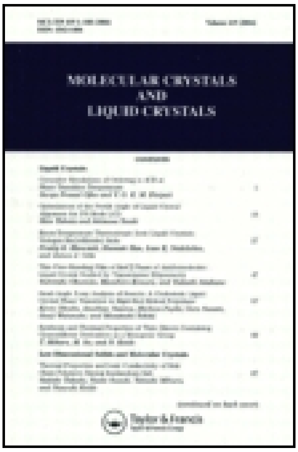

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Electrochemical Studies of the Formation Mechanism of $(\text{cation})_x[\text{Ni(dmit)}_2]$ Conductive Compounds and of their Non-Integer Oxidation State

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Electrochemical Studies of the Formation Mechanism of (cation)$_x$[Ni(dmit)$_2$] Conductive Compounds and of their Non-integer Oxidation State

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The mechanism of electrocrystallization of (cation)$_x$[Ni(dmit)$_2$] (cation = $NHMe_3^+$, NMe_4^+) conductive compounds is studied under non-stationary conditions by cyclic voltammetry using ultramicroelectrodes at high potential-scan rates. It is shown that the formation of non-integer oxidation state compounds proceeds through one-electron transfers combined with chemical reaction between $[Ni(dmit)_2]^-$ and $[Ni(dmit)_2]^0$ electrogenerated species exhibiting integer charges. The non-integer oxidation state in (cation)$_x$[Ni(dmit)$_2$] compounds (cation = NBu_4^+, $AsPh_4^+$, $NH_2Me_2^+$, NH_3Me^+), measured by the non-integer value of x, is determined under stationary conditions by use of the carbon paste electrode at very low potential-scan rates.

Keywords: electrocrystallization, (cation)$_x$[Ni(dmit)$_2$], 1,3-dithia-2-thione-4,5-dithiolato, cyclic voltammetry, ultramicroelectrodes, non-integer oxidation state, carbon paste electrode

INTRODUCTON

The very high number of papers reporting on the so called "organic metals"[1,2] is certainly due, on the one hand, to the interesting electrical and magnetic properties that these compounds exhibit, but also on the other hand, to the fact that these compounds are easy to prepare. With a few exceptions, these compounds are prepared by galvanostatic oxidative electrocrystallization of an appropriate pre-

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cursor molecule. If one has the disposal of these precursors (and this may be the main difficulty, if they are not commercially available), it is not much of a work to connect the electrodes of a two-compartment cell containing a solution of the precursor to a constant-current source, wait for a few days (or weeks), and collect the desired compound grown on the anode.[1,2] The situation, however, is not that bright, for a number of difficulties may be encountered when carrying out such electrosyntheses: poor yields, poor reproducibility (especially in terms of size and quality of crystals), unforeseeable influence of the electrode (nature, size, shape, previous surface processing) and of the solvent (nature, impurities), obtention of several phases in the same batch, etc. . . . Consequently, and in spite of some few attempts towards a better understanding and a better control of the various parameters of the electrolyzation procedure,[1,3–5] the preparation of organic metals is still dependent to date on empirical recipes.

Even more mysterious is the formation mechanism of these conducting species on the electrode. The electrochemical oxidation of the BEDT-TTF precursor molecule (BEDT-TTF = bis-ethylenedithio-tetrathiafulvalene) should lead, in solution and with the assumption of a one-electron transfer, to a monovalent BEDT-TTF salt.[6] How then could it be conceived that, in an appropriate solvent and in presence of an electrolyte containing a given X^- anion ($X^- = \mathrm{ClO}_4^-$, $\mathrm{Cu(NCS)}_2^-$, . . .)[1], crystals of the corresponding $(\mathrm{BEDT\text{-}TTF})_2X$ conducting species are obtained, for which the formal electronic transfer is 0.5 electron? Likewise, why the electrochemical oxidation of the (cation)$[\mathrm{M(dmit)_2}]$ precursor complex (dmit = 1,3-dithia-2-thione-4,5-dithiolato; M = Ni, Pd, Pt, . . .) does not simply lead to the $[\mathrm{M(dmit)_2}]^0$ neutral species, but to $(\mathrm{cation})_x[\mathrm{M(dmit)_2}]$ non-integer oxidation state compounds,[2] for which the formal electronic transfer is $(1 - x)$ electron?

An intuitive answer to those questions—which is still to be experimentally checked—may be the combination of a chemical reaction with the electrochemical charge transfer. However, the study of such chemical-electrochemical processes is often impossible when using conventional electrochemical techniques with standard millimetric electrodes in organic resistive solvents, because the potential-scan rates usable with such millimetric electrodes are too low for observing short-lived species.[7] The use of micrometric electrodes (or ultramicroelectrodes), i.e. electrodes with diameter of a few ten microns, results in reducing the ohmic drop between the electrodes, allowing thus much faster potential-scan rates and leading to a smaller time constant of the electrochemical cell (smaller than that of the chemical perturbation).[8] These ultramicroelectodes are now more and more frequently used for the study of reaction mechanisms.[9]

In this work, we report on the use of such ultramicroelectrodes for a better understanding of the electrochemical formation mechanism of $(\mathrm{cation})_x[\mathrm{Ni(dmit)_2}]$ (cation = NHMe_3^+, NMe_4^+) conductive compounds.

The conducting properties of such $(\mathrm{cation})_x[\mathrm{Ni(dmit)_2}]$ compounds are directly related to their non-integer oxidation state, reflected by the non-integer value of x. The determination of x by elemental analyses gives very unaccurate values, especially when solvent molecules crystallize with the compound.[10] Only a full structure resolution by X-ray diffraction methods may give unambiguous results, but these techniques imply that suitable single crystals are available and may be costly. We also report here on the use of the carbon paste electrode for determining the value of x in (cation)$_x$[Ni(dmit)$_2$] compounds with cation = NBu_4^+, $AsPh_4^+$, $NH_2Me_2^+$, NH_3Me^+.

EXPERIMENTAL

Chemicals. The precursor complexes, (cation)$_n$[Ni(dmit)$_2$] (cation = NMe_4,[11] $NHMe_3$, NH_2Me_2, NH_3Me,[11,12] NBu_4,[13] $AsPh_4$,[14] $n = 2.1$), as well as the corresponding non-integer oxidation state compounds, (cation)$_x$[Ni(dmit)$_2$], were prepared according to already published methods.

Acetonitrile (Aldrich, Gold Label) was used without any further purification. The $(NMe_4)ClO_4$ (Fluka, purum) and $(NBu_4)ClO_4$ (Fluka, puriss) supporting electrolytes were used as received. The $(NHMe_3)BF_4$, $(NH_2Me_2)BF_4$, and $(NH_3Me)BF_4$ salts were prepared by reaction of HBF_4 with the corresponding parent chloride compounds (1:1) dissolved in CH_3CN; the resulting solution was evaporated to dryness, the residue was washed twice with diethyl ether, recrystallized in CH_3CN, and the crystals were dried under vacuum.[10]

Electrochemical Studies. Electrochemical measurements were carried out with a home-made potentiostat using an interfacing hardware with a PC-compatible microcomputer.[15] The positive feedback (scan rate > 1 V.s^{-1}) or interrupt (scan rate < 1 V.s^{-1}) methods were used to compensate for incompensated resistance (IR) drop. Electrochemical experiments were performed in an air-tight three-electrode cell connected to a vacuum/argon line. The cell was degassed and filled according to standard vacuum techniques. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge-compartment filled with a solution of the same supporting electrolyte in the same solvent as used in the cell. The counter-electrode was a spiral of ca. 1 cm^2 apparent surface area, made of a 8 cm-long and 0.5 mm-diameter platinum wire. The working electrode was a rotating disk electrode (RDE) with a 2 mm-diameter Pt disk (Tacussel EDI), or an ultramicroelectrode consisting of a 100 μm-diameter Pt disk.

The carbon paste electrode (CPE) has been previously described.[16] The carbon paste was obtained by mixing a weighted quantity of electroactive compound (ca. 3 mg of (cation)$_x$[Ni(dmit)$_2$] compound) with a known amount of graphite powder (ca. 300 mg Carbone Lorraine 9901, non-pelletable quality). An electrolyte solution (300 μL (cation)$^+$ 0.1 mol/l in CH_3CN) was added and mixed until the carbon appeared evenly wetted. Electrodes were formed by packing the carbon paste into a tube against a carbon contact and covering the paste with a glass frit.[17] Such electrodes were used in a stationary mode and were freshly prepared before each determination. The auxiliary electrode (a platinum wire), the reference electrode (SCE), and the CPE were immersed in an electrochemical cell containing the same electrolyte solution as that used as paste "binder."

RESULTS AND DISCUSSION

A. Electrochemical Behavior

1°) Voltamperometry on Millimetric Electrodes. Figure 1 shows the voltamperogramm of $(NHMe_3)_2[Ni(dmit)_2]$ in CH_3CN obtained using a 2 mm Pt electrode. It shows two oxidation processes. The first one, at ~ -0.17 V, corresponds to a reversible system while the second one is affected by surface phenomena, adsorption or deposition, which results in a sharp reduction peak. Under stationary conditions at a RDE (Figure 2), the voltamperogram shows two waves corresponding to the two oxidation processes. The second wave does not afford a diffusion limit: the current increases with the potential. A black deposit is formed on the surface of the electrode.

As concerns the first oxidation process, the oxidation wave ($E_{1/2} = -0.17$ V) follows a Nernstian shape: the linear-regression calculation of the $E = f(\log I_D/I_D - I)$ straight line yields a slope of 58 mV.[7] The diffusion current obeys the Levich law[7] as for a diffusion-controlled process: the current I_D is linearly related to the square root of the rotation speed; this leads to the determination of the diffusion coefficient $D = 4.5 \times 10^{-6}$ $cm^2.s^{-1}$. Exhaustive electrolysis of a solution of the diamagnetic $(NHMe_3)_2[Ni(dmit)_2]$ divalent salt at constant potential (0.0 V) confirms a monoelectronic transfer: the ESR spectrum of the resulting green solution recorded at 100 K shows a signal at $g = 2.04$ which is due to the paramagnetic $(NHMe_3)[Ni(dmit)_2]$ species. By cyclic voltammetry, and when the potential scan is restricted to the first redox couple, the voltamperogram presents the pattern of a reversible system (peaks (a) and (b) in Figure 1). The peak ratio RI_p is equal to

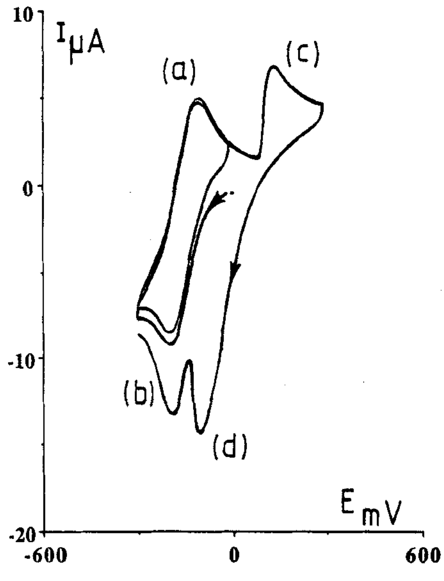

FIGURE 1 Cyclic voltammetry of $(NHMe_3)_2[Ni(dmit)_2]$ 10^{-3} mol/l, in CH_3CN—$(NHMe_3)BF_4$ 0.1 mol/l, at a Pt electrode (2 mm), scan rate 0.1 $V.s^{-1}$; potential in V. vs. ECS

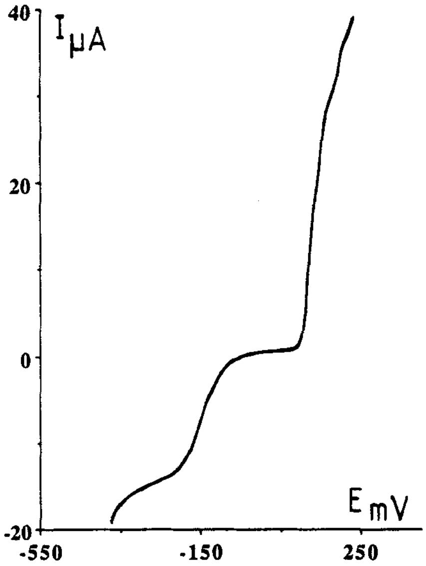

FIGURE 2 Linear voltammetry of (NHMe$_3$)$_2$[Ni(dmit)$_2$] 10^{-3} mol/l, in CH$_3$CN—(NHMe$_3$)BF$_4$ 0.1 mol/l, at a Pt electrode (2 mm), scan rate 5 m V.s^{-1}, rotation speed ω = 1000 rpm; potential in V. vs. ECS.

1 and the oxidation peak I_p is proportional to the square root of the potential-scan rate.[7] The peak separation ΔE_p is slightly increased when the scan speed increases as for a quasi-reversible system. All these results clearly show that the first redox couple corresponds to a simple monoelectronic process according to:

$$[\mathrm{Ni(dmit)_2}]^{2-} \leftrightarrow [\mathrm{Ni(dmit)_2}]^- + e^-$$

As concerns the second redox couple, it is characterized by peaks (c) and (d) in Figure 1. Under stationary conditions (Figure 2), the diffusion wave could not be observed. The oxidation current increases with the potential and a black deposit is formed on the electrode surface. Due to this surface modification, exhaustive electrolysis on the second step cannot be achieved and the determination of the number of exchanged electron is not possible. Likewise, the second oxidation peak of the cyclic voltamperogramm (peak (c) in Figure 1) is not purely diffusion-controlled but is also affected by the modification of the electrode surface: the decrease of the current after the peak does not follow a Cottrell law.[7] Moreover, the backward peak (d) is characteristic of a redissolution process: the intensity of this peak is proportional to the scan rate, v, while, for a diffusion process, it should be proportional to $v^{1/2}$.[7] The redissolution peak intensity is also related to the amount of materials deposited on the electrode: when going to more anodic potentials, an increase in the current is observed (Figure 3), indicating that the black deposit is electrically conductive. This deposit is probably made of the non-integer oxidation state phases (NHMe$_3$)$_{0.5}$[Ni(dmit)$_2$] and (NHMe$_3$)$_{0.4}$[Ni(dmit)$_2$], 0.4 CH$_3$CN which have been independently obtained by galvanostatic electrocrystallization of a solution of (NHMe$_3$)[Ni(dmit)$_2$] and characterized by X-ray diffraction meth-

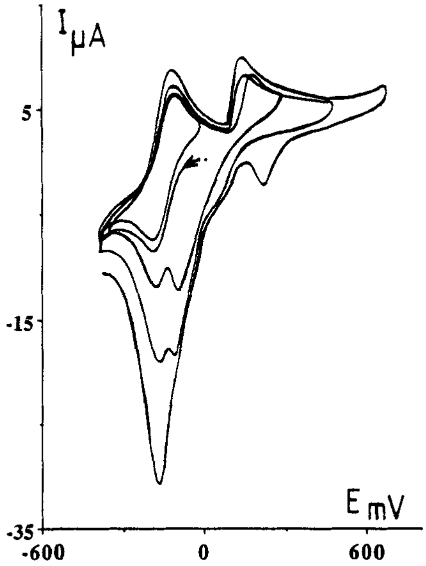

FIGURE 3 Increase of the intensity of the redissolution peak with the potential range observed for $(NHMe_3)_2[Ni(dmit)_2]$ (same conditions as in Figure 1).

ods.[10,12] Hence, the global scheme of the second oxidation step implies a formal partial electron-exchange according to:

$$[Ni(dmit)_2]^- \rightarrow [Ni(dmit)_2]^{x-} + (1 - x)e^-$$

2°) Cyclic Voltammetry on Micrometric Electrodes. Figure 4 shows the cyclic voltamperogramm of $(NHMe_3)_2[Ni(dmit)_2]$ in acetonitrile obtained using a 100 μm diameter Pt electrode. For a potential-scan rate of 305 $V.s^{-1}$ (Figure 4A), the voltamperogramm shows on the backward scan an additional reduction peak (e) at a potential $\approx$ 0.2 V higher than that of the previously observed redissolution peak (d). This reduction peak (e) may be associated with the oxidation step (c). Above $\approx$ 800 $V.s^{-1}$ (see Figure 4B, for which v = 1220 $V.s^{-1}$), the redissolution peak (d) disappears: within this time scale, the deposit is not formed. Figure 5 shows the variation of the intensity of the redissolution peak, $Ip(d)$, as a function of the potential-scan rate, v: (i) at low rate ($v < 100$ $V.s^{-1}$), i.e. when the electrolysis time is important, $Ip(d)$ is proportional to v; (ii) at high rate ($v > 800$ $V.s^{-1}$), $Ip(d)$ tends to zero; (iii) between these two domains, $Ip(d)$ goes through a plateau. It is interesting to note that the ratio of the intensities of peaks (e) and (c), $Ip(e)/Ip(c)$, increases and tends to 1 when the potential-scan rate increases, indicating that the corresponding redox couple becomes reversible.

According to these results, the following mechanism for the formation of $(NHMe_3)_x[Ni(dmit)_2]$ may be proposed:

A) The first electron-transfer, which appears as reversible, may be used as a reference for a simple one-electron transfer

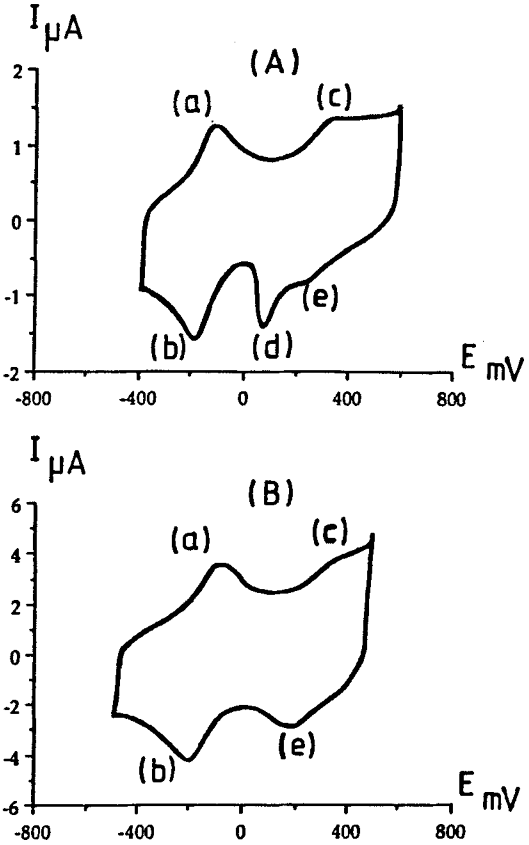

FIGURE 4 Cyclic voltammetry of $(NHMe_3)_2[Ni(dmit)_2]$ 10^{-3} mol/l, in CH_3CN—$(NHMe_3)BF_4$ 0.1 mol/l, at a Pt electrode (100 µm); scan rates: (A) 305 V.s^{-1}, (B) 1220 V.s^{-1}.

$$[Ni(dmit)_2]^{2-} \leftrightarrow [Ni(dmit)_2]^{-} + e^{-} \qquad A$$

B) The second electron-transfer generates the neutral species $[Ni(dmit)_2]^0$

$$[Ni(dmit)_2]^{-} \rightarrow [Ni(dmit)_2]^{0} + e^{-} \qquad B$$

C) The non-integer oxidation state compound is formed by a chemical reaction, in the diffusion layer, between $[Ni(dmit)_2]^-$ and $[Ni(dmit)_2]^0$ species

$$n[Ni(dmit)_2]^{-} + m[Ni(dmit)_2]^{0} \rightarrow \{[Ni(dmit)_2]^{x-}\}_{n+m} \qquad C$$

[where $x = n/(n + m)$]

D) Finally, the non-integer oxidation state compound is deposited on the electrode

$$\{[Ni(dmit)_2]^{x-}\}_{n+m}(\text{in solution}) \rightarrow \{[Ni(dmit)_2]^{x-}\}_{n+m}(\text{on the electrode}) \qquad D$$

It should be mentioned here that a similar mechanism has been proposed by Enkelmann *et al.*[3] for the formation of $(Ar)_2X$ (Ar = fluoranthene or perylene;

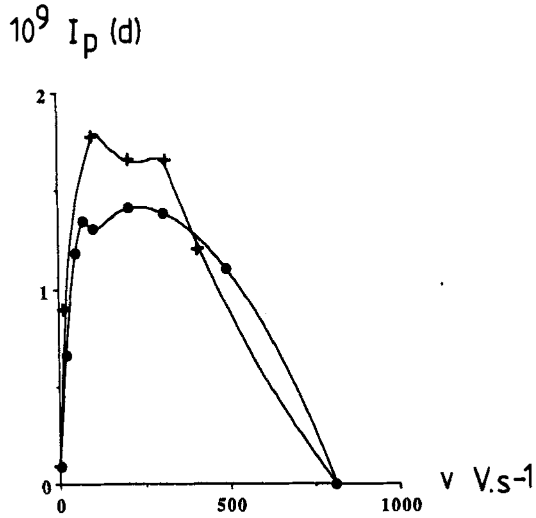

FIGURE 5 Plot of the redissolution peak intensity *Ip*(d) (normalized in comparison with C.D.S.; *C* = concentration of the oxidized species, *D* = diffusion coefficient of the studied species, *S* = area of the micrometric electrode) as a function of the potential-scan rate *v*; (+): $(NHMe_3)_2[Ni(dmit)_2]$, (●): $(NMe_4)_2[Ni(dmit)_2]$.

$X = PF_6, AsF_6, SbF_6, \ldots$) cation radical salts. In this case, the mechanism involves the reaction of an electrogenerated $(Ar)^+$ cation with the starting neutral Ar molecule, and the formation of a $[Ar_2]^+$ dimer radical cation.

As said above, two non-integer oxidation state phases $(NHMe_3)_{0.5}[Ni(dmit)_2]$ and $(NHMe_3)_{0.4}[Ni(dmit)_2]$, 0.4 CH_3CN have been simultaneously obtained by galvanostatic electrocrystallization of a solution of $(NHMe_3)[Ni(dmit)_2]$ and characterized by X-ray diffraction methods.[10,12] In these phases, the default charge, x, is 0.5 and 0.4, respectively. At high potential-scan rate, i.e. $v > 800$ V.s^{-1}, when the deposition step cancels out, and assuming that the diffusion coefficients are identical for both $[Ni(dmit)_2]^{2-}$ and $[Ni(dmit)_2]^-$ species, the ratio of the intensities of the two oxidation peaks, $Ip(c)/Ip(a)$, should be close to $(1 - x)$. In fact, the observed value of ≈ 0.5 is consistent with the formula of both experimental obtained phases.

However, it should be noted that the voltamperogramms recorded on a 25 μm Pt electrode in CH_3CN with very high potential-scan rates ranging from 1,500 V.s^{-1} up to 20,000 V.s^{-1} do not show any longer the second redox couple.[18] This may be due to the occurrence of a chemical reaction prior to the second electron transfer, leading to a possible overall electrochemical-chemical-electrochemical-chemical (ECEC) scheme.

3°) Counter Cation Effects. In order to study the influence of the nature of the counter cation, the $(NMe_4)_2[Ni(dmit)_2]$ compound was studied under similar conditions. The voltamperogramms of a 5.10^{-4} mol/l solution of this compound in CH_3CN—$(NMe_4)ClO_4$ (5.10^{-2} mol/l) are very similar to those obtained for $(NHMe_3)_2[Ni(dmit)_2]$ (and for other $(cation)_2[Ni(dmit)_2]$ complexes when using millimetric electrodes[10,12,14,19]). Two oxidation waves are observed in stationary conditions, only the first step being well-defined with $E_{1/2} = -0.18$ V. Two oxidation steps with a redissolution peak on the backward scan are observed by cyclic voltammetry at 0.1 V.s^{-1}. The redissolution peak disappears when the potential-scan rate increases above ≈800 V.s^{-1} (Figure 5). The only slight difference concerns the plateau observed for Ip(d) for intermediate potential-scan rates ($100 < v < 800$ V.s^{-1}) which is narrower for (NMe$_4$)$_2$[Ni(dmit)$_2$] than for (NHMe$_3$)$_2$[Ni(dmit)$_2$]. Also, the diffusion coefficient of the first oxidation process is higher for (NMe$_4$)$_2$[Ni(dmit)$_2$] than for (NHMe$_3$)$_2$[Ni(dmit)$_2$], 9.6×10^{-6} and 4.5×10^{-6} cm^2.s^{-1}, respectively. In conclusion, the general electrochemical behavior of (cation)$_2$[Ni(dmit)$_2$] does not seem to depend on the nature of the cation, NMe$_4^+$ or NHMe$_3^+$, whereas the electrical properties of the corresponding (cation)$_x$[Ni(dmit)$_2$] conductive phases are quite different: (NMe$_4$)$_2$[Ni(dmit)$_2$] is metallic down to low temperatures at ambient pressure (and undergoes a superconducting transition under pressure)[11] whereas (NHMe$_3$)$_2$[Ni(dmit)$_2$] undergoes a metal to insulator transition at ambient pressure and does not become superconducting under pressure.[10]

B. Electrochemical Analysis of the Deposits

We have reported above that, under stationary conditions, a black material is deposited on the electrode during the second oxidation step of (cation)$_2$[Ni(dmit)$_2$] compounds, precluding voltammetric analysis; for example, exhaustive controlled potential electrolysis cannot lead to the determination of the number of exchanged electrons during this second step, and therefore of the value of the default charge x in the resulting (cation)$_x$[Ni(dmit)$_2$] deposited materials. As described above,

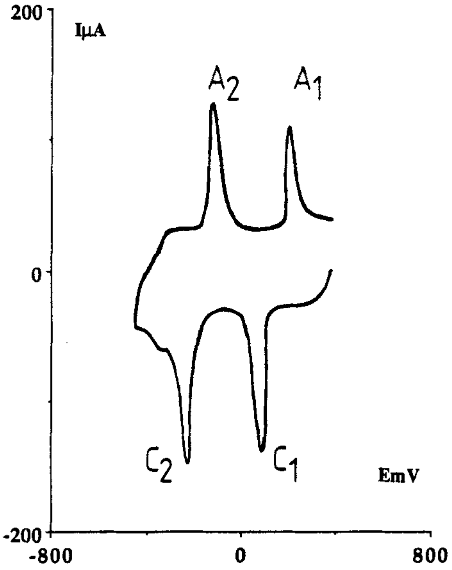

FIGURE 6 Voltammogramm of (NH$_2$Me$_2$)$_{0.5}$[Ni(dmit)$_2$] (3 mg) included in a carbon paste electrode containing (NHMe$_3$)BF$_4$ 0.1 mol/l in CH$_3$CN and 300 mg of graphite powder; scan rate: 2.10^{-5} V.s^{-1}; potential in V. vs. ECS.

TABLE I

Peak potentials (*Ep*; anodic A and cathodic C), half-wave potential ($E_{1/2}$), number of electrons (NE) involved in the electrochemical process for peak C_1 and C_2, and resulting *x* value (experimental error in parenthesis), for $(\text{cation})_x[\text{Ni(dmit)}_2]$ compounds.

Compound	Ep		Ep		$E_{1/2}$	NE		x
	C_1	A_1	C_2	A_2		C_1	C_2	
$(NBu_4)_{0.29}[Ni(dmit)_2]$ **(I)**	0.03	0.21	-0.27	-0.08	-0.15	0.71	1	0,29(2)
$(AsPh_4)_{0.25}[Ni(dmit)_2]$ **(II)**	0.20	0.38	-0.09	-0.10	0.00	0.75	1	0,25(2)
$(NH_2Me_2)_{0.5}[Ni(dmit)_2]$ **(III)**	0.09	0.20	-0.23	-0.13	-0.17	0.50	1	0,50(3)
$(NH_3Me)_{0.4}[Ni(dmit)_2]$, $0.4CH_3CN$ **(IV)**	0.07	0.27	-0.34	-0.14	-0.25	0.53	1	0,47(3)

when using ultramicroelectrodes at high potential-scan rates, a very crude estimation of *x* can be obtained from the ratio of the (a) and (b) peak intensities, but the results depend on the potential-scan rate. The use of the carbon paste electrode (CPE) has been previously proposed for studying electron-exchange processes in solid state organic conductors.[20] This method may be successfully applied to the $(\text{cation})_x[\text{Ni(dmit)}_2]$ because of their sparing solubility in organic solvents such as acetonitrile.

Such a CPE analysis has been carried out on a series of $(\text{cation})_x[\text{Ni(dmit)}_2]$ compounds prepared by galvanostatic electrolysis, namely, $(NBu_4)_{0.29}[Ni(dmit)_2]$ **(I)**,[13] $(AsPh_4)_{0.25}[Ni(dmit)_2]$ **(II)**,[14] $(NH_2Me_2)_{0.5}[Ni(dmit)_2]$ **(III)**,[10] and $(NH_3Me)_{0.4}[Ni(dmit)_2]$, 0.4 CH_3CN **(IV)**.[10] The value of *x* in all these compounds had been previously determined by X-ray structure analysis.[10,13,14] These compounds were selected because the corresponding samples prepared by galvanostatic electrolysis are known to contain a single phase. The CPE method cannot be usefully applied to a sample containing several phases, such as for example the experimentally obtained mixture of $(NHMe_3)_{0.5}[Ni(dmit)_2]$ and $(NHMe_3)_{0.4}[Ni(dmit)_2]$, 0.4 CH_3CN,[10] for which only a weighted average *x* value could be obtained.

The current-voltage curves recorded at very low potential-scan rates (2.10^{-5} $V.s^{-1}$), using a CPE with a very small amount of incorporated electroactive material (ca. 3 mg), usually correspond to the almost complete reduction of the compound (yield = $Q_{\text{theoretical}}/Q_{\text{experimental}} \geq 90\%$). Under these conditions, the voltammogramms (Figure 6) exhibit two symmetric cathodic (C_1 and C_2) and anodic (A_1 and A_2) peaks. The half-sum $(Ep_A + Ep_C)/2$ of the cathodic and anodic peak potentials remains close to the standard potential of the corresponding redox couple (Table I). The first reduction peak C_1 can be formally ascribed to the following reaction:

$$[Ni(dmit)_2]^{x-} + (1 - x)e^- \rightarrow [Ni(dmit)_2]^-$$

The second reduction peak C_2 can be attributed to the following reaction:

$$[\mathrm{Ni(dmit)_2}]^- + e^- \rightarrow [\mathrm{Ni(dmit)_2}]^{2-}$$

which involves one electron per mole of $[\mathrm{Ni(dmit)_2}]^-$ and can be considered as an internal reference for a one-electron transfer. The areas, S_1 and S_2, of peaks C_1 and C_2, respectively, being proportional to the number of exchanged electrons per molecule for each reduction step, the value of x may be determined as follows:

$$S_1/S_2 = (1 - x)/1 \qquad \text{i.e. } x = 1 - S_1/S_2$$

As shown in Table I, the values of x determined by CPE analysis are in good agreement with the values determined by X-ray diffraction methods for compounds **I**, **II** and **III**. There is a discrepancy in the case of compound **IV**, but the two values are still close.

It should be noted that upon reduction the color of the solution, in which the CPE is immersed, turns slightly green, indicating the $[\mathrm{Ni(dmit)_2}]^-$ and $[\mathrm{Ni(dmit)_2}]^{2-}$ species, successively generated, diffuse through the glass frit from the CPE to the solution, and dissolve. The resulting loss of electroactive species in the CPE does not allow to determine the x value by comparison of the area of the A_2 and A_1 peaks observed in the subsequent oxidation scan. Such a diffusion-dissolution process may also explain the discrepancy observed in the case of compound **IV** which is more soluble in acetonitrile than compounds **I**, **II** and **III**.

CONCLUSION

Electrochemical techniques have proven valuable for progressing in the understanding of the formation of (cation)$_x$[Ni(dmit)$_2$] conductive compounds. Under non-stationary conditions, cyclic voltammetry studies using ultramicroelectrodes at high potential-scan rates confirm that the electrocrystallization of these non-integer oxidation state compounds proceeds through one-electron transfers combined with chemical reaction between species exhibiting integer charges. This method could be successfully applied to organic conductors and superconductors.

Under stationary conditions, the use of the carbon paste electrode provides an alternative method for determining the stoichiometry of (cation)$_x$[Ni(dmit)$_2$] non-integer oxidation state conductive compounds. This method, which is much more efficient than elemental analysis, does not give as complete and accurate results than X-ray diffraction methods, but is easier to use, much less costly, and can be applied to compounds for which suitable single crystals are not available.

Note Added in Proof

After submission of this paper, we became aware of a very recent work (R. Carlier, A. Tallec, P. Frère, M. Salle, M. Jubault, A. Gorgues and J. Cousseau, *Synth. Met.*, 1993, in press; and personal communication) about thin layer cyclic voltammetry studies of several cation radical salts of the type C_2X (C = TTF, TMTTF, TMTSF, BEDT-TTF; X = Br, PR_6, BF_4). This method seems to allow a fast determination of the non-integer oxidation state in these salts. Moreover, the interpretation of these results, obtained using a quite different technique, is based on a mechanism identical to that previously proposed by Enkelmann *et al.*,[3] and similar to that proposed in our work in the case of $(\text{cation})_x[\text{Ni(dmit)}_2]$ anion radical salts.

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