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^{1}H-NMR and Electrochemical Studies on Ligated Iron(III)perchlorates in Acetonitrile-d_3**

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Summary. Half-wave potentials, $E_{1/2}$, of Fe(ligand)$_6^{3+/2+}$, as ClO_4^- salt, [ligand = N,N-dimethylformamide (*dmf*), acetamide (*aa*), N,N-dimethylacetamide (*dma*), trimethylphosphate (*tmp*), dimethylsulfoxide (*dmso*), and acetonitrile (*Me*CN)] are given. A linear correlation between $E_{1/2}$ and Gutmann's donor numbers of the ligands, a parameter which expresses quantitatively the Lewis donor properties towards hard acceptors, was found. Ligand replacement on Fe(ligand)$_6^{3+}$ in acetonitrile-d_3 was studied by means of ^{1}H-NMR spectroscopy at 20°C. An average number of ligands coordinated to Fe^{3+}, n_{coord}, is given. n_{coord} increases with the ligand's donor strength; i.e. *tmp* < *dmf* < *dmso*.

Keywords. Half-wave potentials; Iron(III) complexes; Ligand exchange.

^{1}H-NMR- und elektrochemische Untersuchungen an koordinierten Eisen(III)perchloraten in Acetonitril-d_3

Zusammenfassung. Es wurden die Halbwellenpotentiale, $E_{1/2}$, von Fe(Ligand)$_6^{3+}$ als ClO_4^- Salz [Ligand = N,N-dimethylformamid (*dmf*), Acetamid (*aa*), N,N-dimethylacetamid (*dma*), Trimethylphosphat (*tmp*), Dimethylsulfoxid (*dmso*) und Acetonitril (*Me*CN)] bestimmt. Zwischen den $E_{1/2}$-Werten und den Gutmann Donor Zahlen der Liganden (eine Größe, welche die Lewis Basizität in quantitativer Weise ausdrückt) wurde ein linearer Zusammenhang gefunden. Der Ligandenaustausch an Fe(Ligand)$_6^{3+}$ in Acetonitril-d_3 wurde mittels ^{1}H-NMR Spektroskopie bei 20°C untersucht. Eine mittlere Koordinationszahl, n_{coord}, wurde bestimmt. n_{coord} nimmt mit der Donizität der Liganden zu, d.h. *tmp* < *dmf* < *dmso*.

Introduction

Kinetic and mechanistic investigations of chemical reactions in non-aqueous solutions have become an important field of research in the last decade. The simplest fundamental processes (at least in a theoretical sense) such as solvent exchange reactions [1], electron selfexchange reactions [2, 3] and electron transfer reactions between substitution inert complexes [4, 5] have been dealt with.

However, in the case of electron transfer reactions one eventually has to extend such studies to substitution of labile systems since many practical redox agents are

** Dedicated to Prof. Dr. mult. Viktor Gutmann on the occasion of his 70th birthday

labile solvated metal ions, and such studies might prove to be interesting by themselves. A study in this regard is given in [6].

In the present paper we report on electrochemical and ^{1}H-NMR studies on ligated iron(III) perchlorates, $Fe(ligand)_6^{3+}$ in acetonitrile solutions as part of our ongoing effort to study redox systems utilizing labile solvated metal ions as oxidants for substitution of inert complexes [7–9]. Strong donor solvents such as trimethylphosphate (*tmp*), N,N-dimethylformamide (*dmf*), dimethylsulfoxide (*dmso*), acetamide (*aa*), and N,N-dimethylacetamide (*dma*) are used as ligands. As a competitor for possible ligand replacement, acetonitrile (*Me*CN), a solvent with relative poor solvating power towards Fe^{3+}, has been chosen.

Further, the study of solvated metal ions in solvents other than those used as ligands might be an informative and interesting approach to mixed solvents to achieve a better understanding of the relative solvating power of solvents.

Experimental Part

Materials

$[Fe(ligand)_6](ClO_4)_3$ (ligand = *tmp*, *dmf*, *dmso*, *dma*) was made according to standard procedures [10]. $Fe(MeCN)_6)(ClO_4)_2$ was prepared by dissolving $[Fe(OH_2)_6](ClO_4)_2$ in acetonitrile and evaporating the solvent in the presence of 3 Å molecular sieve (activated at 300°C under vacuum). This procedure was repeated four times. The residue was recrystallized from *Me*CN, washed with anhydrous diethyl ether, and dried in vacuum at 50°C. $[Fe(aa)_6](ClO_4)_3$ was synthesized as described in [11]. The complex was precipitated from the reaction mixture upon the addition of anhydrous diethyl ether. The crude complex was recrystallized twice from *Me*CN, washed with anhydrous diethyl ether and dried in vacuum at room temperature for 24 h. Anal. calc. for $C_{18}H_{54}P_6O_{36}Cl_3Fe$ (*tmp*): C 18.10, H 4.56; found: C 17.79, H 4.37. Anal. calc. for $C_{18}H_{42}N_6O_{18}Cl_3Fe$ (*dmf*): C 27.27, H 5.34, N 10.60, Fe 7.04; found: C 27.26, H 5.27, N 10.48, Fe 7.04. Anal. calc. for $C_{12}H_{36}S_6O_{18}Cl_3Fe$ (*dmso*): C 17.52, H 4.41; Fe 6.80; found: C 17.35, H 4.19, Fe 6.81. Anal. calc. for $C_{24}H_{54}N_6O_{18}Cl_3Fe$ (*dma*): C 32.87, H 6.21, N 9.58, Cl 12.13, Fe 6.36; found: C 32.94, H 6.28, N 9.39, Cl 11.99, Fe 5.42. Anal. calc. for $C_{12}H_{30}N_6O_{18}Cl_3Fe$ (*aa*): C 20.34, H 4.27, N 11.86; found: C 20.07, H 4.10, N 11.69. Anal. calc. for $C_{12}H_{18}N_6O_8Cl_2Fe$ (*Me*CN): C 28.58, H 3.57, N 16.67; found: C 26.16, H 3.58, N 15.18. Microanalyses of the *tmp* and *aa* solvates were done by Galbraith Laboratories, Knoxville, TN. All other compounds were analyzed by the Microanalytical Laboratory of the University of Vienna. All solvents used for the synthesis of the iron complexes were purified according to a literature method [12]. Acetamide was purchased from Alpha Chemical Co., recrystallized twice from methanol and dried at 25°C under vacuum. Acetonitrile-d_3 (99.7% D) was obtained from MSD Isotopes Merck, dried over activated 4 Å molecular sieves, degassed by three consecutive freeze-pump-thaw cycles, and stored in an evacuated bulb in the dark until used.

^{1}H-NMR Measurements

Details of sample preparation are given in [2, 3]. Proton NMR spectra were collected on a Nicolet NT 200 WB and IBM NR 300 instruments operating at 200 and 300 MHz, respectively. The acquisition parameters on the Nicolet instrument were a 4.5 μs pulse width, a 500 ms post acquisition delay, a 10 000 to 20 000 Hz sweep width, a 32 K block size and 256 to 2 048 pulses. On the IBM instrument the acquisition parameters were a 2.0 μs pulse width, a 10 000 Hz sweep width, a 32 K block size, and 130 to 4 000 pulses. All measurements were carried out at 20 ± 1°C. The temperature readings were calibrated against the temperature dependence of the proton chemical shifts of acidified (0.5% HCl) methanol [13]. Chemical shifts are given relative to tetramethysilane (*TMS*) or to the signal of the residual protons of CD_3CN (1.939 ppm vs. *TMS*).

Cyclic Voltammetric Measurements

Cyclic voltammetric measurements were carried out at 25°C with a Princeton Applied Research (PAR) 173 potentiostat and a PAR 175 universal programmer equipped with a Houston Instruments Model 2000 XY recorder. A three-electrode system was used with a glassy carbon working electrode and Pt-wire counter electrode. The reference electrode was a silver wire employed as a quasi-reference electrode. Both the counter electrode and the Ag-wire electrode were separated from the working solution by fine glass frits. The reference redox system added to the solutions studied was bis(biphenyl)-chromium(O/I) (BBCr), added as the tetraphenylborate salt (−1.118 V vs. ferrocene/ferricenium). Tetra(*n*-butylammomium)-hexafluorophosphate (0.1 *M*) was used as supporting electrolyte [14].

Results and Discussion

At room temperature the solvated iron(III) complexes show separated signals for coordinated and bulk ligands indicating that ligand exchange is in the slow-exchange regime on the NMR time scale. For the analogous iron(II) complexes dissolved in acetonitrile-d_3 only at temperatures below −40°C seperated signals have been observed [6]. This observation is in line with solvent exchange data reported by Merbach et al. [1]. Pseudo-first-order rate constants were determined to be 9.3 and 61 s^{-1} for the *dmso* and *dmf* solvate, respectively.

Due to the paramagnetism of Fe^{3+} (d^5-high spin) the signals of the coordinated ligands are shifted up to 100 ppm downfield vs. *TMS*. The signals of bulk ligands are not affected, and are found to to be in the usual frequency range for organic compounds between 0 and 10 ppm. However, the signals of the coordinated ligands are in some cases up to ca. 1 000 Hz broad and hence no distinction between different species, $Fe(ligand)_{6-n}(MeCN)_n^{3+}$ ($n = 0$ to 6), could be made.

$Fe(dmf)_6^{3+}$: The concentration range studied was about 3 to 70 m*M*. In all cases coordinated and bulk ligands could be detected. This is illustrated in Fig. 1. In agreement with the spectrum of neat *dmf* the peak at 8.01 ppm (enlarged 200 times) and the slightly broadened doublet at 2.74 and 2.91 ppm, respectively, could

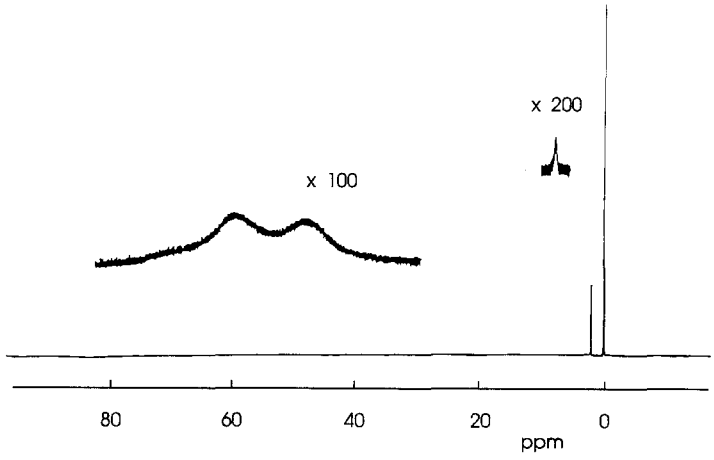

Fig. 1. 200 MHz ^{1}H-NMR spectrum of $[Fe(dmf)_6](ClO_4)_3 = 8.6$ m*M* in acetonitrile-d_3 at 20°C. The formyl proton (200 times enlarged) is observed at 8.01 ppm and the methyl protons of coordinated *dmf* (100 times enlarged) are shifted towards higher frequencies resonating between 20 and 100 ppm. The signal at 1.93 ppm can be assigned to acetonitrile-d_3; all signals are related to *TMS*

be assigned to the formyl proton and the (*cis* and *trans*) methyl protons with regard to the oxygen atom of bulk *dmf*. The formyl peak had to be chosen for peak integration due to peak overlapping of the latter with the solvent resonance signal. The broad peaks between 20 and 100 ppm (enlarged 100 times) were assigned to the methyl protons of coordinated *dmf*. From experience it is reasonable to assume that these signals do not include the formyl protons of coordinated *dmf*. It has been shown that, in the case of *dmf* coordination through oxygen, paramagnetic line broadening is about 10 – 50 times stronger for formyl protons than for methyl protons [6, 15, 16]. An average coordination number of *dmf* coordinated at Fe^{3+}, n_{coord}, calculated from the areas of the peaks between 20 and 100 ppm, and from the peak area at 8.01 ppm is given in Table 1 for various Fe(III) concentrations.

$Fe(tmp)_6^{3+}$: Even at a magnetic field of 300 MHz slight peak overlapping occurred, as shown in Fig. 2. Therefore, peak integration was done manually by weighing the areas under the peaks. In agreement with the ^{1}H-NMR spectrum of neat *tmp* the signal of bulk *tmp* was found at 3.68 ppm. Because of coupling to ^{31}P, in the more diluted samples the signal was split into a doublet. In analogy to the *dmf* complex the broad signal between about 4 to 12 ppm was assigned to coordinated *tmp*. n_{coord} was determined in the same manner as for the *dmf* complex and is given in Table 2.

$Fe(dmso)_6^{3+}$: No evidence for free *dmso* was found. The signal of coordinated *dmso* was found between 20 to 60 ppm. Upon addition of small amounts of extra *dmso* a signal at 2.49 ppm was observed which could be assigned to free *dmso*, which implies that the ligand exchange is slow on the NMR timescale. Current studies on electron-transfer reactions utilizing this complex as an oxidant for ferrocene in *Me*CN and *Me*CN/*dmso* mixtures, however, indicate that some *dmso* is replaced by *Me*CN [9].

$Fe(aa)_6^{3+}$: As for the *dmso* system no free ligand could be detected. Free acetamide exhibits a sharp singlet at 1.48 ppm (methyl protons) and a broad peak at about 5.8 ppm (amide protons). Since the chemical shifts of the protons of *aa* are very sensitive to solvent [17] the singlet of bulk methyl protons is superimposed by the solvent signal. The signal of free amide protons is broadened due to quadrupole relaxation of the adjacent ^{14}N [18] which might be too broad to be detected

Table 1. Numbers, n_{coord} of N,N-dimethylformamide molecules coordinated at Fe^{3+} in solutions of hexakis(N,N-dimethylformamide)iron(III)perchlorate in acetonitrile-d_3 at 20°C

$[Fe^{3+}]$/m*M*	n_{coord}/molecule
1.70	5.19 ± 0.2
3.03	5.32 ± 0.2
6.86	5.55 ± 0.2
9.24	5.75 ± 0.2
21.19	5.77 ± 0.3
76.50	5.89 ± 0.3

Table 2. Numbers, n_{coord}, of Trimethylphosphate molecules coordinated at Fe^{3+} in solutions of hexakis-(trimethylphosphate)iron(III)perchlorate in acetonitrile-d_3 at 20°C

$[Fe^{3+}]$/m*M*	n_{coord}/molecule
3.00	3.90 ± 0.2
7.15	4.56 ± 0.1
11.13	4.70 ± 0.2
30.50	4.89 ± 0.2

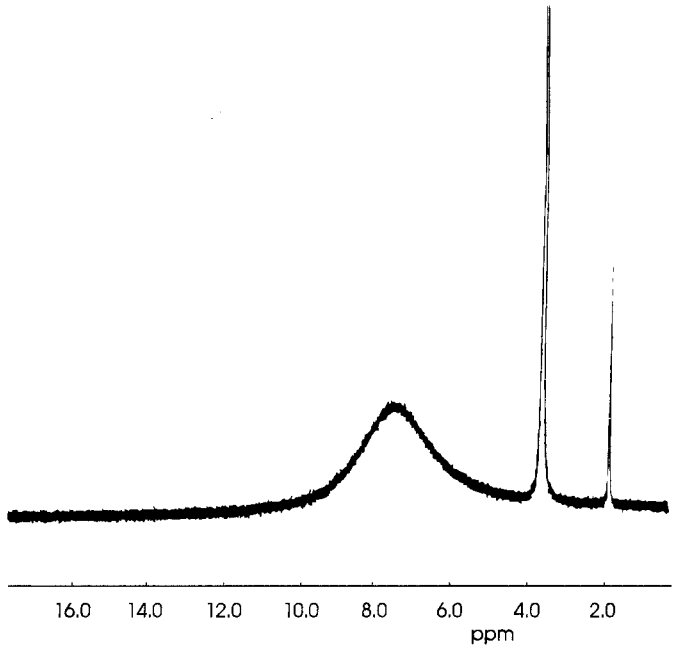

Fig. 2. 300 MHz ^{1}H-NMR spectrum of $[Fe(tmp)_6](ClO_4)_3 = 30.5$ m*M* in acetonitrile-d_3 at 20°C. Methyl protons of bulk *tmp* resonate at 3.68 ppm. The broad signal between about 4 to 12 ppm corresponds to the methyl protons of coordinated *tmp*. The solvent peak is assigned to 1.93 ppm; no *TMS* was added

by NMR. Thus no evidence for ligand replacement can be given though it cannot be conclusively ruled out.

$Fe(dma)_6^{3+}$: No quantitative information could be gained due to extensive peak overlapping between the signals of coordinated and bulk *dma*. However, ligand substitution takes place, and the signals of bulk *dma* are in line with a spectrum of neat *dma* (*cis* and *trans* methyl protons at 3.17 and 3.11 ppm, respectively).

$Fe(H_2O)_6^{3+}$: No conclusive results could be gained due to the formation of several intractable species presumably hydroxo bridged complexes. The spectrum shows more than 6 broad peaks which are strongly overlapped. Further investigation on this subject is planed.

As depicted in the insert of Fig. 3, n_{coord} increases with decreasing donor strength of the ligand. However, ligand replacement is much less pronounced than in the Fe^{2+} case. From the above results, together with previous results from kinetic studies [6, 7], the speciation for both $Fe(dmf)_6^{2+}$ and $Fe(dmf)_6^{3+}$ dissolved in acetonitrile could be given. For the first $Fe(dmf)_2(MeCN)_4^{2+}$ is the predominant species, for the latter $Fe(dmf)_6^{3+}$ and $Fe(dmf)_5(MeCN)^{3+}$, respectively, are the predominant species in acetonitrile as a solvent.

The results of the electrochemical measurements are depicted in Fig. 3. They agree well with the values reported in [11]. A linear relationship between half-wave potentials and Gutmann's donor numbers was found [19]. The stronger the donor the more stable is the oxidized form of these redox couples. The *Me*CN solvate, however, does not follow this pattern. Acetonitrile is known to stabilize metal ions in lower oxidation states due to its ability to accept electron density from filled metal orbitals to form a type of π bonding that supplements the σ bonding arising

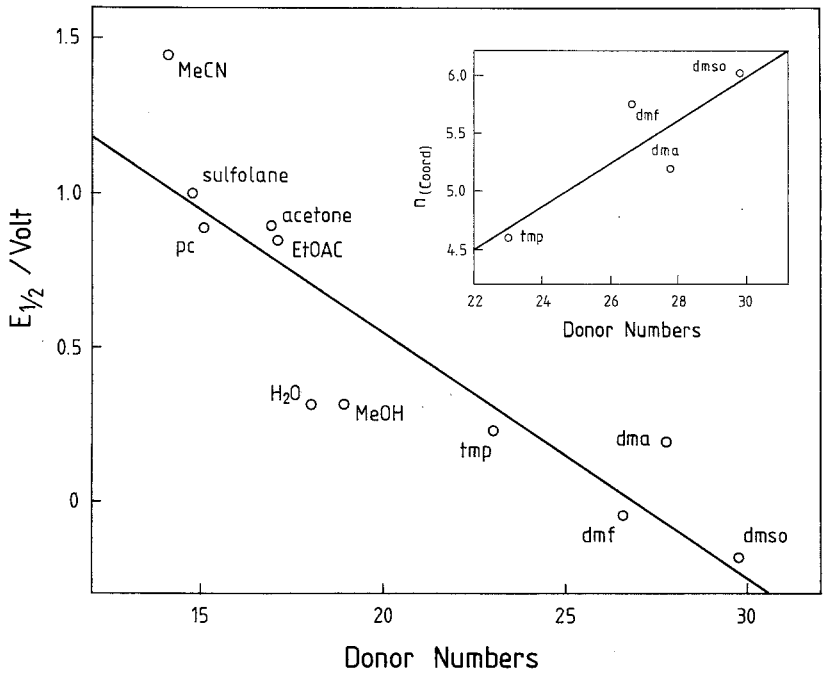

Fig. 3. Plot of half-wave potentials of Fe(ligand)$_6^{3+}$, as the perchlorate salt, vs. Gutmanns Donor Numbers. $E_{1/2}$ values for sulfolane, propanediolcarbonate (*pc*), acetone, ethylacetate (*EtOAc*), H_2O and methanol (*MeOH*) were taken from Ref. [11]. Insert: Average number of coordinated *tmp*, *dmf*, *dma* and *dmso*, coordinated at Fe^{3+} ([Fe(III)] $\approx$ 9.2 m*M*, except for [Fe(*dmso*)$_6$(ClO$_4$)$_3$] as saturated solution $\approx$ 2 m*M*) vs. Donor Numbers. The value for *dma* was taken from kinetic data [9]

from the lone-pair donation. As can be seen from Fig. 3 the redox potential of the $Fe^{3+/2+}$ couple increases from -0.05_8 V in the case of Fe(*dmf*)$_6^{3+/2+}$ to as high as 1.44_6 V in the case of Fe(*Me*CN)$_6^{3+/2+}$ (reference redox system is ferrocene/ferricenium). Fe(ligand)$_6^{3+}$ dissolved in *Me*CN (ligand $\neq$ *Me*CN) did not show a reversible oscillographic wave. In [11] a similar behaviour was reported. There, a cyclic voltammogram of Fe(OH$_2$)$_6^{3+}$ in 0.1 *M* tetraethylammonium perchlorate acetonitrile solution taken at 100 mV/s reveals a broad oxidation wave at about 1.4 V (vs. ferrocene/ferricenium). On the return scan there is a single irreversible reduction wave at about 0.0 V (vs. ferrocene/ferricenium).

The cyclic voltammogram of Fe(*dmf*)$_6^{3+/2+}$ in *Me*CN shows the same pattern . This suggests an ECEC mechanism [20] which indeed is in line with the speciation given for the Fe(*dmf*)$_6^{3+/2+}$ system in acetonitrile. On the basis of these studies [6, 7] a scheme of a cyclic ECEC mechanism is given in Fig. 4.

In conclusion, even though high spin Fe^{3+} is not considered as a good π base *Me*CN is able to replace a significant amount of strong donor ligands such as *tmp*, *dma*, and *dmf* coordinated at Fe^{3+}. No evidence for the replacement of *dmso* could be found in the present study. However, kinetic studies on electron-transfer reactions between Fe(ligand)$_6^{3+}$ and ferrocene in acetonitrile suggest that even in the *dmso* case ligand substitution occurs [9]. Further research on similar systems such as V(ligand)$_6^{3+}$ and Mn(ligand)$_6^{3+}$ and so called "poorly coordinating" solvants other than acetonitrile such nitromethane and propylene carbonate might prove to be of interest.

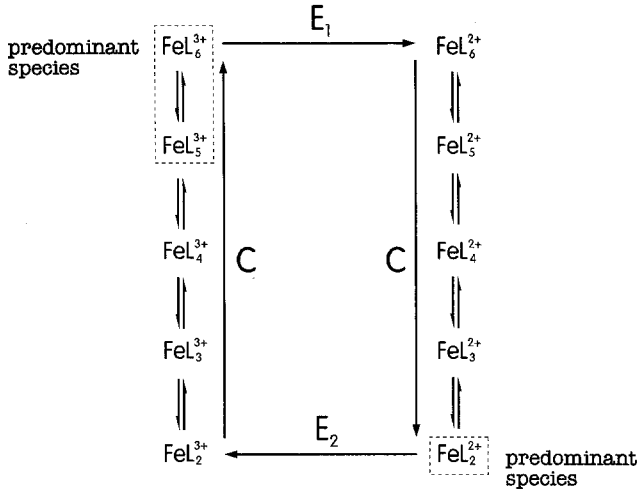

Fig. 4. A schematic presentation of a cyclic ECEC mechanism for $Fe(dmf)_6^{3+}$ (counterion is ClO_4^-) dissolved in acetonitrile at 20°C [$Fe(dmf)_6^{3+} = FeL_6^{3+}$, coordinated *Me*CN is omitted]

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References

[1] Merbach A. E. (1982) Pure Appl. Chem. **54**: 1479
[2] Kirchner K., Dodgen H. W., Wherland S., Hunt J. P. (1989) Inorg. Chem. **28**: 3606
[3] Anderson K., Wherland S. (1989) Inorg. Chem. **28**: 601
[4] Borchardt D., Pool K., Wherland S. (1982) Inorg. Chem. **21**: 93
[5] Gribble J., Wherland S. (1989) Inorg. Chem. **28**: 2859
[6] Schmid R., Kirchner K., Dickert F. L. (1988) Inorg. Chem. **27**: 1530
[7] Schmid R., Kirchner K., Sapunov V. N. (1989) Inorg. Chem. **28**: 4171
[8] Schmid R., Han L-F., Kirchner K., Sapunov V. N. to be submitted.
[9] Jedlicka R. (1990) Dissertation, TU-Wien
[10] Schmid R., Sapunov V. N., Gutmann V. (1976) Ber. Bunsenges. Phys. Chem. **80**: 1302
[11] Kotani E., Kobayashi S., Ishii Y., Tobinaga S. (1984) Chem. Pharm. Bull. **11**: 4281
[12] Riddick J. A., Bunger W. B. (1970) Organic Solvent, Wiley-Interscience, New York 3rd ed. Techniques of Chemistry, Vol. II
[13] Raiford D. S., Fisk C. L., Becker E. D. (1979) Anal. Chem. **51**: 2050
[14] Gritzner G. J. (1983) Electroanal. Chem. Interfacial Electrochem. **144**: 259
[15] Matwioff N. A. (1966) Inorg. Chem. **5**: 788
[16] Dickert F. (1977) Z. Phys. Chem. (Munich) **106**: 155
[17] Gonzales G, Chavez I. (1981) J. Chem. Soc., Faraday Trans. 2 **77**: 2231
[18] Liler M. (1971) J. Magn. Reson. **5**: 333
[19] Schmid R. (1983) J. Solution Chem. **12**: 135
[20] Harman D. W., Fairlie D. P., Taube H. (1986) J. Am. Chem. Soc. **108**: 8223
[21] Kirchner K., (1987) Dissertation, TU-Wien

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