

A New Paramagnetic Pd(dmit)₂ Salt: Tris(2,2'-Bipyridine)Nickel(II) Bis(1,3-Dithiole-2-Thione-4,5-Dithiolato)Palladate(II) Mono-Acetonitrile; [Ni(bpy)₃][Pd(dmit)₂] · CH₃CN

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Combination of the [Ni(bpy)₃]²⁺ cation complex and the [Pd(dmit)₂]⁻ anion (dmit = C₃S₅²⁻ = 1,3-dithiole-2-thione-4,5-dithiolate) has resulted in the paramagnetic [Ni(bpy)₃][Pd(dmit)₂] · CH₃CN compound, a suitable precursor for a molecular magnetic conductor. Its crystal structure consists of a Pd(dmit)₂ anion arrangement that is quite different from segregated stack layers often found for M(dmit)₂-based compounds. The reduction of the [Pd(dmit)₂]⁻ to the 2- charged anion in the title compound most probably is the result of a charge disproportionation between Pd(dmit)₂ anions. © 2002

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Key Words: palladium nickel complexes; dithiolate complexes; crystal structure.

1. INTRODUCTION

One of the important recent challenges in the synthesis of molecular conductors is the combination of paramagnetic and conducting species (1). This has already been accomplished in 1986 with the preparation of the metallic conductor ($\sigma_{RT} = 10^3 \Omega^{-1} \text{cm}^{-1}$) (phtalocyaninato)copper iodide, [Cu(Pc)][I₃]_{0.33} with a localized unpaired *d*-electron ($S = \frac{1}{2}$) on the Cu²⁺ ion situated within the partially oxidized Pc ring that contains the mobile conduction electrons (2, 3). An interaction between the localized and mobile spins has been reported. The combination of conducting and paramagnetic molecular moieties has resulted in the preparation of (Per)₂[M(mnt)₂]-type compounds (mnt = *cis*-(2,3-dimercapto-2-butenedinitrile)) (4, 5) with the conducting electron-donor perylene (Per) and with localized spin on the anion-stacks when *M* = Ni,

Fe, Pd, Pt. Interaction between localized and conduction electrons is present, but does not influence the metal-insulator transition present in these materials. In the area of chalcogen-rich (S,Se,Te) electron-donor materials many examples of interesting compounds can be given. Three of them are the β' -(BEDT-TTF)₄Fe(C₂O₄)₃(C₆H₅CN)(H₂O) (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene), which is a superconductor ($T_c = 7.0 \text{ K}$) with weakly antiferromagnetically coupled anions (6), the λ -(BETS)₂FeCl₄ (BETS = bis(ethylenedithio)tetraselenafulvalene) showing an interaction between the conduction electrons in the BETS layers and the spins localized on the (FeCl₄)⁻ anions (7) and the [BEDT-TTF]₃[MnCr(C₂O₄)₃] which is a metallic conductor ($\sigma_{RT} = 250 \Omega^{-1} \text{cm}^{-1}$) and a ferromagnet (8) with $T_c = 5.5 \text{ K}$. In the area of the organic electron-acceptor-based materials some Cu(II) complexes have been combined with the TCNQ (TCNQ = 7,7',8,8'-tetracyanoquinodimethane) molecule, yielding [Cu(Me₂phen)₂]₂[TCNQ]₂ (Me₂phen = 2,9-dimethyl-1,10-phenanthroline) (9), [Cu(di-2-pyridylamine)₂][TCNQ]₂ (10) and [Cu(phen)₃][TCNQ]₂ (11), all exhibiting either conductivity, or localized magnetic moments, but no coexistence of the two properties. [Fe(4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole)₂](TCNQ)₂ shows a spin transition (12) at $T = 280 \text{ K}$. Other TCNQ-based compounds with Cu(II) complexes have been reported (10, 13–17). These compounds (powder samples) exhibit magnetic, as well as conducting properties. However, the absence of crystal structures did not permit an explanation for the observed properties.

Combination of paramagnetic complex cations with Ni(dmit)₂ anions (dmit = C₃S₅²⁻ = 1,3-dithiole-2-thione-4,5-dithiolate), which are conducting when they are fractionally oxidized, has resulted in several interesting compounds. [Fe(CpMe₃)₂][Ni(dmit)₂] displays ferromagnetic behavior which crosses over at low temperatures to

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antiferromagnetic behavior, because of the dominant antiferromagnetic interactions between the Ni(dmit)₂ anions, but does not show conductivity (18). The compounds $[M(\text{cyclam})(\text{CH}_3\text{CN})][\text{Ni}(\text{dmit})_2]_2$ with $M = \text{Cu}, \text{Ni}$ (19) consist of magnetically isolated cations and strongly antiferromagnetically coupled anions, but do not electrically conduct. After publication of the crystal structure of $[\text{Co}(\text{Cp})_2][\text{Ni}(\text{dmit})_2]$ (20) the preparation of the partially oxidized $[\text{Co}(\text{Cp})_2][\text{Ni}(\text{dmit})_2]_3 \cdot 2\text{CH}_3\text{CN}$ (21) and its semiconducting behavior were reported; but the $[\text{Co}(\text{Cp})_2]$ cation is not paramagnetic. More recently (22) the crystal structure of $[\text{Cu}(\text{bpy})_3][\text{Ni}(\text{dmit})_2]_2$ (bpy = 2,2'-bipyridine) was reported. The conductivity was not determined, but was expected to be low, because of the integer charge on the anion. Recently, the preparation of $[M(\text{CpMe}_5)_2][M'(\text{dmit})_2]$ -type compounds ($M = \text{Mn}, \text{Ni}$ and $M' = \text{Ni}, \text{Fe}$) and their magnetic properties have been reported (23). The $[\text{Mn}(\text{CpMe}_5)_2][\text{Ni}(\text{dmit})_2]$ displays the behavior of a magnet, which was later characterized as that of a ferromagnet (24). Also the $[\text{Fe}(\text{CpMe}_5)_2][M(\text{dmix})_2]$ compounds ($M = \text{Ni}, \text{Pd}, \text{Pt}$ and $\text{dmix} = \text{dmio}, \text{dmit}$) have been prepared (25) showing ferro- and antiferromagnetic interactions depending on the type of metal M and the crystal structure. For the $[\text{Co}(\text{15-crown-5})][\text{Ni}(\text{dmit})_2]_2 \cdot 2\text{CH}_3\text{CN}$ (26) no high conductivity was reported and the $[\text{Ni}(\text{dmit})_2]^-$ anions form a one-dimensional antiferromagnetic chain, while the cation has a free d -spin of the Co^{2+} . Recently Sakai *et al.* (27) reported the crystal and electronic band structure of the first partially oxidized Ni(dmit)₂-salt with a transition metal cation, $\text{Cu}_{0.39}[\text{Ni}(\text{dmit})_2]$. Its magnetic and electric properties are being studied. This paper reports on another precursor material for such compounds.

2. EXPERIMENTAL

2.1. Syntheses

$[\text{Ni}(\text{bpy})_3](\text{BF}_4)_2$. This paramagnetic complex has been prepared using a method described by Dunnach and Perichon (28) by mixing ethanol solutions of stoichiometric amounts of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and 2,2'-bipyridine with triethylorthoformate as a drying agent. The resulting pink precipitate was filtered off, washed with ethanol and diethylether and dried *in vacuo*.

$[\text{Bu}_4\text{N}][\text{Pd}(\text{dmit})_2]$. This compound was prepared using a well-developed method described by Steimecke *et al.* (29).

$[\text{Ni}(\text{bpy})_3][\text{Pd}(\text{dmit})_2] \cdot \text{CH}_3\text{CN}$. This metathesis product has been prepared by adding a filtrated solution of 35 mg (0.05 mmol) of $[\text{Ni}(\text{bpy})_3](\text{BF}_4)_2$ in 10 ml acetonitrile to a filtrated solution of 37 mg (0.05 mmol) of

$[\text{Bu}_4\text{N}][\text{Pd}(\text{dmit})_2]$ in 75 ml acetonitrile. The immediately formed black precipitate was filtered off. The filtrate was kept at 0°C. After 2 weeks black platelets had formed in the flask. A crystal structure has been determined. The quality of the crystals rapidly deteriorated after having been isolated from their mother solution. Evaporation of the lattice acetonitrile was suspected. Therefore, the X-ray data were collected at 150 K on a crystal immediately taken from the solution. Elemental analysis: found (calculated) C 42.26 (42.76); H 2.23 (2.55); N 9.20 (9.19). IR (cm⁻¹): 3100–3000 w (aromatic C–H stretch bpy), 1596 s (bpy), 1440 s (C = C stretch dmit), 1055 s, 1020 s (C = S stretch dmit), 898 m (dmit), 765 s (bpy), 735 m, 465 m (dmit).

Elemental analysis of the obtained black powder suggests a composition with a cation:anion ratio much smaller than 1:2 (1:2 ratio: C 33.07; H 1.59; N 5.51), the expected stoichiometry, when taking the charge on $[\text{Ni}(\text{bpy})_3]^{2+}$ and $[\text{Pd}(\text{dmit})_2]^-$ of the starting compounds into account. The stoichiometry optimized for best C:N ratio, is $[\text{Ni}(\text{bpy})_3][\text{Pd}(\text{dmit})_2]_{6.16}$; found (calculated for 1:6.16, cation:anion) C 24.31 (22.32); H 0.54 (0.67); N 2.54 (2.33)%. IR (cm⁻¹): 1596 s, 1470 s, 1440 s (bpy), 1289 s, 1056 s (C=C, C=S stretch band dmit). The two point DC powder conductivity of $5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ is not as high as found for other fractionally oxidized compounds (30).

2.2. Physical Measurements

Magnetic susceptibility was measured on the crystals in the temperature range 5–300 K on a Quantum Design MPMS-5S SQUID operating at 2.0 Tesla. Data were corrected for magnetization of the sample holder and diamagnetic contributions, which were estimated using Pascal constants ($\chi_{\text{dia}} = -5.13 \times 10^{-4} \text{cm}^3 \text{mol}^{-1}$) (31). X-ray data collection and cell refinement were performed on an IPDS Stoe diffractometer, by using the IPDS software (32) version 2.86 at 150 K. The crystal-to-detector distance was kept at 70 mm. One hundred and eighty-three exposures (3 min per exposure) were obtained with $0 < \phi < 220^\circ$ and with the crystals rotated through 1.2° in ϕ . Crystal decay was monitored by measuring a maximum of 200 reflexions per image. All calculations were carried out using the WinGX package (33) with Sir92 (34) for the structure solution and Shelx197 (35) for the subsequent refinements. Geometrical calculations have been performed with the computer program PLATON (36).

3. RESULTS AND DISCUSSION

3.1. Crystal Structure of $[\text{Ni}(\text{bpy})_3][\text{Pd}(\text{dmit})_2] \cdot \text{CH}_3\text{CN}$

The crystallographically independent unit (Fig. 1) consists of two $\text{Ni}(\text{bpy})_3$ complexes, one entire $[\text{Pd}(\text{dmit})_2]$ anion and two-half $\text{Pd}(\text{dmit})_2$ units (each unit builds up its

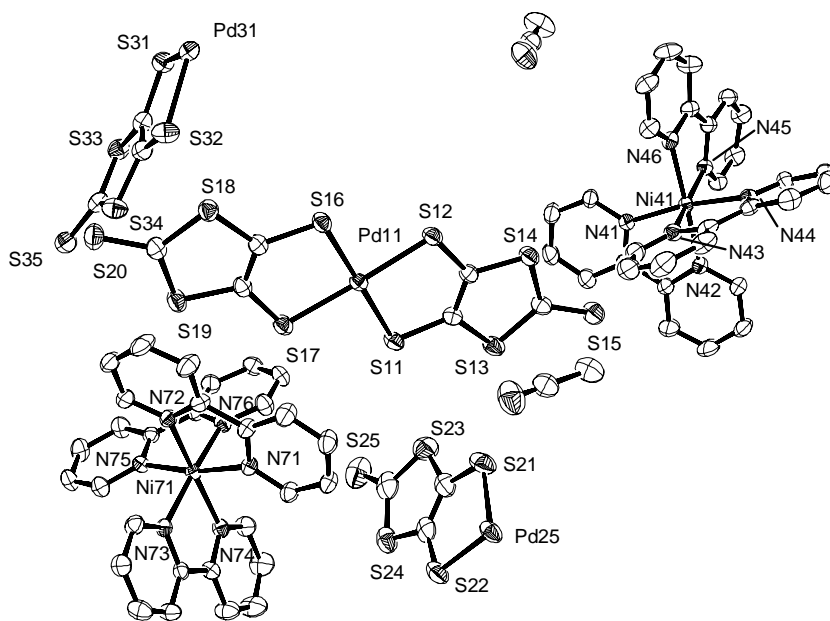


FIG. 1. Thermal ellipsoid drawing (36) of the crystallographically independent units in $[\text{Ni}(\text{bpy})_3][\text{Pd}(\text{dmit})_2] \cdot \text{CH}_3\text{CN}$; hydrogen atoms are omitted for clarity.

TABLE 1
Crystallographic Data of $[\text{Ni}(\text{bpy})_3][\text{Pd}(\text{dmit})_2] \cdot \text{CH}_3\text{CN}$

Identification code	$[\text{Ni}(\text{bpy})_3][\text{Pd}(\text{dmit})_2] \cdot \text{CH}_3\text{CN}$
Empirical formula	$\text{C}_{38}\text{H}_{27}\text{N}_7\text{NiPdS}_{10}$
Formula weight	1067.48
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/a$ (No. 14)
Unit cell dimensions	$a = 23.969(3)$ Å $\alpha = 90^\circ$ $b = 14.2768(11)$ Å $\beta = 103.726(13)^\circ$ $c = 25.879(3)$ Å $\gamma = 90^\circ$
Volume	$8602.9(15)$ Å ³
Z	8
Density (calculated)	1.648 g cm ⁻³
Absorption coefficient	1.380 mm ⁻¹
$F(000)$	4304
Crystal size	$0.38 \times 0.35 \times 0.08$ mm ³
Theta range for data collection	2.08 – 26.10°
Index ranges	$-29 \leq h \leq 29$, $-17 \leq k \leq 17$, $-31 \leq l \leq 31$
Reflections collected	73530
Independent reflections	16578 [$R(\text{int}) = 0.0536$]
Completeness to $\theta = 26.10^\circ$	97.1%
Absorption correction	Empirical (DIFABS)
Max. and min. transmission	0.9618 and 0.7854
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	16578/0/1228
Goodness-of-fit on F^2	0.950
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0341$, $wR_2 = 0.0752$
R indices (all data)	$R_1 = 0.0577$, $wR_2 = 0.0831$
Largest diff. Peak and hole	1.877 and -1.113 e Å ⁻³

other half of the anion via the inversion centers situated on the Pd atom) and two acetonitrile molecules (Table 1).

The Ni–N distances in the cation complex with Ni41 have a range of 2.064(3)–2.113(3) Å and an average of 2.087(3) Å and in the complex with Ni71 a range of 2.074(3)–2.093(3) Å and an average of 2.086(3) Å (Table 2). Ni–N distances for $\text{Ni}(\text{bpy})_3$ compounds found in the Cambridge Structural Database are in the range 2.049(5)–2.138(5) Å and with an average of 2.087(5) Å, making the present distances quite normal. The dihedral angles between the pyridine least-squares planes in the bpy molecules are in the range of 1.1(2)–8.5(2)°. The Me–C–N angles in the acetonitrile molecules are 178.3(5)° and 179.7(5)°.

The average Pd–S distance of 2.309(1) Å is in agreement with the average Pd–S distance of 2.314(2) Å in $[\text{Bu}_4\text{N}]_2[\text{Pd}(\text{dmit})_2]$ (37). The $[\text{Pd}(\text{dmit})_2]$ anions are slightly bent in a z -like manner.

The unit cell contains eight formula units. Six $[\text{Ni}(\text{bpy})_3]^{2+}$ cation complexes are almost completely situated within the unit cell and four cations are shared by neighboring unit cells. In the $[\text{Ni}(\text{bpy})_3][\text{Pd}(\text{dmit})_2] \cdot \text{CH}_3\text{CN}$ structure both $[\text{Ni}(\text{bpy})_3]^{2+}$ enantiomers Λ and Δ are present, as would be expected for a monoclinic $P 2_1/a$ space group.

Four $[\text{Pd}(\text{dmit})_2]^{2-}$ anions (Pd11 units) are situated within the unit cell, whereas the other $\text{Pd}(\text{dmit})_2$ units are

TABLE 2
Coordination Bond Distances (Å) and Angles (deg)
of [Ni(bpy)₃][Pd(dmit)₂]·CH₃CN

Ni(41)–N(41)	2.064(3)	Ni(41)–N(44)	2.092(3)
Ni(41)–N(42)	2.089(3)	Ni(41)–N(45)	2.077(3)
Ni(41)–N(43)	2.087(3)	Ni(41)–N(46)	2.113(3)
N(45)–Ni(41)–N(46)	78.2(1)	N(45)–Ni(41)–N(41)	95.1(1)
N(41)–Ni(41)–N(42)	78.6(1)	N(45)–Ni(41)–N(42)	98.3(1)
N(43)–Ni(41)–N(44)	79.2(1)	N(45)–Ni(41)–N(43)	167.3(1)
N(46)–Ni(41)–N(44)	87.8(1)	N(45)–Ni(41)–N(44)	92.0(1)
N(46)–Ni(41)–N(43)	92.2(1)	N(44)–Ni(41)–N(41)	170.9(1)
N(46)–Ni(41)–N(42)	175.8(1)	N(44)–Ni(41)–N(42)	94.8(1)
N(46)–Ni(41)–N(41)	99.3(1)	N(43)–Ni(41)–N(41)	94.7(1)
		N(43)–Ni(41)–N(42)	91.6(1)
Ni(71)–N(71)	2.093(3)	Ni(71)–N(74)	2.083(3)
Ni(71)–N(72)	2.093(3)	Ni(71)–N(75)	2.079(3)
Ni(71)–N(73)	2.074(3)	Ni(71)–N(76)	2.091(3)
N(75)–Ni(71)–N(76)	78.7(1)	N(75)–Ni(71)–N(71)	169.6(1)
N(71)–Ni(71)–N(72)	78.3(1)	N(75)–Ni(71)–N(72)	95.1(1)
N(73)–Ni(71)–N(74)	78.8(1)	N(75)–Ni(71)–N(73)	98.3(1)
N(76)–Ni(71)–N(74)	94.6(1)	N(75)–Ni(71)–N(74)	92.0(1)
N(76)–Ni(71)–N(73)	172.7(1)	N(74)–Ni(71)–N(71)	95.2(1)
N(76)–Ni(71)–N(72)	91.7(1)	N(74)–Ni(71)–N(72)	171.3(1)
N(76)–Ni(71)–N(71)	93.2(1)	N(73)–Ni(71)–N(71)	90.4(1)
		N(73)–Ni(71)–N(72)	95.2(1)
Pd(11)–S(11)	2.3041(9)	Pd(11)–S(16)	2.3235(9)
Pd(11)–S(12)	2.2978(9)	Pd(11)–S(17)	2.3040(9)
S(11)–Pd(11)–S(16)	177.55(3)	S(16)–Pd(11)–S(17)	90.84(3)
S(12)–Pd(11)–S(17)	175.66(4)	S(12)–Pd(11)–S(16)	89.99(3)
S(11)–Pd(11)–S(12)	90.64(3)	S(11)–Pd(11)–S(17)	88.70(3)
Pd(21)–S(21)/S(21a) ^a	2.312(1)	Pd(21)–S(22)/S(22a) ^a	2.304(1)
S(21)–Pd(21)–S(22)	91.33(4)	S(21)–Pd(21)–S(22a) ^a	88.67(4)
Pd(31)–S(31)/S(31a) ^b	2.321(1)	Pd(31)–S(32)/S(32a) ^b	2.3039(9)
S(31)–Pd(31)–S(32)	91.28(3)	S(31)–Pd(31)–S(32a) ^b	88.72(3)

Symmetry transformations used to generate equivalent atoms:
^a $-x+1, -y+1, -z$; ^b $-x+2, -y+1, -z+1$.

shared by neighboring unit cells. Eight anions (Pd21) are situated at the cell corners and six anions (Pd21 and Pd31) on the faces of the cell. The acetonitrile molecules are scattered across the unit cell.

Anions lying in the *bc* plane are present, as well as anions directed in the *a* direction. The angles between the least-squares planes of the anions Pd11–Pd21 and Pd11–Pd31 are, respectively, 88.96(4)° and 81.71(3)°. As would be expected for a 1:1 stoichiometry with such a bulky cation, very few intermolecular close S...S contacts (distance < 3.70 Å = 2*r*_{VanderWaals}) are present. Two types of S...S contacts with distances 3.522(1) and 3.543(1) Å are present and they propagate, via an *ABACABAC*-like anion array, in the [101] direction, as can be seen in Figs. 2 and 3.

The anion arrangement is remarkably different from the lamellar, separate anion slab structures, very often found for [Pd(dmit)₂]-based compounds (30).

3.2. Magnetic Properties

Only the cation complex Ni(bpy)₃²⁺ (O_h d⁸, S = 1) is the origin of the paramagnetic response of the [Ni(bpy)₃][Pd(dmit)₂]·CH₃CN crystals to a magnetic field, since the [Pd(dmit)₂]²⁻ anions are diamagnetic species. The compound displays a slight deviation from Curie behavior (38) ($\theta = -1.7$ K, $C = 1.26$ cm³ mol⁻¹ calculated in the 20–100 K temperature range). The Curie constant is lower than the calculated $C = 1.80$ cm³ mol⁻¹ for an S = 1 system. The latter two observations may be attributed to a zero-field splitting present in the Ni(bpy)₃²⁺ cation (38).

3.3. Reduction of the [Pd(dmit)₂]¹⁻ Anion

The crystals have stoichiometry [Ni(bpy)₃][Pd(dmit)₂]·CH₃CN. The assumption that the [Ni(bpy)₃]²⁺ has retained its charge during the metathesis would imply a charge of 2– on the [Pd(dmit)₂] anion. Infrared data of the crystals support this suggestion. The C=C stretch vibration of the dmit ligand is sensitive to the charge on the [Pd(dmit)₂] anion (39). This vibration of [Ni(bpy)₃][Pd(dmit)₂]·CH₃CN at 1440 cm⁻¹ is exactly equal to the corresponding vibration in the precursor compound [Bu₄N]₂[Pd(dmit)₂] with charge 2– on the anion.

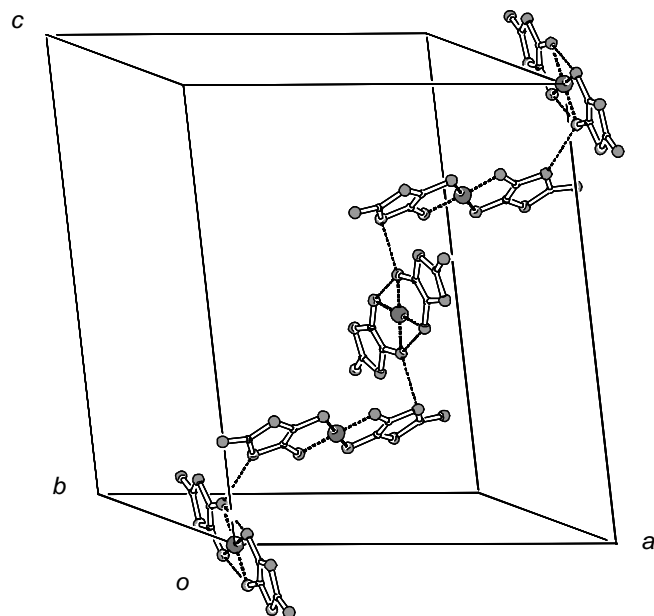


FIG. 2. Arrangement of Pd(dmit)₂ anions with close S...S contacts indicated by dotted lines in [Ni(bpy)₃][Pd(dmit)₂]·CH₃CN.

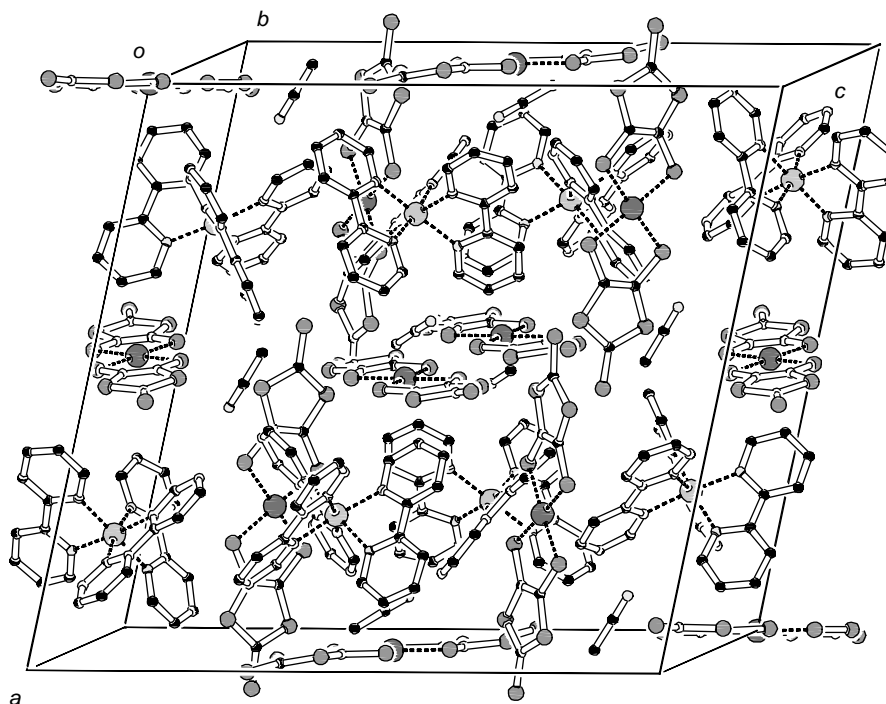


FIG. 3. Unit cell and packing details of $[\text{Ni}(\text{bpy})_3][\text{Pd}(\text{dmit})_2] \cdot \text{CH}_3\text{CN}$.

The anion in this compound has been reduced from a 1- to a 2- charged anion. This reduction cannot be easily explained. All compounds present in the reaction mixture have been screened as potential reducers, but no species possibly present in the reaction mixture has a redox potential low enough to be the reductor of the $[\text{Pd}(\text{dmit})_2]^{1-}$ anion (Table 3).

The solvent, acetonitrile, well known for its electrochemical inertness and often used for electro-analytical measurements, also cannot be responsible for this reduction. Taking into account the probable stoichiometry of cation:anion = 1:6.16 of the black powder, that has precipitated immediately after mixing solutions of the starting compounds, a disproportionation of charge could be an explanation

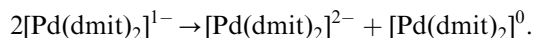


TABLE 3

Redox Potentials of all Reactants Possibly Present in the Reaction Mixture of the Synthesis of $[\text{Ni}(\text{bpy})_3][\text{Pd}(\text{dmit})_2] \cdot \text{CH}_3\text{CN}$

Redox couples	$E_{1/2}$ vs SCE (V)	References
$[\text{Pd}(\text{dmit})_2]^{1-/-}$	0.05	(41)
$[\text{Pd}(\text{dmit})_2]^{x-/-}$	0.20	(41)
$[\text{Ni}(\text{bpy})_3]^{3+/2+}$	1.63	(43)
$\text{bpy}^{+}/^0$	2.08	(43)

A similar phenomenon has been reported earlier by Sun *et al.* (40) when the simultaneous preparation of $[\text{MDA}]_2[\text{Pd}(\text{dmit})_2]$ and $[\text{MDA}][\text{Pd}(\text{dmit})_2]_2$ ($\text{MDA}^+ = 2$ -dimethylamino-1,3-dithiolanylium) starting from $[\text{MDA}][\text{Pd}(\text{dmit})_2]$ was described. Sun states that the stabilization of the $[\text{M}(\text{dmit})_2]^-$ anion strongly depends on the counter cation and solvent. Our observations agree with this. Apparently, just the addition of another counter cation, here the $\text{Ni}(\text{bpy})_3^{2+}$ complex, induces this disproportionation of charge. A cyclic voltammogram (41) of $[\text{Bu}_4\text{N}][\text{Pd}(\text{dmit})_2]$ shows that the two waves for the redox couples $2-/1-$ ($E_{1/2} = 0.05$ V vs SCE) and $1-/x-$ ($0 < x < 1$) ($E_{\text{ox}} = 0.16$ V vs SCE) of $[\text{Pd}(\text{dmit})_2]$ are very close ($\Delta E = 0.11$ V), as opposed to the voltammogram of $[\text{Bu}_4\text{N}][\text{Ni}(\text{dmit})_2]$ which contains two waves for the two redox couples $2-/1-$ and $1-/x-$ of $[\text{Ni}(\text{dmit})_2]$ at $E_{1/2} = -0.15$ V vs SCE and $E_{1/2} = 0.21$ V vs SCE, respectively ($\Delta E = 0.36$ V) (42). This suggests a relative instability of the monovalent $[\text{Pd}(\text{dmit})_2]^-$ anion, which might easily be reduced to $[\text{Pd}(\text{dmit})_2]^{2-}$ causing the observed disproportionation of charge.

4. CONCLUSIONS

Combination of $[\text{Ni}(\text{bpy})_3]^{2+}$ and $[\text{Pd}(\text{dmit})_2]^{1-}$ has resulted in two products. The first product is an immediately precipitated black powder with the composition $[\text{Ni}(\text{bpy})_3][\text{Pd}(\text{dmit})_2]_{6.16}$. The second product, crystallized

from the filtrate, is the paramagnetic [Ni(bpy)₃][Pd(dmit)₂]·CH₃CN, a compound with charge 2⁻ on the anion, which most probably is the consequence of a disproportionation reaction. The crystal structure of [Ni(bpy)₃][Pd(dmit)₂]·CH₃CN consists of an anion arrangement, which is significantly different from structures with segregated [Pd(dmit)₂] stack layers often observed for [Pd(dmit)₂]-based compounds.

Since this compound is readily soluble in acetonitrile, it is a promising precursor material for oxidized materials of general composition [Ni(bpy)₃][Pd(dmit)₂]_n with $n > 2$ and a non-integer formal charge on the anion. These materials can be obtained via electro-oxidation, with the purpose to obtain electrically conducting materials.

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