)](OH)_2$: C 61.97, N 14.46, H 4.37. The agreement between these calculations and the experimental results is a good support to consider partial decomposition of the Os and Ru complexes.

The Fe derivative is more reactive in the atmosphere than the other two compounds. This could lead to more complex decomposition pathways. The oxidation states 2+ and 3+ for the central metal atom could be considered in the decomposition schemes, which would make the interpretation of the elemental analysis results even more difficult. Since these additional possibilities result in potentially complicated schemes, and fitting the data would entail the use of multiple independent parameters, these were not attempted. Therefore, the Fe system was characterized on the basis of its electrochemical behavior, its ^{1}H-NMR spectra, and its similarity with the Ru and Os compounds.

Other experimental results showed that $[Fe(bpy)_3]$ does behave similarly. Controlled potential electrolyses of solutions of 1 mM $[M(bpy)_3](PF_6)_2$, M = Fe, Ru or Os, containing 0.1M Bu_4NPF_6 in MeCN were conducted at room temperature. The cyclic voltammograms were first recorded using a glassy C electrode in a specially designed cell equipped to do bulk electrolysis without exchanging electrodes. This cell required only 1 ml of solution and was pumped to 10^{-5} Torr for a period of 30 min, before the solvent was vapor-transferred under vacuum. Controlled potential electrolyses were performed at -2.00 V *vs.* the ferrocene/ferricenium couple using a Pt mesh (2 cm^2) both as the working and as the counter electrodes, while keeping the compartments separated by a porous glass plug (porosity $\leqslant 4$ µm). For each experiment, the initial reduction yielded a soluble substance of intensely red coloration, ascribed to the monoreduced species $[M(bpy)_3]^+$. Exactly at the point corresponding to the completion of the first reduction, a black precipitate started to form and to adhere to the Pt mesh cathode. At the completion of the reduction sequence, determined by a decrease in the current to 4% of its initial value, the number of electrons calculated by integration of the current-time curve was 2.0 ± 0.1 e^-/molecule. It is important to mention that the solutions are essentially colorless at the completion of the electrolysis process. Although these controlled-potential electrolysis experiments differ from the actual electrocrystallizations, where the process is conducted at controlled current, the appearance of the color of the solutions and the black precipitates is very similar under both experimental conditions. This means that the crystalline materials deposited in the controlled-current mode must be a doubly reduced product of the metallic complexes, probably $[Fe(bpy)_3]$, $[Ru(bpy)_3]$, and $[Os(bpy)_3]$.

Spectroscopic characterization of samples before and after electrocrystallization have also been conducted to establish that the crystalline material returns to the original complex when exposed to the atmosphere. The electrocrystals were exposed to moist air and dissolved in distilled water; HPF_6 was added to these solutions to precipitate the final products, which were washed several times with distilled water before being vacuum dried. The UV/VIS spectrum of an authentic sample of $[Fe(bpy)_3](PF_6)_2$ is presented in *Fig. 2,* along with the spectrum for a sample generated *via* reoxidation of $[Fe(bpy)_3]$ in

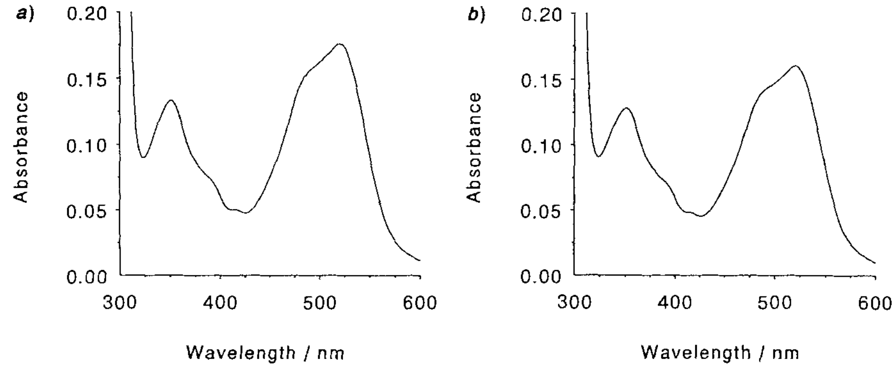


Fig. 2. *UV/VIS Spectra for:* a) *$[Fe(bpy)_3](PF_6)_2$ in MeCN* (0.14mM) *and* b) *$[Fe(bpy)_3]$ after reoxidizing the sample* (see text for details) *and dissolving it in MeCN.* Both spectra are identical, indicating that the chromophore has remained intact after the electrocrystallization-reoxidation process.

moist air as described before. There is no perceptible difference between these spectra, a result that is similar to the ones of the Ru and Os derivatives.

^{1}H-NMR spectroscopy at 400 MHz was also used to characterize the materials before and after electrocrystallization. For these experiments, the electrocrystals were also decomposed by following the protocol mentioned before. The aromatic region showed that the signals remain virtually unchanged between the starting material and the product obtained after the electrocrystals reoxidation, as is shown in *Fig. 3* for the Fe complex.

The most unexpected result encountered during the characterization of the crystalline materials was the lack of an ESR signal. As mentioned above, ESR signals have been observed for all of the reduced $[M(bpy)_3]$ species, where M = Fe, Ru, and Os [8]. These solid materials were prepared *via* electrolyses of MeCN solutions of the parent complexes, in a similar way as described in the present work, except that they were not conducted under high vacuum. We agree with these authors' observation of immediate precipitation of a dark solid material, when two electrons are transferred to MeCN solutions containing $[M(bpy)_3]^{2+}$ [8]. They also characterized these powdery materials as $[M(bpy)_3]$, but they reported relatively strong and broad ESR signals [8]. In contrast, both our shiny crystalline material prepared by controlled current electrocrystallization under vacuum and the powdery material prepared *via* controlled-potential electrolysis, also under vacuum, were ESR silent. No signals were observed for the relatively large sample sizes that were placed in 3-mm-diameter tubes. The lack of paramagnetism indicates that the reduction electrons are somehow paired in the new crystalline material. If the microsymmetry of these species in the solid state is considered to be D_3, which is the starting symmetry of the parent compounds, then the lowest unoccupied molecular orbital is singly degenerate and the two reduction electrons would be paired [11]. A recent photochemical study with related compounds $[M(bpy)_3]^{2+}$ (M = Zn, Os), concluded that there is electronic delocalization of the excited state [12]. Such a conclusion could support the observations made here if the reduction electrons are delocalized. However, further structural data will be required for a final resolution of this issue.

In view of the morphology of the electrocrystals (*Fig. 1*), and the fact that there are no ESR signals, it could be that the crystalline materials behave as conductors or perhaps as

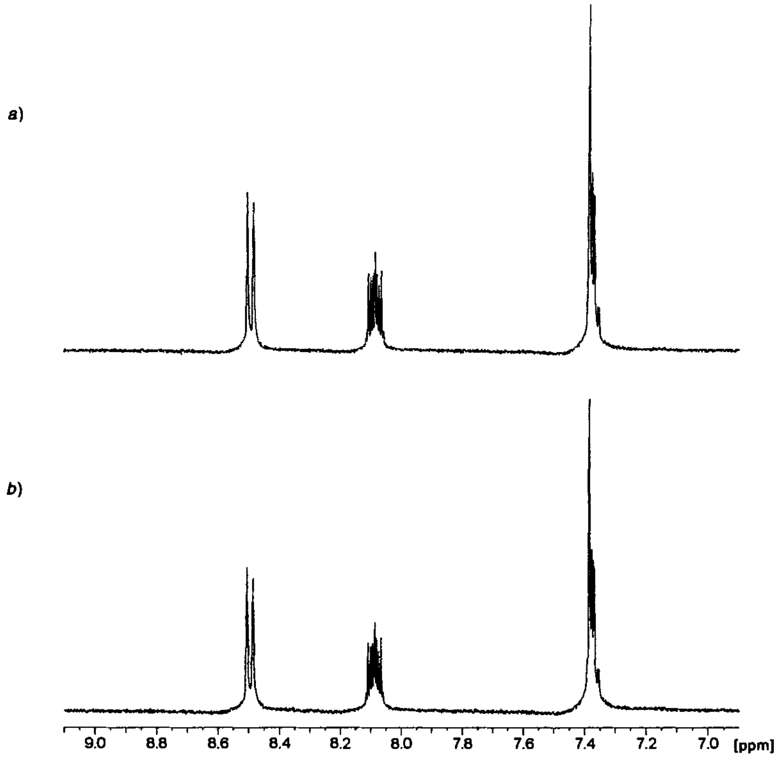


Fig. 3. *Expansion of the aromatic region of the* ^{1}*H-NMR spectra for:* a) *[Fe(bpy)$_3$](PF$_6$)$_2$ in CD$_3$CN, and* b) *[Fe(bpy)$_3$] after reoxidizing the sample* (see text for details) *and dissolving it in CD$_3$CN*

semiconductors. Single-crystal electrical conductivity measurements are currently underway to establish their transport properties. X-Ray analyses have been attempted with all of these samples but unfortunately these have not been successful due to inherent disorder in the crystals.

Many other analogous complexes are currently being explored in an attempt to generate new crystalline materials.

The authors wish to thank the Division of Materials Research of the National Science Foundation for the support of this work (DMR-9119986). They also wish to thank *Marielle Gómez* for taking the picture shown in *Fig. 1*, and *Johnny Ramirez* for the ^{1}H-NMR spectra.

Experimental Part

General. HPLC-Grade CH_3CN, CD_3CN (99.5% D), P_2O_5 (98+%), and HPF_6 (60 wt.-% soln. in H_2O) were purchased from *Adrich Chemical Company, Inc.* Electrochemical-grade Bu_4NPF_6 was purchased from *Fluka Chemical Corp.* The complexes [Fe(bpy)$_3$](PF$_6$)$_2$ (**2**), [Ru(bpy)$_3$](PF$_6$)$_2$ (**3**), and [Os(bpy)$_3$](PF$_6$)$_2$ (**4**) were prepared by following published procedures [1]. ^{1}H-NMR Spectra at 400 MHz were obtained using a *Varian* model *VXR-400* spectrometer. Quant. elemental analyses for C, H, and N were effected by *Atlantic Microlab, Inc.*, Norcross, Georgia.

1. *Electrochemical Procedures. Electrocrystallization at Constant Current.* The electrochemical cell used was similar to that described by *Echegoyen et al.* [4]. Typically, 7.5 μmol of the electroactive compound (6.1 mg of **2**, 6.4 mg of **3**, or 7.1 mg of **4**) were placed in the cathodic compartment; 290 mg (750 μmol) of Bu_4NPF_6 as received from *Fluka* were placed in each cathodic and anodic compartments. MeCN was dried (P_2O_5), degassed by repeated freeze-pump-thaw cycles, and pumped to 10^{-5} Torr. Typically, 15 ml of this highly purified solvent were vapor-transferred into the high-vacuum electrochemical cell [4]. The cathode and anode were similar and made of a Pt wire 0.7 mm in diameter and 20 mm in length. The energy source was a *Hewlett-Packard-Harrison* DC power supply model *6200 B*, the current output of which was monitored by a *John Fluke Mfg. Co., Inc.* True RMS multimeter model 87.

After the first 30 min of the electrolysis, a dark liquid layer formed around the cathode and the first small crystals appeared on the electrode surface. After 48 h of electrolysis, the cathode with the shiny crystals attached to it was removed from the cell under a dry O_2-free Ar atmosphere and transferred to a *Schlenk* tube, where the crystals were carefully removed, placed in 4-mm diameter tubes, and pumped to 10^{-5} Torr for 10 min before the sample tubes were flame sealed for subsequent experiments.

Electrolysis at Constant Potential. A *Bioanalytical Systems, Inc.*, electrochemical analyzer model *BAS 100 W* was used to perform cyclic voltammetry and bulk electrolysis at controlled potential in a home-made high-vacuum cell. Typically, 2.0 μmol of the electroactive species (1.6 mg of **2**, 1.7 mg of **3**, or 1.9 mg of **4**), and 38.5 mg (100 μmol) of Bu_4NPF_6, recrystallized at least three times from 95% aq. EtOH, were placed in the cathodic compartment. After heating and pumping the cell to a pressure of 10^{-5} Torr for several min, 1.0–2.0 ml of pure MeCN were vapor transferred into the cell by following the procedure previously described.

2. *Characterization of [Fe(bpy)$_3$]* (**5**), *[Ru(bpy)$_3$]* (**6**), *and [Os(bpy)$_3$]* (**7**). Samples of the crystalline materials **5**, **6**, and **7** were slowly exposed to moist air for a few days. After this time, the solids were dissolved in distilled H_2O and a few drops of HPF_6 added to the solns. to precipitate the products **5a** (red), **6a** (orange), and **7a** (green), respectively. These solids were washed several times by following a cycle of addition of distilled H_2O, sonication, centrifugation, and decantation. The final products were vacuum-dried at 50° and a pressure of 10^{-5} Torr for 3 h.

UV/VIS Spectrophotometry. MeCN Solns. of 0.11 mg/ml of **2**, **3**, **4**, **5a**, **6a**, and **7a** were prepared, and their absorption spectra recorded in a 0.1-mm-pathlength quartz cell using a *Hewlett-Packard* diode array spectrophotometer model *8452 A*.

REFERENCES

[1] M. Biner, H.-B. Bürgi, A. Ludi, C. Röhr, *J. Am. Chem. Soc.* **1992,** *114,* 5197.

[2] a) G. F. Strouse, P. A. Anderson, J. R. Schoonover, T. J. Meyer, F. R. Keene, *Inorg. Chem.* **1992,** *31,* 3004; b) H. B. Ross, M. Boldaji, D. P. Rillema, C. B. Blanton, R. P. White, *ibid.* **1989,** *28,* 1013; c) J. N. Gex, M. K. DeArmond, K. W. Hanck, *J. Phys. Chem.* **1987,** *91,* 251; d) Y. Ohsawa, M.-H. Whangbo, K. W. Hanck, M. K. DeArmond, *Inorg. Chem.* **1984,** *23,* 3426; e) D. P. Rillema, G. Allen, T. J. Meyer, D. Conrad, *ibid.* **1983,** *22,* 1617.

[3] a) M. K. DeArmond, M. L. Myrick, *Acc. Chem. Res.* **1989,** *22,* 364; b) M. K. DeArmond, K. W. Hanck, D. W. Wertz, *Coord. Chem. Rev.* **1985,** *64,* 65; c) P. S. Braterman, G. A. Heath, L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.* **1985,** 1081; d) G. A. Heath, L. J. Yellowlees, P. S. Braterman, *Chem. Phys. Lett.* **1982,** *92,* 646; e) A. H. Graham, L. J. Yellowlees, P. S. Braterman, *J. Chem. Soc., Chem. Commun.* **1981,** 287.

[4] a) L. Echegoyen, A. DeCian, J. Fischer, J.-M. Lehn, *Angew. Chem. Int. Ed.* **1991,** *30,* 838; b) L. Echegoyen, Q. Xie, E. Pérez-Cordero, *Pure Appl. Chem.* **1993,** *65,* 441.

[5] S. Herzog, H. Präkel, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, September 7–11, 1964, p. 214.

[6] F. S. Hall, W. L. Reynolds, *Inorg. Chem.* **1966,** *5,* 931.

[7] N. Tanaka, T. Ogata, S. Niizuma, *Bull. Chem. Soc. Jpn.* **1973,** *46,* 3299.

[8] D. E. Morris, K. W. Hanck, M. K. DeArmond, *Inorg. Chem.* **1985,** *24,* 977.

[9] a) D. E. Morris, K. W. Hanck, M. K. DeArmond, *J. Am. Chem. Soc.* **1983,** *105,* 3032; b) Y. Ohsawa, M. K. DeArmond, K. W. Hanck, D. E. Morris, *ibid.* **1983,** *105,* 6522; c) A. G. Motten, K. W. Hanck, M. K. DeArmond, *Chem. Phys. Lett,* **1981,** *79,* 541.

[10] J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, A. J. Schultz, M.-H. Whangbo, 'Progress in Inorganic Chemistry', Ed. S. J. Lippard, John Wiley & Sons, Inc., New York, 1987, Vol. 35, pp. 51–218.

[11] N. E. Tokel-Takvoryan, R. E. Hemingway, A. J. Bard, *J. Am. Chem. Soc.* **1973,** *95,* 6582.

[12] P. Huber, H. Yersin, *J. Phys. Chem.* **1993,** *97,* 12705.