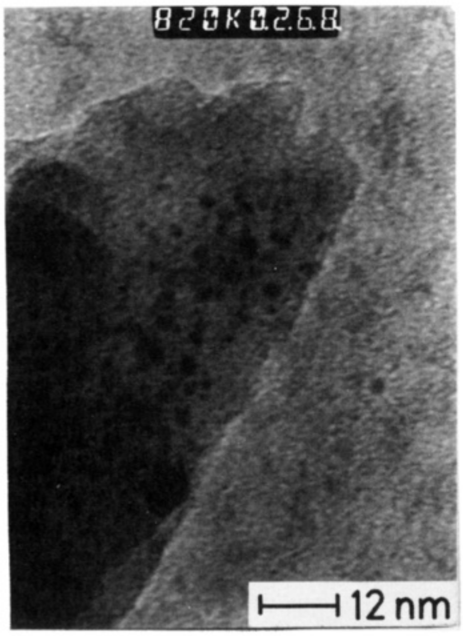

Figure 2. Scanning transmission electron micrograph of **5** (x = 70), prepared from $Pd(acac)_2$, **2**, and $Si(OEt)_4$ and containing 2.38 wt% Pd.

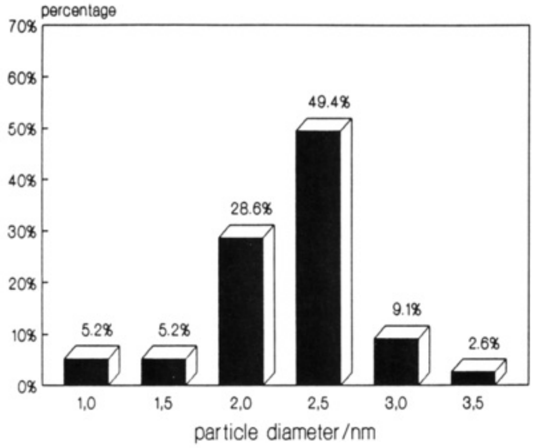

Figure 3. Pd particle size distribution of $Pd-SiO_2$ composite **5** (x = 70) (same as in Figure 2). Mean particle diameter 2.2 nm (calculated from 77 particles).

tions are very similar to those given in Figure 3.

To find out how anchoring of the metal complex via ligand **1** or **2** during polycondensation influences particle size and particle distribution of the resulting composites, we also prepared $PdO\cdot xSiO_2$ from $Pd(acac)_2$, ethylenediamine, and TEOS, without using **1** or **2**. Apart from this, the reaction conditions during polycondensation, calcination, and reduction were not altered, in order to avoid an influence of these parameters on the results. The Pd particle diameters in the thus-obtained composite $Pd\cdot 70SiO_2$ were between 2.25 and 9.75 nm (average 5.0 nm) and did not give an approximately Gaussian distribution curve.

Although preparation of the composites has not yet been optimized, these results show the soundness of our approach to prepare small metal particles in a ceramic matrix by sol–gel processing of metal complexes. Future efforts will be directed toward a generalization of this method.

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A New Molecular Metal: $(NHMe_3)_{0.5}[Ni(dmit)_2]$ (dmit = 4,5-Dimercapto-1,3-dithia-2-thione)

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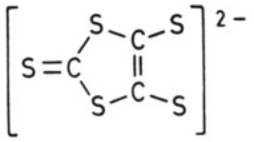
Transition-metal complexes of the dmit ligand (dmit = 4,5-dimercapto-1,3-dithia-2-thione) have been used as



precursors for the preparation of a number of conducting and superconducting π donor–acceptor or fractional oxidation state compounds.[1-6] Namely, four superconducting phases have been described: $TTF[Ni(dmit)_2]_2$ (TTF = tetrathiafulvalene, T_c = 1.7 K/7 kbar),[3] α- and α'-$TTF[Pd(dmit)_2]_2$ (T_c = 1.7 K/20 kbar and 6.5 K/21 kbar, respectively),[4] and $(NMe_4)_{0.5}[Ni(dmit)_2]$ (T_c = 5 K/7 kbar).[5] Band structure calculations[6,7] and previous experimental studies[1-5] suggest that small modifications of the chemical environment in these systems could lead to new compounds exhibiting quite different transport properties.

We were thus tempted to check whether substitution of hydrogen atom(s) for methyl group(s) in the countercation of the $(NMe_4)_{0.5}[Ni(dmit)_2]$ superconductor would result in dramatic changes in the transport properties. We report here on the synthesis and electrochemical study of the $(NH_yMe_{4-y})_n[Ni(dmit)_2]$ series of precursor complexes (n = 2, 1; y = 1, 2, 3), the electrocrystallization of the $(NHMe_3)_{0.5}[Ni(dmit)_2]$ and $(NH_2Me_2)_x[Ni(dmit)_2]$ fractional oxidation state compounds, and the preliminary structural and conductivity studies of $(NHMe_3)_{0.5}[Ni(dmit)_2]$.

Due to the low stability of the $[NH_yMe_{4-y}]^+$ cations in the strong basic medium in which the dmit ligand generated from $dmit(COPh)_2$ is stable[1] and the high solubility of the $(NH_yMe_{4-y})_2[Ni(dmit)_2]$ complexes, the standard

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procedure used for preparing analogous tetraalkylammonium salts[8] was modified. Typically, 686 mg of Na (29.84 mmol) were dissolved in 23 mL of distilled methanol. The solution was stirred for 30 min in a cold water bath. The dmit(COPh)$_2$ (3 g, 7.38 mmol) was then added to the methanolate solution. After 30 min of stirring, the yellow solid dissolved, leading to a deep red solution of dmitNa$_2$. A solution of 762 mg of NiCl$_2$·6H$_2$O (3.21 mmol) in 50 mL of methanol was prepared and canula transferred to the dmitNa$_2$ solution, whose color turned violet. A large excess of the appropriate (NH$_y$Me$_{4-y}$)Cl salt (26.95 mmol in 50 mL of methanol) was then added (i) to neutralize to a weakly basic pH and (ii) to precipitate the corresponding (NH$_y$Me$_{4-y}$)$_2$[Ni(dmit)$_2$] complex. The resulting mixture was stirred under nitrogen for 1 h. Upon addition of (NHMe$_3$)Cl or (NH$_2$Me$_2$)Cl, immediate precipitation of the corresponding complexes, (NHMe$_3$)$_2$[Ni(dmit)$_2$] or (NH$_2$Me$_2$)$_2$[Ni(dmit)$_2$] was observed. After 2 h of cooling at −30 °C, the solid was filtered off under nitrogen and washed with 3 × 10 mL of methanol. Recrystallization was carried out in acetone/isopropyl alcohol for (NHMe$_3$)$_2$[Ni(dmit)$_2$] and in acetonitrile/isopropyl alcohol for (NH$_2$Me$_2$)$_2$[Ni(dmit)$_2$] (shiny violet crystals). When (NH$_3$Me)Cl was added, no precipitation was observed. The reaction mixture was evaporated to dryness. The remaining solid was dissolved in 150 mL of acetonitrile at 40 °C. After filtration, the solution was concentrated to 30 mL, and 150 mL of ether was added. After 2 h of cooling at −30 °C, a dark violet powder of (NH$_3$Me)$_2$[Ni(dmit)$_2$] was filtered off and washed with 3 × 10 mL of ether.

The three (NH$_y$Me$_{4-y}$)$_2$[Ni(dmit)$_2$] compounds with y = 1, 2, and 3 (yields 85, 83, and 89%, respectively) have been characterized by elemental analysis and IR spectroscopy.[8,9] An alternative and even better route for obtaining these three complexes involves in a first step the reaction of the dmitNa$_2$ solution with the appropriate (NH$_y$Me$_{4-y}$)Cl salt (in excess, for the same reason noted above) followed by the addition of NiCl$_2$·6H$_2$O. Efforts to obtain the corresponding (NH$_4$)$_2$[Ni(dmit)$_2$] by either method were not successful.

Oxidation of the (NH$_y$Me$_{4-y}$)$_2$[Ni(dmit)$_2$] complex salts (y = 1, 2, 3) using iodine[8] leads to the corresponding (NH$_y$Me$_{4-y}$)[Ni(dmit)$_2$] complexes. Recrystallization of (NHMe$_3$)[Ni(dmit)$_2$] is carried out in acetone/isopropyl alcohol, and those of (NH$_2$Me$_2$)[Ni(dmit)$_2$] and (NH$_3$Me)[Ni(dmit)$_2$] are in acetonitrile/isopropyl alcohol. These dark-blue solids (yields 60, 74, and 54%, respectively) were characterized by elemental analysis and IR spectroscopy.[8,9]

Cyclic voltammograms of the (NH$_y$Me$_{4-y}$)$_2$[Ni(dmit)$_2$] complexes in the CH$_3$CN/(NH$_y$Me$_{4-y}$)BF$_4$ medium have been obtained by using previously described techniques.[10] They consist of two waves. The first wave corresponds to the reversible $[\mathrm{Ni(dmit)_2}]^{2-} \rightleftarrows [\mathrm{Ni(dmit)_2}]^{-}$ one-electron exchange process. The half-wave potential of this wave depends on the nature of the countercation (−167, −175, and −248 mV vs Ag/AgCl, 0.1 N KCl, for y = 1, 2, and 3, respectively). The second quasi-reversible wave (anodic peak potentials at +72, +132, and +72 mV for y = 1, 2, and 3, respectively) exhibits features characteristic of the buildup on the electrode of conducting partially oxidized C$_x$[Ni(dmit)$_2$] species.[11]

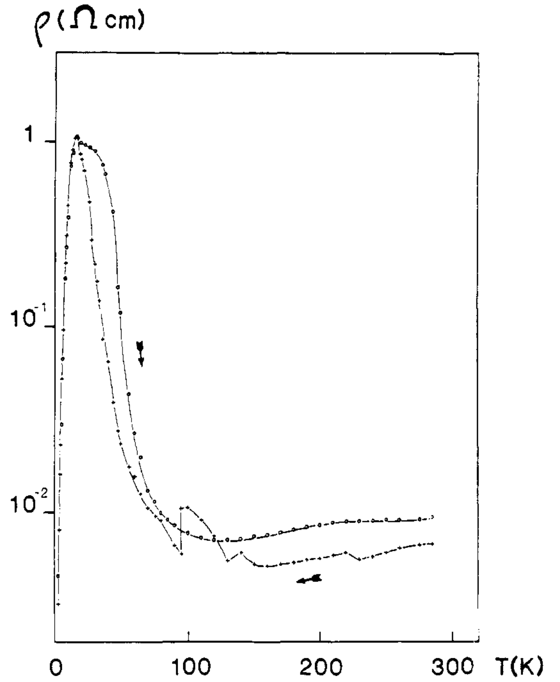

Figure 1. Resistivity vs temperature for a crystal of (NHMe$_3$)$_{0.5}$[Ni(dmit)$_2$] between 300 and 2 K, measured on cooling (+) and subsequent warming (O).

Using this observation, we were able to grow single crystals of (NHMe$_3$)$_x$[Ni(dmit)$_2$] and (NH$_2$Me$_2$)$_x$[Ni(dmit)$_2$] on a platinum electrode by standard[1] galvanostatic anodic oxidation of the appropriate monoanionic salts (NH$_y$Me$_{4-y}$)[Ni(dmit)$_2$] (5 × 10^{-3} M) in acetonitrile containing (NH$_y$Me$_{4-y}$)BF$_4$ (5 × 10^{-3} M) at 20 °C with a constant current of 1 μA. Due to the low yield of these electrosyntheses, the value of x could not be estimated at this point by elemental analysis.

Elongated hexagonal-shaped black platelets of (NHMe$_3$)$_x$[Ni(dmit)$_2$] were mounted on a CAD4 Enraf-Nonius automatic diffractometer. Unit cell parameters were derived from a least-squares refinement based on the setting angles of 25 reflections: triclinic, space group $P1$ or $P\bar{1}$; a = 7.535 (1), b = 17.558 (2), c = 6.623 (1) Å, α = 100.61 (1), β = 113.88 (1), γ = 87.37 (1)°, V = 787 Å^3, Z = 2. From the observed density, d_{obs} = 2.02 (2) g·cm^{-3} (flotation) the unit weight M_w = 481 can be calculated, resulting in $x = 0.50 \pm 0.02$. The complete determination of the crystal structure is in progress; preliminary results unambiguously confirm the stoichiometry, x = 0.5.

The electrical conductivity of (NHMe$_3$)$_{0.5}$[Ni(dmit)$_2$] has been measured as a function of temperature by using the standard four-probe mounting with gold-evaporated precontacts. The room-temperature conductivity, measured along the longest dimension of the elongated hexagonal-shaped crystals, is equal to 300 ± 200 S/cm, depending on the sample. All samples exhibit metallike behavior from room temperature to ca. 120 K (Figure 1). At this temperature they undergo a metal-to-insulator transition, accompanied by several resistance *jumps*. This behavior is similar to that observed from room temperature to ca. 50 K for (NMe$_4$)$_{0.5}$[Ni(dmit)$_2$].[5] However, in the case of (NHMe$_3$)$_{0.5}$[Ni(dmit)$_2$] a striking feature is observed at lower temperatures: all samples exhibit a maximum in the

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[9] Major IR absorptions (in cm^{-1}): (NH$_y$Me$_{4-y}$)$_2$[Ni(dmit)$_2$] (y = 1, 2, 3) 1449, 1452, 1426 (C=C); 1043 and 1023, 1060 and 1010, 1052 and 1032 (C=S); 913 and 897, 915 and 834, 910 and 830 (C-S); 467 and 325, 471 and 324, 466 and 323 (Ni-S). (NH$_y$Me$_{4-y}$)[Ni(dmit)$_2$] (y = 1, 2, 3) 1337, 1330, 1333 (C=C); 1056 and 1018, 1072 and 1050, 1084 and 1061 (C=S); 922, 920, 919 (C-S); 508 and 330, 505 and 324, 510 and 328 (Ni-S).

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resistance at ca. 15 K. Below this temperature, a sharp decrease of the resistance is observed down to 2 K. Upon heating again the samples exhibit reversible behavior in the low-temperature range, but hysteresis is observed in the insulator regime. The temperature of the resistance maximum is sample dependent (from 9 to 25 K), and this may be due to order–disorder transitions in the cation or subtle changes in the stoichiometry. However, the overall behavior is reproducible and has been observed for more than six samples. This behavior is also reminiscent of that observed at higher temperatures for some samples of the superconducting κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$] phase.[12]

Additional work is in progress so as to better characterize the new molecular metal (NHMe$_3$)$_{0.5}$[Ni(dmit)$_2$] and elucidate its properties (sample dependence, nature of both transitions, pressure effects, etc.). However, these promising preliminary results open a new area of investigation on (NH$_y$Me$_{4-y}$)$_x$[M(dmit)$_2$] systems with different y values as well as with different metals, M; for example, parallel studies on such systems with M = Pd and Pt are underway and will be reported shortly.

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Articles

Structural, Chemical, and Physical Properties of Rare-Earth Metal Rhodium Carbides LnRhC$_2$ (Ln = La, Ce, Pr, Nd, Sm)[†]

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The title compounds were prepared by arc melting and subsequent annealing. LaRhC$_2$ and CeRhC$_2$ melt congruently, while the others are formed by peritectic reactions. LaRhC$_2$ and CeRhC$_2$ crystallize with a tetragonal structure of space group $P4_3$ (and $P4_1$), which was determined from single-crystal X-ray data of CeRhC$_2$ (a = 392.45 (9) pm, c = 1526.0 (7) pm; R = 0.037 for 692 structure factors and 26 variable parameters). PrRhC$_2$, NdRhC$_2$, and SmRhC$_2$ crystallize with the orthorhombic CeNiC$_2$ type structure, which was refined from single-crystal X-ray data of SmRhC$_2$ (space group $Amm2$, a = 358.91 (6) pm, b = 469.29 (7) pm, c = 656.7 (1) pm; R = 0.027 for 373 F values and 12 variables). The compounds contain C$_2$ pairs with C–C distances of 139 (2) pm (CeRhC$_2$) and 134 (1) pm (SmRhC$_2$), thus indicating double bonds. The hydrolyses with hydrochloric acid yield mixtures of methane, ethane, propane, and the various isomers of butane, pentane, and hexane but little (LaRhC$_2$) or no (SmRhC$_2$) unsaturated hydrocarbons. LaRhC$_2$ is diamagnetic at room temperature, while the carbides LnRhC$_2$ (Ln = Ce, Pr, Nd) show Curie–Weiss behavior with magnetic moments corresponding to those of the trivalent rare-earth metal ions. SmRhC$_2$ is Van Vleck paramagnetic. The samples of LaRhC$_2$ and CeRhC$_2$ are semiconducting, while those of PrRhC$_2$ and NdRhC$_2$ show metallic behavior. The crystal structures and properties of these carbides are discussed.

Introduction

Because of their importance to the nuclear reactor industry, the ternary systems of the actinoids with transition metals and carbon have been studied for some time, and several ternary carbides were reported.[1] The corresponding rare-earth transition-metal carbides are of interest because of their potential as superconductors and ferromagnets. Their exploration has begun more recently.

These carbides have the structural characteristics of intermetallics with high coordination numbers for all atoms. In the combinations with the early transition metals and in carbides with low carbon content, the carbon atoms are usually isolated from each other, while C$_2$ pairs are found frequently in ternary carbides with the late transition metals. Thus isolated carbon atoms were found in the structures of UMoC$_2$,[2] URu$_3$C$_{1-x}$,[3] U$_2$IrC$_2$,[4] Ce$_2$Ni$_{22}$C$_3$,[5] Gd$_2$Fe$_{14}$C,[6,7] LaMn$_{11}$C$_{2-x}$,[8] Pr$_2$Mn$_{17}$C$_{2-x}$,[9] Ho$_2$Cr$_2$C$_3$,[10]

[†] Dedicated to Professor Reginald Gruehn on the occasion of his 60th birthday.

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