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Crystal Structure and Electrical and Magnetic Properties of Tris(*N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine) Bis(4,5-dimercapto-1,3-dithiole-2-thionato)nickelate

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The electrochemical synthesis and characterization of a new member of the family of $[\text{cat}]_x[\text{Ni(dmit)}_2]$ coordination compounds, with "cat" being the radical cation of *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (abbreviated as tmpd), $\text{dmit}^{2-} = C_3S_5^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolate, and $x = 3$, is reported. $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$ has an extremely low electrical conductivity of about 10^{-12} S cm^{-1}. The high resistivity contrasts with many materials based on both $[\text{Ni(dmit)}_2]$ alone or tmpd alone. A single-crystal structure determination was carried out. The crystals are triclinic, space group $P\bar{1}$ with $a = 9.423$ (1) Å, $b = 9.883$ (1) Å, $c = 14.728$ (2) Å, $\alpha = 102.99$ (2)°, $\beta = 93.33$ (2)°, $\gamma = 125.30$ (2)°, and $Z = 1$ for formula $C_{36}H_{48}N_6NiS_{10}$. The structure was solved by Patterson, Fourier, and least-squares techniques. $R_w = 0.043$ for 3792 independent significant reflections. The Ni atoms are located at centers of symmetry. The unit cell contains three tmpd units, two of which being dimerized and one isolated. The structure displays shortests S···S contacts of about 4.2 Å; these very long contacts explain the observed high resistivity. The mean Ni–S distance is 2.193 Å, which indicates that the Ni atom carries an average positive charge of about 2.24. This picture is consistent with the EPR and susceptibility data, which can be explained by the occurrence of $[\text{Ni(dmit)}_2]^-$ and $[\text{tmpd}]_2^+$ radicals, together with $[\text{Ni(dmit)}_2]^{2-}$ anions and $[\text{tmpd}]_2^{2+}$ dimers, the latter having a thermally accessible triplet state.

Introduction

Conducting compounds based on the radical cation of *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (hereafter abbreviated as tmpd) have been known for a long time; one of the most well-known compounds in this class is the so-called "Würsters Blue", $(\text{tmpd})\text{ClO}_4$,[1] with a room-temperature conductivity of about 10^{-3} S cm^{-1}. An even more successful class of molecular conductors is based on the radical anion $[\text{Ni(dmit)}_2]^{\bullet-}$ ($\text{dmit}^{2-} = C_3S_5^{2-}$ = 4,5-dimercapto-1,3-dithiole-2-thionate); some of these conductors are even superconductors at low temperature. One of the first $[\text{Ni(dmit)}_2]$-based superconductors reported was $[\text{ttf}][\text{Ni(dmit)}_2]_2$,[2] with ttf standing for the sulfur-rich tetrathiafulvalene radical cation. We therefore tried to replace ttf in the latter compound by the planar nitrogen-containing radical $\text{tmpd}^{\bullet+}$, with the aim to accomplish fractional charge transfer between the anion and the cation, which is one of the origins of the conductivity in $[\text{ttf}][\text{Ni(dmit)}_2]_2$.[2] Apart from this, tmpd-containing compounds may display very interesting triplet exciton EPR spectra due to stacking of tmpd cations with alternating intermolecular distances.[3] In the present work the synthesis, X-ray structure, and electrical conductivity as well as magnetic susceptibility and EPR data of $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$ are reported.

Experimental Section

Synthesis of $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$. $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$ was prepared by dissolving 0.1 mmol of neutral *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (obtained commercially) and 0.1 mmol of $[\text{Bu}_4\text{N}][\text{Ni(dmit)}_2]$ (prepared according to the general recipe of Steimecke[4]) in 10 mL of acetonitrile. Electrooxidation of the solution yielded thick, hexagonal, dark violet crystals. The results of the elemental analysis were in agreement with the molecular formula proposed for the compound. Anal. Calcd: C, 45.8; N, 8.9; H, 5.1; Ni, 6.2; S, 34.0. Found: C, 46.1; N, 8.8; H, 5.6; Ni, 6.0.

Magnetic Measurements. Susceptibility data were obtained with a Faraday balance in the temperature range 80–300 K. Data obtained in the cooling cycle were identical to data obtained in the heating cycle. EPR spectra were recorded on a Varian E3 spectrometer (9.4 GHz) at 300 and 77 K.

Single-Crystal X-ray Analysis. A hexagonally shaped single crystal of high quality with approximate dimensions 0.4 × 0.3 × 0.15 mm^3 was mounted on a CAD-4 diffractometer, and diffraction data were collected using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Intensity data were measured by the $\omega/2\theta$ scan technique in the 2θ range 2–33°; $h = -12$ to $+11$, $k = -14$ to $+11$, and $l = 0$ to $+22$. Transmission coefficients ranged from 89.90 to 107.33. Data were corrected for Lorentz and polarization effects. An absorption correction ($\mu = 9.68$ cm^{-1}) was applied by use of Monte Carlo methods.[5] Atomic scattering factors were taken from the literature.[6] The structure was solved from the Ni position, obtained from a Patterson synthesis map, by automatic

Table I. Crystallographic Parameters for $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$

chem formula	$C_{36}H_{48}N_6NiS_{10}$	Z	1
fw	944.17	space group	$P\bar{1}$ (No. 2)
a	9.423 (1) Å	ρ_{obs}	1.47 g cm^{-3}
b	9.883 (1) Å	ρ_{calc}	1.479 g cm^{-3}
c	14.728 (2) Å	T	300 K
α	102.99 (2)°	λ(Mo Kα)	0.71073 Å
β	93.33 (2)°	μ	9.68 cm^{-1}
γ	125.30 (2)°	R^a	0.0357
V	1059.8 (4) Å^3	$R_w{}^b$	0.0431

[a] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [b] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $w = 1/\sigma^2(F)$.

Table II. Atomic Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms in $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$ (Standard Deviations in Parentheses)

	x/a	y/b	z/c	B_{iso},^{a} Å^2
Ni	1	0	1	2.73 (1)
S(1)	0.7133 (9)	0.1244 (9)	0.9676 (7)	3.47 (2)
S(2)	0.9901 (8)	0.1217 (9)	0.8527 (7)	3.28 (2)
S(3)	0.4279 (9)	0.3692 (9)	0.7813 (8)	3.60 (2)
S(4)	0.6766 (9)	0.3694 (9)	0.6776 (7)	3.51 (2)
S(5)	0.2917 (10)	0.5809 (10)	0.5759 (8)	4.07 (2)
C(1)	0.649 (3)	0.242 (3)	0.848 (3)	2.97 (6)
C(2)	0.766 (3)	0.243 (3)	0.799 (2)	2.92 (6)
C(3)	0.457 (3)	0.446 (3)	0.672 (3)	3.23 (6)
C(4)	0.294 (3)	0.357 (3)	0.038 (3)	3.22 (6)
C(5)	0.241 (3)	0.530 (2)	0.000 (2)	3.63 (7)
C(6)	0.120 (3)	0.640 (2)	0.916 (2)	3.32 (6)
C(7)	0.040 (3)	0.589 (3)	0.861 (3)	2.96 (6)
C(8)	0.090 (3)	0.419 (2)	0.900 (2)	3.46 (7)
C(9)	0.212 (3)	0.308 (2)	0.986 (2)	3.35 (7)
C(10)	0.477 (1)	0.062 (1)	0.156 (1)	4.12 (8)
C(11)	0.514 (2)	0.290 (1)	0.175 (1)	4.95 (9)
C(12)	0.132 (2)	0.638 (2)	0.711 (1)	5.57 (10)
C(13)	0.112 (2)	0.867 (1)	0.731 (1)	5.51 (10)
N(1)	0.418 (2)	0.245 (2)	0.122 (1)	3.86 (6)
N(2)	0.075 (2)	0.700 (2)	0.775 (1)	3.86 (6)
C(4')	0.635 (3)	0.047 (3)	0.447 (3)	3.02 (6)
C(5')	0.566 (3)	0.141 (3)	0.468 (2)	3.67 (7)
C(6')	0.435 (3)	0.094 (3)	0.519 (2)	3.72 (7)
C(10')	0.864 (2)	0.263 (1)	0.382 (1)	4.72 (9)
C(11')	0.870 (1)	0.029 (2)	0.402 (1)	4.96 (9)
N(1')	0.762 (2)	0.089 (2)	0.391 (1)	3.73 (6)

[a] $B_{\text{iso}} = {}^8/_3\pi^2\text{Tr(U)}$.

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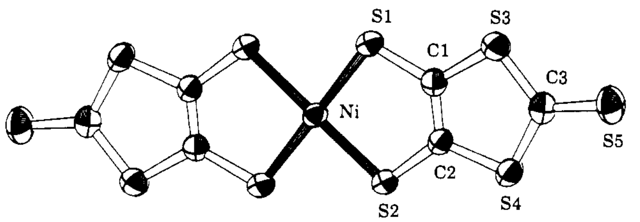

Figure 1. ORTEP drawing of the $[\text{Ni(dmit)}_2]$ unit in $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$ with the atomic labeling system used.

Table III. Intramolecular Distances (Å) and Angles (deg) in $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$ (Standard Deviations in Parentheses)[a]

Ni–S(1)	2.1876 (7)	Ni–S(2)	2.1987 (6)
S(1)–C(1)	1.728 (3)	S(2)–C(2)	1.729 (3)
S(3)–C(1)	1.750 (3)	S(3)–C(3)	1.723 (3)
S(4)–C(2)	1.749 (2)	S(4)–C(3)	1.734 (3)
S(5)–C(3)	1.647 (3)	C(1)–C(2)	1.349 (3)
S(1)–Ni–S(2)	92.96 (2)	Ni–S(1)–C(1)	101.50 (9)
Ni–S(2)–C(2)	101.54 (8)	S(1)–C(1)–S(3)	122.0 (1)
S(2)–C(2)–S(4)	122.4 (1)	C(1)–S(3)–C(3)	98.3 (1)
C(2)–S(4)–C(3)	97.9 (1)	S(3)–C(3)–S(4)	112.3 (1)
S(3)–C(3)–S(5)	123.0 (2)	S(4)–C(3)–S(5)	124.7 (2)
C(4)–C(5)	1.426 (3)	C(5)–C(6)	1.352 (2)
C(6)–C(7)	1.417 (3)	C(7)–C(8)	1.415 (3)
C(8)–C(9)	1.375 (2)	C(9)–C(4)	1.384 (3)
C(4)–N(1)	1.360 (3)	C(7)–N(2)	1.354 (3)
N(1)–C(10)	1.457 (2)	N(1)–C(11)	1.462 (2)
N(2)–C(12)	1.435 (2)	N(2)–C(13)	1.471 (2)
C(4′)–C(5′)	1.395 (3)	C(4′)–C(6′*)	1.388 (3)
C(5′)–C(6′)	1.387 (3)	C(4′)–N(1′)	1.407 (3)
N(1′)–C(10′)	1.455 (2)	N(1′)–C(11′)	1.463 (2)
C(9)–C(4)–C(5)	117.4 (2)	C(4)–C(5)–C(6)	121.4 (2)
C(5)–C(6)–C(7)	121.2 (2)	C(6)–C(7)–C(8)	117.4 (2)
C(7)–C(8)–C(9)	120.6 (2)	C(8)–C(9)–C(4)	122.0 (2)
C(5)–C(4)–N(1)	121.3 (2)	C(6)–C(7)–N(2)	121.1 (2)
C(4)–N(1)–C(10)	121.5 (2)	C(4)–N(1)–C(11)	122.1 (2)
C(10)–N(1)–C(11)	115.3 (1)	C(7)–N(2)–C(12)	122.4 (2)
C(7)–N(2)–C(13)	121.1 (2)	C(12)–N(2)–C(13)	114.7 (1)
C(6′*)–C(4′)–C(5′)	116.5 (2)	C(4′)–C(5′)–C(6′)	121.7 (2)
C(4′*)–C(6′)–C(5′)	121.8 (2)	C(5′)–C(4′)–N(1′)	121.8 (2)
C(4′)–N(1′)–C(10′)	117.2 (1)	C(4′)–N(1′)–C(11′)	116.7 (1)
C(10′)–N(1′)–C(11′)	112.9 (1)		

[a] An asterisk indicates the symmetry operation $1 - x, -y, 1 - z$.

Fourier methods using the program AUTOFOUR[7] and difference Fourier maps to locate the hydrogen atoms. Full-matrix least-squares refinement in space group $P\bar{1}$ (322 variables, anisotropic thermal parameters for all non-hydrogen atoms) converged to $R = 0.036$ and $R_w = 0.043$ for 3792 independent significant reflections $[I > 2\sigma(I)]$ out of a total of 7968 reflections. The value for R_{int} proved to be 0.0267. During the refinement constraints according to the method of Waser[8] for all distances involving hydrogen atoms were applied. Table I lists all relevant crystallographic data. Atomic coordinates and thermal parameters are listed in Table II.

Results and Discussion

Description of the Structure of $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$. A projection of the anionic unit is shown in Figure 1, together with the atomic labeling system used. Relevant intramolecular distances and angles are tabulated in Table III. The observed bond lengths are comparable to the bond lengths found for other Ni(dmit)_2 compounds, except for the Ni–S bonds, which are 2.19 Å. For Ni(III) species the Ni–S bond is usually about 2.156 Å, while for Ni(II) complexes the Ni–S bond is about 2.21 Å (see Table IV). This is indicative for a charge between the Ni(II) and Ni(III) species. For isolated anions the Ni–S distance is a direct measure of the oxidation state of the Ni atom, as can be seen from Table IV. If one places $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$ between the Ni(II) and the Ni(III) species in this table, an effective mean charge of about 2.24 for the Ni atom would be obtained.

Table IV. Intermolecular Contacts between tmpd Units Shorter than 3.6 Å in $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$ (Standard Deviations in Parentheses)[a]

C(4)–C(7*)	3.366 (3)	C(4)–C(8*)	3.286 (4)
C(5)–C(8*)	3.341 (4)	C(6)–C(8*)	3.582 (3)
C(6)–C(9*)	3.344 (4)	C(7)–C(9*)	3.253 (3)
C(8)–C(9*)	3.443 (3)	N(1)–N(2*)	3.451 (2)

[a] An asterisk indicates the symmetry operation $-x, -1 - y, 2 - z$.

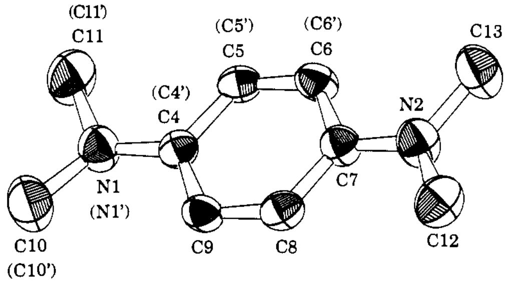

Figure 2. ORTEP drawing of one tmpd unit (tmpd(1)) with the labeling system used. The labeling scheme used for the tmpd(3) unit is indicated in parentheses.

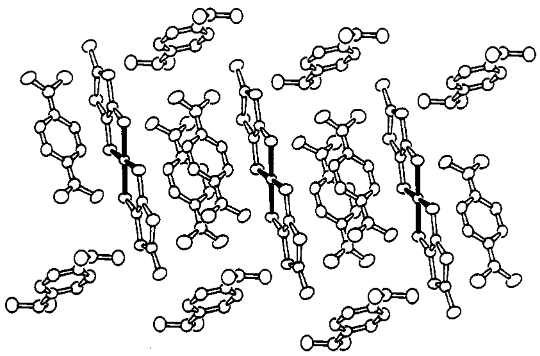

Figure 3. View of the packing of the anions and cations in $[\text{tmpd}]_3[\text{Ni(dmit)}_2]$.

As is shown by a calculation of a plane through Ni, S(1), and S(2), the anion is almost completely planar. The largest deviations from the mean plane are observed for S(3) and S(5) (deviations of 0.026 (6) and 0.025 (5) Å, respectively).

In Figure 2 a drawing of the tmpd unit with the used atomic labeling system is shown. The two crystallographically equivalent tmpd units (hereafter abbreviated as tmpd(1) and tmpd(2)) lie between two $[\text{Ni(dmit)}_2]$ molecules, as can be seen from the overview of the unit cell (Figure 3). The third tmpd unit (hereafter abbreviated as tmpd(3)) lies on a center of inversion and has no close contacts to any of the other molecules. The most prominent difference between the two crystallographically independent tmpd molecules is the difference in the bond lengths between the nitrogen atoms and the ring carbon atoms. In tmpd(1) and tmpd(2) this distance is 1.36 Å, whereas in tmpd(3) this distance is 1.41 Å. This discrepancy may be accounted for by the presence of a positive charge on both tmpd(1) and tmpd(2), which increases the bonding interaction of the nitrogen with the ring system. Distances in the ring itself also show differences (see Table III), though they are not as drastic. The ring systems of tmpd(1) and tmpd(2) are clearly not hexagonal, in agreement with

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Table V. Ni–S Bond Lengths for Different [Ni(dmit)$_2$] Coordination Compounds

compd	M–S, Å	ref
[Bu$_4$N]$_2$[Ni(dmit)$_2$]	2.21	4
[Me$_4$N][Ni(dmit)$_2$]	2.158	12
[Et$_4$N][Ni(dmit)$_2$]	2.157	13
[Pr$_4$N][Ni(dmit)$_2$]	2.160	12
[Bu$_4$N][Ni(dmit)$_2$]	2.157	14
[Et$_4$N][Ni(dmit)$_2$]$_2$	2.152	15
[tmpd]$_3$[Ni(dmit)$_2$]	2.193	this paper

bond distances found in (tmpd)ClO$_4$[1] and [tmpd]$_2$[Ni(mnt)$_2$].[10] In contrast, the benzene ring in tmpd(3) is hexagonal within experimental error, as expected for an uncharged species.[9] The observed C(4′)–N(1′) distance (1.41 Å), however, is somewhat larger (1.39 Å) than predicted by the calculations in ref 9. Also, the ring system of tmpd(3) is completely planar (within experimental error) with the nitrogen atom N(1′) in this plane (deviation 0.07 (1) Å) and the carbon atoms C(10′) and C(11′) pointing out of this plane (deviations −0.31 (1) and −0.40 (1) Å, respectively).

The presence of a positive charge on tmpd(1) and tmpd(2) is further supported by the observation that tmpd(1) and tmpd(2) form a dimer. This is illustrated in Table V, where the shortest intermolecular distances are tabulated. Molecular interactions between the tmpd(1) and tmpd(2) units are even more enhanced by the fact that a least-squares calculation of a plane through the ring carbon atoms indicates that each tmpd molecule is planar. Moreover, crystal symmetry requires these molecules to be parallel to each other. The largest deviation from the plane is observed for the methyl carbon atoms (about 0.2 Å), tending to bend away from the other tmpd molecule. All other atoms have a deviation from the plane less than 0.01 Å.

Electrical Conductivity. [tmpd]$_3$[Ni(dmit)$_2$] displays an extremely low electrical conductivity of less than 10^{-12} S cm^{-1}, which is the lower limit of the measurement. This value can be understood from the long intermolecular S···S contacts; the shortest observed S···S contact (between the exocyclic sulfur atoms) is as long as 4.2 Å, which is obviously too large for any substantial molecular overlap. In contrast, the shortest cation···anion contacts are only 3.46 Å, but the overlap angle (70°) prevents the existence of a large overlap integral. This observation eliminates the possibility of the fractional charge on the Ni atom being a result of partial charge transfer, which would give rise to high conductivity, due to the resulting high mobility of the electrons. Therefore, the net fractional charge on the Ni atom, as discussed in the previous section, is a result of a statistical average of Ni(II) and Ni(III) species, each having a definite charge, and each accompanied by a (tmpd)$_2$ dimer with charge 2+ or 1+, respectively. The absence of satellite reflections ruled out the possibility of a supercell consisting of 3 Ni(II) and 1 Ni(III) species, which is the ratio that would give an average positive charge on the Ni atom of 2.25.

EPR Measurements. In Figure 4 a typical EPR spectrum of a polycrystalline sample is shown. The spectrum is dominated by a central, very intense peak at $g = 2.01$, which is split up. At the low- and high-field sides of the central peak fine structure is observed, which appears to be superposed with a hyperfine structure. In order to assign the peaks, the analysis of the spectrum will be split up in three parts: the intense, central absorption at $g = 2.01$, the hyperfine structure, and the fine structure. Starting with the last one, it is easily recognized that (tmpd)$_2^{2+}$ dimers have readily accessible triplet states. When there is some interdimer exchange possible, these can give rise to triplet excitons, which have been studied very extensively.[3,10] Due to the large interdimer distance, however, a pure triplet spectrum is expected. The spin Hamiltonian for such a system is given by

$$H = \beta SgH + D(S_z^2 - \tfrac{2}{3}) + E(S_x^2 - S_y^2) \qquad (1)$$

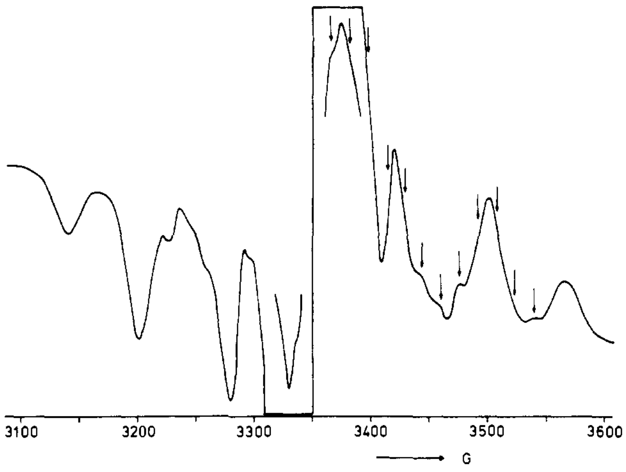

Figure 4. EPR spectrum at room temperature of [tmpd]$_3$[Ni(dmit)$_2$] (x axis in G). The arrows represent the positions of the absorptions due to the hyperfine interaction.

where D and E are the zero-field splitting parameters. If the **g** tensor is not too anisotropic, the doublet splittings are given by[11]

$$d_1 = |D + 3E| \qquad (2a)$$

$$d_2 = |D - 3E| \qquad (2b)$$

$$d_3 = 2|D| \qquad (2c)$$

where d_1, d_2, and d_3 represent the measured splittings along the principal axis. From these relations the following values for g, D, and E are obtained:

$$g = 2.01\ (1) \qquad |D| = 220\ (1)\ \mathrm{G} \qquad |E| = 27.4\ (4)\ \mathrm{G}$$

These are in very close agreement with the values obtained for [tmpd]$_2$[Ni(mnt)$_2$] ($|D| = 215$ G, $|E| = 28$ G).[10] Evidence for the triplet state being an excited state comes from the fact that, on cooling the salt to liquid-nitrogen temperatures, the intensity of the fine structure decreases dramatically. When the intensity is approximated by

$$I = Ce^{-\Delta E/kT} \qquad (3)$$

where C is a proportionality constant and ΔE is the energy splitting between the singlet and triplet state, an estimated value for ΔE of 0.22 (5) eV is obtained.

The next part of the spectrum consists of a hyperfine pattern. This part of the spectrum also originates from the triplet state, as the hyperfine structure disappears when the temperature is lowered to 77 K. The (tmpd)$_2^{2+}$ dimer contains 8 equivalent methyl groups, each having an effective spin $I = {}^3/_2$. The triplet ($S = 1$) thus interacts with an effective spin $I = 12$, which corresponds with a pattern of 25 lines in the EPR spectrum. By the fitting of the hyperfine pattern in Figure 4 to the usual spin Hamiltonian

$$H = \beta SgH + SAI \qquad (4)$$

g and A are obtained:

$$g = 2.01\ (1) \qquad A = 9.0\ (1)\ \mathrm{G}$$

This value for A is fairly reasonable if compared to the hyperfine coupling constants for the methyl protons in doublet tmpd$^+$ (7 G).[16]

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The last part of the spectrum originates from the $[Ni(dmit)_2]^-$ and $(tmpd)_2^+$ species and merely gives an intense single absorption at $g = 2.01$. No hyperfine structure due to the methyl groups of the dimer is found. In Figure 4, all absorptions according to the fitted parameters are indicated and only minor deviations from the recorded spectrum can be observed.

Susceptibility Measurements. The magnetic susceptibility of $[tmpd]_3[Ni(dmit)_2]$ shows paramagnetic behavior, which follows a Curie law with an effective magnetic moment of only 0.7 μ_B per unit cell (80–300 K). This very low magnetic moment clearly indicates that, in $[tmpd]_3[Ni(dmit)_2]$, Ni is not in its Ni(III) oxidation state, as this would give rise to a magnetic moment of at least 1.7 μ_B. However, the low moment can be explained by the distribution of Ni(II) and Ni(III) units.

From the analysis carried out in the previous sections it follows that only roughly 25% of the Ni atoms possess a charge of 1+ and thus carry a spin; the Ni^{2+} atoms are in the low-spin state and consequently do not have a moment. The same accounts for the $(tmpd)_2$ dimers, as only the singly charged species carry an unpaired spin. Using these numbers for the spin-carrying species and ignoring any interactions, a magnetic moment of 0.8 μ_B per unit cell is obtained, close to the observed value of 0.7 μ_B. Due to the fact that the susceptibility is completely dominated by the spins on $(tmpd)_2^{2+}$ and $[Ni(dmit)_2]^-$, no effect of the triplet state of the $(tmpd)_2^{2+}$ dimer could be observed.

Concluding Remarks

To the best of our knowledge $[tmpd]_3[Ni(dmit)_2]$ is the first $[Ni(dmit)_2]$-based compound containing a nitrogen-rich radical cation known sofar. Although the starting material in the electrochemical synthesis was a Ni(III) complex, the charge-transfer salt probably contains both Ni(II) and Ni(III) species. This mixed valence, however, is static, at least on the time scale of EPR spectroscopy, as is shown by the EPR spectrum containing both $(tmpd)_2^+$ and $(tmpd)_2^{2+}$ parts, the latter characterized by its triplet state. When $[tmpd]_3[Ni(dmit)_2]$ and $[ttf][Ni(dmit)_2]_2$, a metallic conductor, are compared, the enormous difference in conductivity may be explained from the fact that in the ttf compound large intermolecular overlaps exist, which are absent in $[tmpd]_3[Ni(dmit)_2]$. The angle between the planes of the $Ni(dmit)_2$ and tmpd units (70°) prevents conductivity via the cation.[17]

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Supplementary Material Available: Tables of crystallographic details, anisotropic thermal parameters, hydrogen positions and thermal parameters, bond distances and angles involving hydrogen atoms, and equations of least-squares planes and deviations (10 pages); a table of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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Comparative Study of NS_2 Ligands, *S*-Alkyl vs *S*-Aryl. Molecular Structure of [2,6-Bis(((2-(methoxycarbonyl)phenyl)thio)methyl)pyridine]dichlorocopper(II)

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Three new NS_2 aza–dithia *S*-aryl ligands have been synthesized and their Cu(II) and Cu(I) complexes reported. The ligand donor properties of these ligands are compared with similar NS_2 *S*-alkyl molecules. The NS_2 *S*-aryl ligands are softer and display a larger π-acid character than the corresponding NS_2 *S*-alkyl compounds. The molecular structure of [2,6-Bis(((2-methoxycarbonyl)phenyl)thio)methyl)pyridine]dichlorocopper(II) has been solved by X-ray diffraction methods: $C_{23}H_{21}Cl_2CuNO_4S_2$, monoclinic, space group $P2_1/c$, $a = 20.138$ (4) Å, $b = 8.173$ (1) Å, $c = 15.533$ (3) Å, $\beta = 111.20$ (2)°, $V = 2384$ (1) Å^3, $Z = 4$, $D_c = 1.600$ g·cm^{-3}.

Introduction

Relatively little work has been carried out on the NS_2 aza–thia compounds either as podand[1–3] or as macrocyclic[2,4–12] ligands. All these compounds contain the group 2,6-bis(thiomethyl)pyridine, which is the source of the NS_2 coordinating moiety. Recently, the macrocycle $[9]NS_2$ (7-aza-1,4-dithiacyclononane) has been reported by two independent groups (Ag(I) complex,[13] Ni(II) complex[14]). All these ligands contain both the hard N-donor and soft S-donor atoms. Interest in such mixed-donor ligands stems from metal ion selectivity and from the possible presence of such coordination environments around metal centers in methanogenic bacterial enzymes.[15,16]

Recent studies in our group have been shown that there is little discrimination of Cu(II) vs Ni or Co(II) ($K^{Pot}_{Cu,Ni} = 0.1$) in the all-solid-state electrode based on PVC, a mediating solvent (tris(2-ethylhexyl) phosphate), and the NS_2 sensor MO1[10] (Figure 1). This result stimulated us to study similar NS_2 ligands but

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