Inorganica Chimica Acta, *117* (1986) 97–101

Solvent Effects on the Electrochemical Properties of $IrCl_2(bpy)_2^+$

BERNADETTE DIVISIA-BLOHORN*

Laboratoires de Chimie (UA CNRS no 321), Centre d'Etudes Nucléaires de Grenoble 85 X, 38041 Grenoble Cedex, France

(Received July 22, 1985; revised February 24, 1986)

Abstract

To investigate the solvent dependence of the d-d contribution to the redox orbital of the *cis*-dichloro-bis-(2,2'-bipyridine) iridium(III) ion, the first reduction electron transfer has been studied in various non-aqueous and aqueous solvents by cyclic voltammetry and spectroelectrochemistry. Totally irreversible electrochemical processes and chloride release have been observed in water, methanol and formamide, which are consistent with the proposed predominantly metallic nature of the redox orbital in these solvents. In other solvents the electron reduction sequence and the low chemical reaction rate of chloride release suggest a strong interaction between the ligand and metal-centered redox orbitals. Correlation of the reduction potential with the Gutmann's acceptor number and dielectric constant of the solvents indicates that chloride release depends strongly upon the dissociative properties of the solvent. The electrochemical behaviour and photochemical observations are compared.

Introduction

Numerous studies [1] have been made on multiple state emission and related phenomena in transition metal complexes. In particular the luminescence turning [2] of the 2,2'-bipyridine and 1,10-phenanthroline complexes of iridium(III) in fluid solution have stimulated widespread interest in recent years. Previous studies on the luminescence properties [3] of *cis*-dichloro-bis-(2,2'bipyridine) iridium(III) ($IrCl_2(bpy)_2^+$) suggest that this complex is able to luminesce from two different low-energy orbitals, *i.e.*, the lowest-energy ligand field (LF) excited states and the low-energy charge transfer (CT) excited states of slightly higher energy than the LF excited states. Recent studies [4, 5] on triplet–triplet absorption attribute the luminescence to the lowest-energy CT excited states. Moreover, different photophysical and photochemical behaviours of this complex have been observed in different solvents. Generally a higher photosolvation rate constant occurs in protic solvents relative to non-protic ones, attributed to an energy increase of the CT states [6].

Conversely, it is known that the redox properties of complexes, depending [7] on the ionization energy, the electron affinity, and on the modified electron distribution in the reacting species, have allowed the characterization of the nature of the redox orbitals of porphyrins [8], metallophthalocyanines [9], bipyridine or phenanthroline complexes [10–14] and the evaluation of ligand–metal and molecular interactions [15–25]. In the case of $IrCl_2(bpy)_2^+$, two electrochemical studies have been reported. Roffia and Ciano [26] described the cyclic voltammetry in dimethylformamide (DMF). Their results suggest that, in this solvent, each reversibly added electron in the first two reduction processes occupies a π^* orbital localised on a single bipyridine ligand. A similar electron transfer sequence in acetonitrile (AN) was observed by Hanck and De Armond [27–28] indicating that the redox orbital character is apparently independent of the solvent. However, the first electron reduction species is unstable and undergoes chloride elimination. These authors attributed this instability to the first reduction electron's occupation of a partially metal-localized redox orbital. Thus, comparison of these two studies suggests a solvent influence on the electrochemical properties of $IrCl_2(bpy)_2^+$. In this paper are reported cyclic voltammetry measurements and spectroelectrochemical data of the first reduction electron transfer in various non-aqueous and aqueous solvents. A comparison is made with photochemical observations.

Experimental

The iridium complex was synthesised as described previously [29] as the chloride or perchlorate. All solvents and background electrolytes were purified according to the usual procedure under argon. Solution preparation and electrochemical measurements were performed under argon.

---

*Member of the 'Université de Savoie'.

0020-1693/86/$3.50

Cyclic voltammetry measurements were made at 25 °C with a Princeton Applied Research (PAR) model 173 potentiostat with a PAR 176 current-to-voltage convertor with IR compensation. A triangular wave generator based on a PAR 175 universal programmer was interfaced to the PAR 173. For rapid scan cyclic voltammetry measurements, an explorer III oscilloscope (digital memory) was used. The Harrick rapid scan spectrometer (HRSS) has been described elsewhere [30].

The working electrode was a dropping mercury electrode (DME) (drop time 2s), a hanging mercury drop (HME) [31], or a platinum electrode; the reference electrode was a saturated calomel electrode connected to the electrolysis cell through an ionic bridge filled with solvent and the background electrolyte; the auxiliary electrode was a platinum wire electrode. Whenever possible, benzene chromium(I)/bis-benzenechrome(0) was used as internal standard for the half potentials, according to the literature procedure [21, 32]. See also 'Supplementary Material'.

Results

(a) Cyclic Voltammetry Measurements

The cyclic voltammetry data of $IrCl_2(bpy)_2ClO_4$ in AN and DMF with TEAP as supporting electrolyte are analogous to those already reported by De Armond *et al.*, and Ciano *et al.* at the same scan rate and scale. But when in AN the chloride instead of the perchloride ion is used as the counter ion, the third reduction peak disappears and two successive one-electron reduction processes are observed as in DMF (Fig. 1).

The cyclic voltammetry data for the first reduction process of $IrCl_2(bpy)_2^+$ in aqueous and non-aqueous solvents are shown in Table I. No anodic peak is observed in FA, MeOH and water for the first reduction process (Figs. 2 and 3). In MeOH, two very close successive totally irreversible one-electron transfers are observed (Fig. 2), while only one totally irreversible two-electron transfer step occurs in FA (Fig. 3). In water, the reduction peak is only a limiting cathodic current shoulder, so that it was not possible to study this reduction process. In MeOH, with chloride as counter ion, the reverse peak is not observed until 1 V/s scan rate. On the contrary, in the other solvents the anodic peak is always observed even at very slow scan rate. The

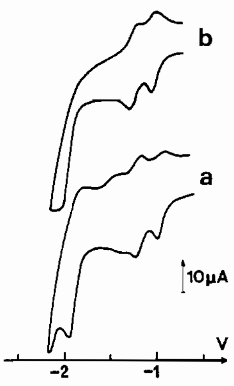

Fig. 1. Cyclic voltammograms of $IrCl_2(bpy)_2^+$ 5 × 10^{-4} M at 29.3 V/s in CH_3CN *vs.* SCE with HME: (a) 0.1 M TEAP; (b) 0.1 M TEACl.

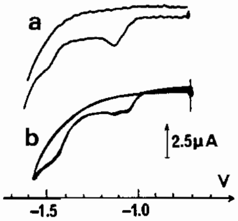

Fig. 2. Cyclic voltammograms of $IrCl_2(bpy)_2^+$ 10^{-3} M and Bu_4NPF_6 0.1 M in MeOH *vs.* SCE with DME: (a) scan rate 2 V/s; (b) scan rate 500 mV/s.

TABLE I. Characteristics of the First Reduction Step of $IrCl_2(bpy)_2^+$ *vs.* Solvent Properties Defined as the Guttman's Acceptor (AN) and Donor (DN) Number and Dielectric Constant

Solvents	Background electrolyte	ν^a (V/s)	E_{pc}^b (V)	E_{pa}^c (V)	$E_{1/2}^d$ (V)	i_{pa}^d	ΔE_{ir} (mV)	ΔE_{cr} (mV)	AN	DN	ϵ
THF	nBu_4PF_6	0.100	−0.465	−0.365	−0.415	0.9	100	70	8	20	7.4
CH_2Cl_2	TBAP	0.05	−0.403	−0.332	−0.380		70	75	20.4		8.9
Ac	TEAP	0.100	−0.385	−0.330	−0.357	0.95	60	100	12.5	17	20.7
DMF	TEAP	0.050	−0.380	−0.320	−0.350	1	60	60	16	26.6	36.7
AN	TEAP	0.050	−0.355	−0.285	−0.320	0.9	70	60	19.3	14.1	36
DMSO	TEAP	0.100	−0.357	−0.297	−0.327	0.9	60	60	19.3	29.8	46.7
MeOH	Bu_4PF_6	0.500	−0.200			0			41.3	32.6	32.6
H_2O	KCl	0.1	−0.210			0			54.8	18	78.5
FA	TBAP	0.050	−0.180			0			39.8	24	109.5

ªScan rate. ᵇCathodic peak. ᶜAnodic peak. ᵈSee text. Potentials are measured *vs.* bisbenzenechromium/bisbenzene chrome as internal reference with HME.

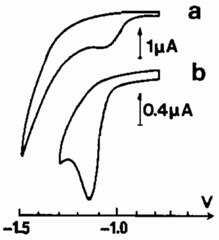

Fig. 3. Cyclic voltammograms of $IrCl_2(bpy)_2^+$ 5 × 10^{-4} M at 200 mV/s: (a) 0.1 M KCl in water with HME; (b) 0.1 TBAP in FA, with HME.

difference $E_{pc} - E_{pa}$ is only 60 mV in DMF and DMSO, but the ratio i_{pa}/i_{pc} calculated according to Nicholson's method [33] is less than 1 except in DMF, indicating a complicated mechanism for this electron reduction. However, an $E_{1/2}$, which is not the thermodynamic value, is calculated from $(E_{pc} + E_{pa})/2$ in order to correlate these potentials with solvent properties referred to as the Gutmann's acceptor and donor number [34] or dielectric constant [35].

As the first two one-electron reductions of $IrCl_2(bpy)_2^+$ appear reversible in DMF from 100 mV/s to 2 V/s scan rate (see for example Fig. 4a), these reduction steps have been studied with thin layer platinum electrodes at scan rates as low as 10 mV/s. On scanning only until the first one-electron reduction, the reverse peak is observed (Fig. 4b, curve 1). But going further than the second electron reduction, a new peak appears at −1.48 V *vs.* SCE with its reverse peak at 1.42 *vs.* SCE, while the anodic peaks of the first two reduction steps of $IrCl_2(bpy)_2^+$ disappear (Fig. 4b, curve 2). On the last scan (Fig. 4b, curve 3) only the cathodic and anodic peaks of the one-electron reduction process of a new species, attributed to $IrCl(bpy)_2^+$ [27], are observed. These data indicate that a chloride elimination also takes place in DMF, but very slowly.

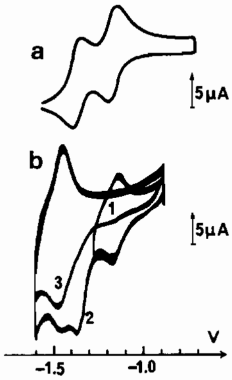

Fig. 4. Cyclic voltammograms of $IrCl_2(bpy)_2^+$ 10^{-3} M in DMF and Bu_4NPF_6 *vs.* SCE: (a) DME, scan rate 2 V/s; (b) thin layer Pt electrode, scan rate 10 mV/s.

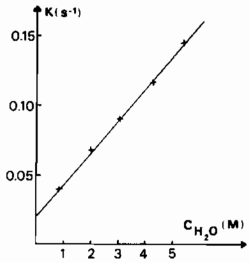

Fig. 5. Variation of the rate constant following the first one-electron reduction in DMF at various H_2O concentrations.

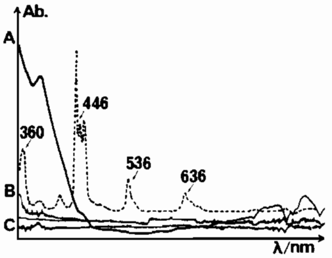

Fig. 6. Spectroelectrochemistry of $IrCl_2(bpy)_2^+$ 1.7 × 10^{-3} M in DMF. Dashed line: UV and visible absorption spectrum of the reference filter; (a) UV–Vis absorption spectrum of $IrCl_2(bpy)_2^+$ solution; (b) after 1024 steps at the first one-electron reduction potential; (c) base line.

Cyclic voltammetry measurements of $IrCl_2(bpy)_2^+$ have been made in various DMF/water mixtures. At low water concentration, there is no net water influence on the cyclic voltammetry shape. At higher concentration (1 M to 5 M), there is no change in the E_{pa} and E_{pc} values but the ratio i_{pa}/i_{pc} decreases and allows us to obtain the first order or pseudo first order rate constant of the chemical reaction that follows the electron transfer [36] (Fig. 5). However, the decrease of this ratio needs such a high water concentration that it is difficult to determine whether the irreversibility of the first one-electron reduction arises from a kinetic factor or from a change in the physical properties of the solvent. Assuming that the chemical reaction is first order, the extrapolation to pure DMF gives a value of 2 × 10^{-2} s^{-1} for this rate constant according to the order of magnitude obtained from thin layer voltammetry. This rate constant is at least 10^3 larger in pure water, MeOH and FA.

Spectroelectrochemistry

The first one-electron reduction step of $IrCl_2(bpy)_2^+$ produces a species stable enough for its spectroelectrochemical study. So we attempted to obtain its UV–Vis absorption spectrum using an HRSS. Similar results have been obtained using chloride or perchlorate as the counterion. The spectrum shown in Fig. 6 was obtained after averaging 1024 combined potential steps plus a scan of a

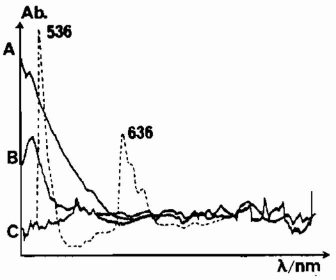

Fig. 7. Spectroelectrochemistry of $Ru(bpy)_3^{2+}$ 8.6 × 10^{-4} M in DMF: (a) UV–Vis absorption spectrum of $Ru(bpy)_3^{2+}$ solution; (b) after 1024 steps at the first one-electron reduction potential; (c) base line.

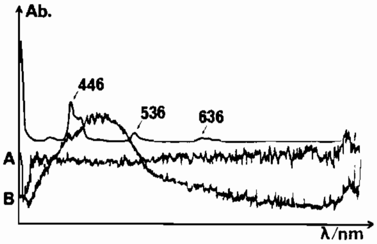

Fig. 8. Spectroelectrochemistry of $IrCl_2(bpy)_3^+$ 6 × 10^{-4} M in DMF; (a) base line; (b) after 1024 steps at −2 V.

1.7×10^{-3} M $IrCl_2(bpy)_2^+$ solution in DMF. The potential excursion was programmed for 50 ms from zero to the potential of the first one-electron reduction and return. The HRSS was triggered for the last 20 ms. Each excursion was made with a 5 s interval at OV, in order to allow the solution to relax. No new absorption band appeared in the area 450–725 nm. Under the same conditions, an 8.6×10^{-4} M $Ru(bpy)_3^{2+}$ solution produced an absorption in this area that can be attributed to the reduced $Ru(bpy)_3^+$ species (Fig. 7) [37]. When the experiment is carried out on the $IrCl_2(bpy)_2^+$ solution at very low potential, where it is known that the $Ir(bpy)_2^-$ species is produced [27], a new absorption appears at 500 nm (Fig. 8) with a molar extinction coefficient of 2.08×10^5 mol^{-1} cm^{-1} l, which is in good agreement with the electronic absorption spectrum of the radical anion of the bipyridine ligand [38]. During the first minutes of a continuous electrolysis at the potential of the first one-electron reduction of a 10^{-3} M $IrCl_2(bpy)_2^+$ solution in DMF analysed by the HRSS, a regular increase of $IrCl_2(bpy)_2^+$ absorption bands is observed. After this time, some variations corroborate the complex first one-electron reduction process of $IrCl_2(bpy)_2^+$.

Discussion

Our own results and previously described results [26–28] are interpreted by the square diagram where the reaction pathway depends on the solvent and the experimental scan rate (Scheme 1). In DMF, at fast enough scan rate, the first two reversible one-electron reduction waves correspond to E_{I} and E_{II}. At very low scan rate the pathway is a mixture of $E_{\mathrm{I}}C_{\mathrm{I}}E_{\mathrm{III}}$ and $E_{\mathrm{I}}E_{\mathrm{II}}C_{\mathrm{II}}$. The third peak of the thin layer experiment corresponds to the process E_{III}. In water, MeOH and FA, the chloride release is so fast that the electron reductions are totally irreversible even at very high scan rate. In the other solvent, the first one-electron reductions E_{I} and E_{II} are followed by the chloride elimination C_{I} and C_{II}, but the rate is slower and the reduction processes are partially irreversible. The chloride elimination can be prevented in AN at high scan rate by using chloride as the counter ion.

$$\begin{tikzcd}
\mathrm{IrCl_2(bpy)_2^+} \arrow[r, leftrightharpoons, "+e^-", "E_{\mathrm{I}}"'] & \mathrm{IrCl_2(bpy)_2^0} \arrow[r, leftrightharpoons, "+e^-", "E_{\mathrm{II}}"'] \arrow[d, shift left, "-\mathrm{Cl}^-"] & \mathrm{IrCl_2(bpy)_2^-} \arrow[d, shift left, "-\mathrm{Cl}^-"] \\
 & \mathrm{IrCl(bpy)_2^+} \arrow[r, leftrightharpoons, "+e^-", "E_{\mathrm{III}}"'] \arrow[u, shift left, "C_{\mathrm{I}}"] & \mathrm{IrCl(bpy)_2^0} \arrow[u, shift left, "C_{\mathrm{II}}"]
\end{tikzcd}$$

Scheme 1.

No correlation of the $E_{1/2}$ of the first one-electron reduction with the solvent donor number has been observed, but only a light potential shift is noted toward the positive potential values by increasing acceptor number except for CH_2Cl_2. The solvent interaction with the reduced species depends slightly on the solvent donor and acceptor properties, as expected by its neutral charge. On the other hand, the first electron reduction is totally irreversible in solvents of high acceptor number or high dielectric constant. When the solvent has a high acceptor number but a very low dielectric constant, for example CH_2Cl_2, the first one-electron reduction potential is lower than in DMF and AN, which have about the same acceptor number but a higher dielectric constant. The dielectric constant reflects the charge separating ability of the solvent and correlate better than the acceptor number the extent to which the solvent weakens the Ir–Cl bond by stabilising the developing charge on the chloride during the reduction step. This interaction becomes strong enough to induce the cleavage of the Ir–Cl bond. In FA of the highest dielectric constant, the reduction process becomes an irreversible two-electron step similar to the reduction process of the rhodium complex [28].

The Nature of the Redox Orbital

The electrochemical properties of $IrCl_2(bpy)_2^+$ parallel quite well the photochemical behaviour of this complex in various solvents, where the photosolvation of the chloride ion is observed in protic solvents such as water and MeOH [6]. The very fast chemical reaction following the electron reduction transfer in water, MeOH and FA can be explained by the predominantly metallic nature of the redox orbital in these solvents. In MeOH, the apparent potential of the first one-electron reduction is higher than the apparent potential of the second one-electron reduction, and two successive one-electron reductions are observed. In FA, this second reduction is shifted toward the positive potential values and becomes higher than the first one-electron reduction. The second one-electron reduction is easier than the first, and the reduction process is a two-electron transfer. This might be explained both by the pure metal redox orbital of the complex in this last solvent, as postulated for the analogous rhodium complex, and by the dielectric properties of the solvent.

On the other hand, the electron reduction sequence and the low chemical reaction rate observed in the other solvents are in good agreement with a strong interaction between the ligand and metal-centered redox orbitals [39]. The spectroelectrochemical data show that in the time scale experiments the first electron reduction is not localized on a bipyridine ligand; this suggests an interaction between the metal and the delocalised ligand orbitals. However, these results do not allow an evaluation of the importance of the d–d participation in the redox orbital but support that this participation depends strongly upon the dissociative properties of the solvent.

Supplementary Material

Further experimental details are available from the author.

Acknowledgements

I would like to thank Professor E. Genies for his collaboration in the spectroelectrochemical experiments and Dr. Y. Mugnier for the electrochemical data on DME. I am also grateful to Professor Cauquis for his interest in this work.

References

1 M. K. De Armond and C. M. Carlin, *Coord. Chem. Rev., 36,* 325 (1981).
2 R. J. Watts, *Inorg. Chem., 20,* 2302 (1981).
3 R. J. Watts, S. Efrima and H. Metiu, *J. Am. Chem. Soc., 101,* 2742 (1979).
4 Y. Ohashi and T. Kobayashi, *Bull. Chem. Soc. Jpn., 52,* 2214 (1979).
5 Y. Ohashi, *Bull. Chem. Soc. Jpn., 54,* 3673 (1981).
6 B. Divisia, P. C. Ford and R. J. Watts, *J. Am. Chem. Soc., 102,* 7264 (1980).
7 A. A. Vlcek, *Electrochim. Acta, 13,* 1063 (1968).
8 A. Giraudeau, H. J. Callot, J. Jordan, I. Ezhar and M. Gross, *J. Am. Chem. Soc., 101,* 3857 (1979).
9 A. B. P. Lever, S. R. Pickens, P. C. Minor, S. Licoccia, B. S. Ramaswamy and K. Magnell, *J. Am. Chem. Soc., 103,* 6800 (1981).
10 T. Saji and S. Aoyagui, *J. Electroanal. Chem., 58,* 401 (1975).
11 T. Saji and S. Aoyagui, *J. Electroanal. Chem., 60,* 1 (1975).
12 T. Saji and S. Aoyagui, *J. Electroanal. Chem., 63,* 405 (1975).
13 T. Saji and S. Aoyagui, *Bull. Chem. Soc. Jpn., 49,* 1399 (1976).
14 T. Saji and S. Aoyagui, *J. Electroanal. Chem., 108,* 223 (1980).
15 T. Matsumura-Inoue, H. Tomono, M. Kasai and T. Tominaga-Morimoto, *J. Electroanal. Chem., 95,* 109 (1979).
16 T. Matsumura-Inoue and T. Tominaga-Morimoto, *J. Electroanal. Chem., 93,* 127 (1978).
17 T. Saji and S. Aoyagui, *J. Electroanal. Chem., 110,* 329 (1980).
18 G. Gritzner, K. Danksagmuller and V. Gutmann, *J. Electroanal. Chem., 72,* 177 (1976).
19 G. Gritzner, H. Murauer and V. Gutmann, *J. Electroanal. Chem., 101,* 185 (1979).
20 A. Seurat, P. Lemoine and M. Gross, *Electrochim. Acta, 25,* 675 (1980).
21 U. Mayer, A. Kotocova and V. Gutmann, *J. Electroanal. Chem., 103,* 409 (1979).
22 A. Messia and G. Gritzner, *J. Electroanal. Chem., 101,* 201 (1979).
23 G. Gritzner, K. Danksagmuller and V. Gutmann, *J. Electroanal. Chem., 90,* 203 (1978).
24 U. Mayer, A. Kotocova, V. Gutmann and W. Gerger, *J. Electroanal. Chem., 100,* 875 (1979).
25 V. Gutmann, 'The Donor–Acceptor Approach to Molecular Interaction', Plenum, New York/London, 1978, p. 121.
26 S. Roffia and M. Ciano, *J. Electroanal. Chem., 87,* 267 (1978).
27 J. L. Kahl, K. W. Hanck and M. K. De Armond, *J. Phys. Chem., 82,* 540 (1978).
28 K. W. Hanck, M. K. De Armond, G. Kew, J. L. Kahl and H. Caldararu, in G. Mamantov (ed.), 'Spectroscopic and Electrochemical Characterization of Solute Species in Non-aqueous Solvents', Plenum, New York, 1977, p. 197.
29 R. J. Watts, J. S. Harrington and J. Van Houten, *J. Am. Chem. Soc., 99,* 2179 (1977).
30 G. Cauquis, M. Genies and E. Vieil, *Nouv. J. Chim., 1,* 307 (1977).
31 A. J. Bellamy, *Anal. Chem., 52,* 607 (1980).
32 R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem., 19,* 2854 (1980).
33 R. S. Nicholson, *Anal. Chem., 38,* 1406 (1966).
34 V. Gutmann, 'The Donor–Acceptor Approach to Molecular Interaction', Plenum, New York/London, 1978.
35 U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem., 106,* 1235 (1975).
36 R. S. Nicholson, *Anal. Chem., 37,* 1351 (1965); R. S. Nicholson and I. Shain, *Anal. Chem., 36,* 706 (1964).
37 G. A. Heath and L. J. Yellowlees, *J. Chem. Soc., Chem. Commun.,* 287 (1981); C. M. Elliot and E. J. Hershenhart, *J. Am. Chem. Soc., 104,* 7519 (1982).
38 C. Mahon and W. L. Reynolds, *Inorg. Chem., 6,* 1297 (1967); E. Konig and S. Kremer, *Chem. Phys. Lett., 5,* 87 (1970); Y. Torii, S. Murasato and Y. Kaizu, *Nippon Kajakv Zasshi, 91,* 549 (1970); *Chem. Abstr., 73,* 93426 (1970); C. Creutz, *Comm. Inorg. Chem., 1,* 293 (1982).
39 A. A. Vlcek, *Rev. Chim. Miner., 5,* 299 (1968).