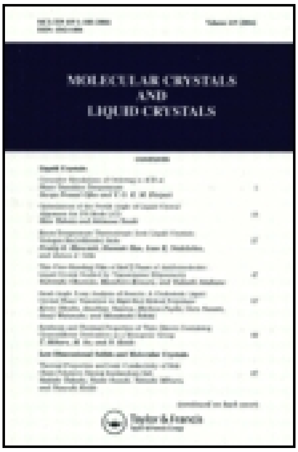

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2-Dicyanomethylene-1,3-Dithiole-4,5-Dithlolate-A New Dithiolene Ligand and Its Metal Complexes

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2-DICYANOMETHYLENE-1,3-DITHIOLE-4,5-DITHIOLATE – A NEW DITHIOLENE LIGAND AND ITS METAL COMPLEXES

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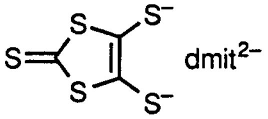
Abstract 2-Dicyanomethylene-1,3-dithiole-4,5-dithiolate (DCDD) has been prepared and used for the synthesis of transition metal complexes $(Bu_4N)_2[M(DCDD)_2]$, M = Ni, Cu, Zn. The redox properties of the nickel complex are similar to that of $(Bu_4N)_2[Ni(dmit)_2]$ (dmit: 1,3-dithiole-2-thione-4,5 dithiolate). Oxidation of $(Bu_4N)_2[Ni(DCDD)_2]$ yields the monoanionic complex $Bu_4N[Ni(DCDD)_2]$ the electron spectrum of which is characterized by a strong NIR absorption at 1135 nm. The crystal structure of $Bu_4N[Ni(DCDD)_2]$ shows the anion to be almost planar. Face-to-face stacking of the anions with alternating Ni-Ni distances results in a columnar structure of dimeric anions. The spins of the anions within a dimer are antiferromagnetically coupled. The complex $Fc^*[Ni(DCDD)_2]$ (Fc^*: decamethylferrocene) has been prepared by a metathesis reaction using Fc^*BF_4.

INTRODUCTION

The quest for molecular materials with unusual optical, magnetic or electrical properties has produced a multitude of interesting results in the last 20 years. Transition metal dithiolene complexes[1] are an important class of compounds in this field; they can be reversibly oxidized, form stable radical anions and show strong absorptions in the near infrared (NIR). Metal-metal, metal-sulfur and sulfur-sulfur interactions in planar dithiolene metal complexes give rise to the formation of dimers or stacking of the molecular units in the crystalline state.[2] As a consequence of these cooperative phenomena magnetic ordering or electrical conductivity are frequently observed. A careful choice of metal ions, substituents, counter cations and stoichiometry is necessary for optimum intermolecular interactions. Materials containing dithiolene complexes have been reported to be electrically conducting with semiconductor or metal characteristics.[3] Several compounds even undergo a phase transition to the superconducting state upon cooling.[4] Complexes with 1,3-dithiole-2-thione-4,5-dithiolate (dmit) **1** proved to be particularly useful in this respect.[5] Dithiolene metal complexes have magnetic ordering states ranging from intradimer spin coupling[6] to long range interactions[7]. Ferromagnetic interactions have been observed with charge transfer salts derived from dithiolene complexes[8] including $Fc^*[Ni(dmit)_2]$[7a] (Fc^*: decamethylferrocene).



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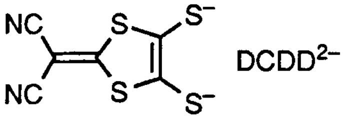
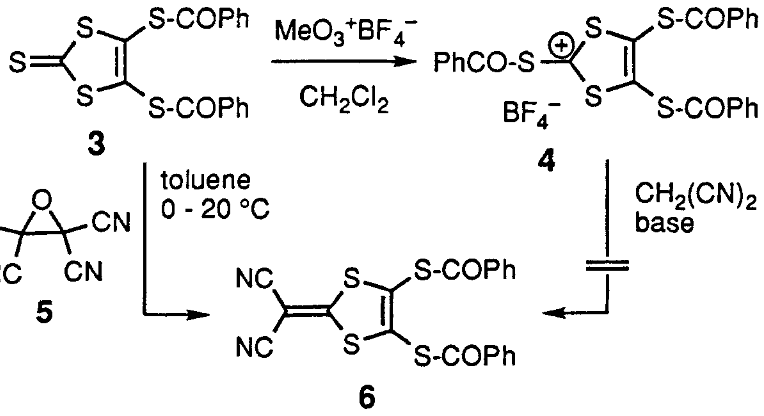


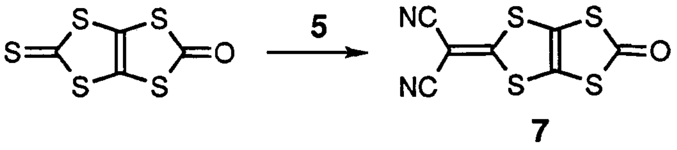
2

Several other sulfur heterocycles bearing the 1,2-dithiolate functionality have been synthesized, e.g., 1,2,5-thiadiazole-3,4-dithiolate,[9] 5-cyano-1,2-thiazole-3,4-dithiolate,[10] or 5,6-dihydro-1,4-dithiine-2,3-dithiolate[11] (DDDT), and transformed into metal complexes. In another approach to extend the range of interesting ligands the thiocarbonyl group in **1** has been replaced by carbonyl or selenocarbonyl groups; examples are 1,3-dithiole-2-one-4,5-dithiolate[12] (dmid) and 1,3-dithiole-2-selenone-4,5-dithiolate[13] (dmise). Based on the well established and often used analogy between carbonyl or thiocarbonyl compounds[14] and the corresponding dicyanovinyl derivatives we expected 2-dicyanomethylene-1,3-dithiole-4,5-dithiolate (DCDD) **2** to have a chemistry similar to that of **1**. In this paper we report the synthesis of **2**, the isolation of transition metal complexes $[M(DCDD)_2]^{n-}$ and their characterization by X-ray crystallography and magnetic susceptibility measurements.

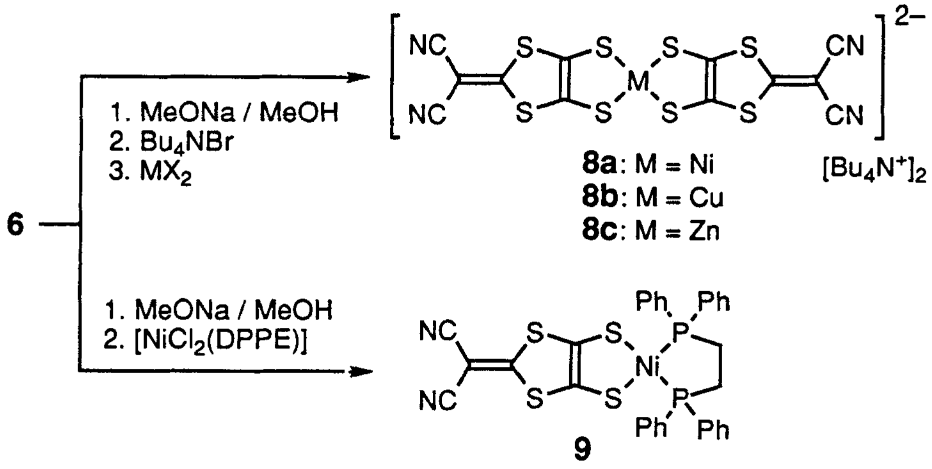
RESULTS AND DISCUSSION

Surprisingly, attempts to prepare **6**, the potential precursor of **2**, by condensation of the dithiolium salt **4**[15] with malononitrile under standard conditions[16] (e. g., heating the starting materials in pyridine/glacial acetic acid or triethylamine/acetonitrile) failed.[17] A simple and efficient synthesis of **6** was found in the reaction of **3**[5] with tetracyanoethylene oxide **5**[18] in toluene at 0-20 °C. The transformation of thiocarbonyl compounds into the corresponding dicyanomethylene derivatives using **5** has been described before,[19] but to the best of our knowledge it has not been applied to 1,3-dithiole-2-thiones. Using the same procedure, **7** can be prepared from 5-thioxo-1,3-dithiolo[4,5-d]-1,3-dithiole-2-one.[15a]





Treatment of **6** with sodium methanolate in methanol leads to a deep pink solution containing the disodium salt of **2**. By adding tetrabutylammonium bromide and transition metal salts to this solution the dianionic dithiolene metal complexes **8** are produced. The neutral complex **9** can be synthesized by heating a solution of **2**-(2 Na^+) in methanol with 1,2-bis(diphenylphosphino)ethane-nickel(II) chloride ($NiCl_2$(DPPE)).

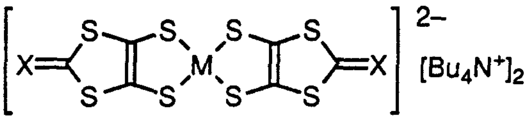


The DCDD metal complexes **8** are deeply coloured crystalline compounds which are soluble in polar solvents (acetone, DMF, etc.) and can be recrystallized from acetone-isopropanol. Surprisingly, they show solvatochromism (**8a**: $\Delta\nu(\mathrm{CHCl_3/Acetone}) = 1336\ \mathrm{cm^{-1}}$) which is even stronger than that of the highly dipolar pyridiniophenolates[20] (4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenolate: $\Delta\nu(\mathrm{CHCl_3/Acetone}) = 1112\ \mathrm{cm^{-1}}$).

The IR spectra of **6**, **7** and **8**, **9** show nitrile bands ($\nu_{\mathrm{CN}} = 2200\ \mathrm{cm^{-1}}$) and bands at 1400-1450 $\mathrm{cm^{-1}}$ assigned to the semicyclic double bonds of the $\mathrm{(NC)_2C{=}C_{ring}}$ moieties. The "dithiolene" bands[3a] partially overlap with the $\mathrm{(NC)_2C{=}C_{ring}}$ bands and can be separately observed only in case of the Ni complex **8a** ($\nu = 1390\ \mathrm{cm^{-1}}$) and the Cu complex **8b** ($\nu = 1386\ \mathrm{cm^{-1}}$).

The large differences in the ^{13}C NMR shifts of the carbon atoms of the semicyclic double bonds are indicative of a strong polarization of the $\mathrm{(NC)_2C{=}C_{ring}}$ group even if the anisotropic shielding by the cyano groups is taken into account. IR and ^{13}C NMR data suggest an increase in the polarization of the $\mathrm{(NC)_2C{=}C_{ring}}$ double bond on going from **7** to **8**. Obviously, the negative charge of the dithiolene complexes increases the contribution of the dipolar resonance structure $\mathrm{(NC)_2C^{-}{-}C^{+}_{ring}}$.

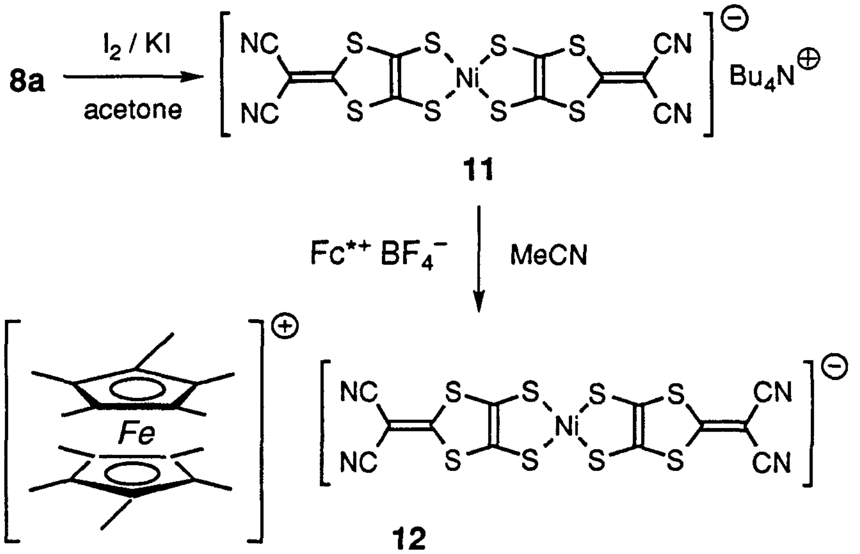
The Ni complex **8a** can reversibly be oxidized by cyclic voltammetry at $E_1 = -0.06$ V (vs. Ag/AgCl; dianion → monoanion) and quasireversibly at $E_2 = +0.27$ V (monoanion → neutral state). In the related dithiolene nickel complexes **10** the redox potential E_1 increases on going from **10a** to **10b** and to **10c**.[12b,13c] In the same sequence the ^{13}C NMR signals of the ring atoms C-4/5 are shifted downfield. This correlation does not hold with **8a**. Although the ^{13}C NMR sig-



10a: X = O, **10b**: X = S, **10c**: X = Se

nal of C-4/5 in **8a** is found at higher field (δ = 132.49 ppm) than that of the dmit-complex **10b** (δ = 137.9 ppm[12b]), E_1 of **8a** is more positive (not negative as expected) than that of **10b** (E_1 = –0.16 V). As compared to Ni complexes of DDDT and mnt (E_1 = +0.26 V; mnt: maleonitriledithiolate) the difference in redox behaviour between DCDD and dmit Ni complexes is rather small. The neutral complex **9** can reversibly be oxidized to a radical cation at +0.57 V (cyclic voltammetry in CH_2Cl_2, vs. Ag/AgCl). Furthermore, a quasireversible reduction wave at –1.57 V for the formation of a radical anion is observed.

The oxidation of **8a** to a monoanionic species can also be performed on a preparative scale. Addition of iodine to the deep green solution of **8a** gives rise to an olive-coloured solution from which **11** crystallizes in dark olive-green needles. The IR spectrum of **11** shows the same characteristic bands as that of **8a**, however the band of the $(NC)_2C{=}C_{ring}$ moiety is shifted to $\nu_{C=C}$ = 1442 cm^{-1} (**8a**: ν = 1401 cm^{-1}). The smaller negative charge of the monoanion as



compared to that of the dianion reduces the high intrinsic polarity of the $(NC)_2C=C_{ring}$ moiety. These observations underline the description of dithiolene metal complexes as delocalized π-electron systems in which the ligands are strongly involved in the redox process.[1]

The dithiolene band in the IR spectrum of **11** is observed at smaller wave numbers ($\nu = 1363\ cm^{-1}$) than in that of the dianionic complex **8a** ($\nu = 1390\ cm^{-1}$) as is general with dithiolene metal complexes.[1a] The electron spectrum of **11** shows a strong absorption maximum at 1135 nm (lg $\varepsilon = 4.344$). Obviously, as $[NBu_4][Ni(dmit)_2]$ absorbs at 1129 nm (lg $\varepsilon = 4.212$),[5] the replacement of the thiocarbonyl sulfur atom by a dicyanomethylene group has only little effect on the NIR absorption. Nevertheless, only a few dithiolene metal complexes have been reported to absorb at longer wavelengths.[21]

Crystal Structure

The crystal structure[22] of **11** (cf. Figure 1) shows the $[Ni(DCDD)_2]^-$ anion to be planar with only a small deviation from an ideal D_{2h} symmetry. Bond distances and angles are similar to those reported for other monoanionic dithiolene Ni complexes.[9-13,23] The average bond length of Ni-S (216.1(8) pm), C1-C2 (135.4(4) pm) and C1-S1 (171.2(3) pm) are typical for the coordination geometry of dithiolene metal complexes. As a result of its strong polarization the semicyclic C3-C4 double bond (139.3(4) pm) is longer than a normal C=C bond. An important feature of the crystal structure of **11** is the face-to-face

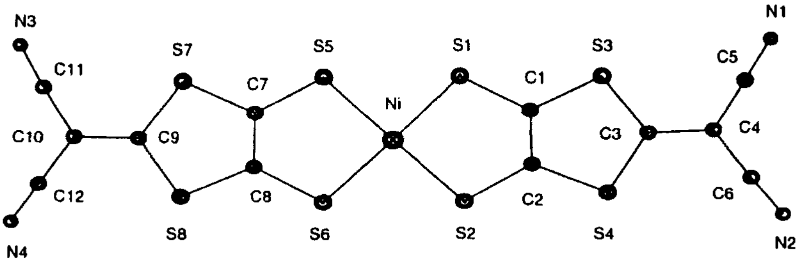


FIGURE 1 Molecular structure of the complex anion of **11**.[22] Selected bond lengths [pm] and angles [°]: Ni-S1 215.28(8), Ni-S2 216.91(8), S1-C1 171.2(3), S3-C1 174.6(3), S3-C3 171.0(3), C1-C2 135.4(4), C3-C4 139.3(4), C4-C5 141.3(4), C5-N1 114.4(5); S1-Ni-S2 93.29(3), C1-S1-Ni 101.92(9), C2-C1-S1 121.8(2), S3-C1-C2 116.8(2), C3-S3-C1 95.8(1), S4-C3-S3 115.6(1), C4-C3-S3 121.9(2), C3-C4-C5 120.7(2).

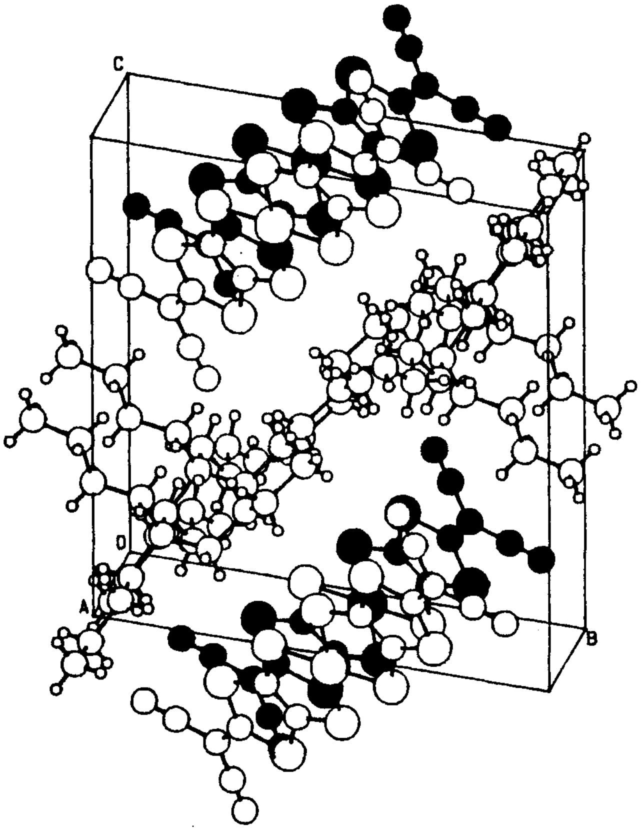


FIGURE 2 Crystal structure of **11**.[22] Packing diagram, view down the a axis.

stacking of the $[Ni(DCDD)_2]^-$ anions along the a-axis (cf., Figure 2). The stacks are separated from each other by stacks of cations. The segregated stacks of anions have short intermolecular S-S, Ni-Ni and Ni-S distances (cf., Table 1). The Ni-Ni distances are alternating (409.4 pm, 596.4 pm) along the stack. Thus, the stacks may be viewed as columns of slipped dimers. The molecules within a dimer are only slightly shifted against each other along the long molecular axis allowing six of eight sulfur atoms in each molecule to have close contact to six sulfur atoms of the neighbouring molecule. Between the dimers

TABLE 1 Intermolecular distances between neighbouring anions in the crystal structure of **11** [pm]

	intradimer	interdimer
Ni-Ni	409.4	596
Ni-S	378.4 (Ni-S5') 425.0 (Ni-S6')	378.9 (Ni-S3") 400.6 (Ni-S4")
S-S	376.6 (S1-S8', S8-S1') 382.2 (S2-S7', S7-S2') 388.4 (S5-S6', S6-S5')	383.9 (S1-S4", S4-S1") 382.5 (S2-S3", S3-S2")

a larger shift in the same direction allows only four close S-S contacts. The shortest Ni-S distances are the same within and between the dimers, but the intradimer interaction (Ni-S5' 378.4 pm) connects a dithiolato sulfur atom with the adjacent nickel atom while the interdimer interaction (Ni-S3" 378.9 pm) takes place between a heterocyclic sulfur atom and the next nickel atom. The short Ni-Ni distance of 409.4 pm is unusual for monoanionic Ni dithiolene complexes containing the tetrathioethylene backbone. The two crystal forms of $Bu_4N[Ni(dmit)_2]$ are characterized by short S-S (340-370 pm) and larger Ni-Ni distances (788.2 pm[23a], 585.1 pm[23b]). The structure of $Et_4N[Ni(dmit)_2]$ which is similar to that of **11** consists of alternating stacks (Ni-Ni 416.3 pm and 423.3 pm, S-S 366.0 pm and 371.1 pm).[23c] Independant of the cations in $R_4N[Ni(DDDT)_2]$ complexes (R = Bu,[11b,c] Et,[11a], Me[11d]) well separated anions (Ni-Ni distances > 800 pm) and short S-S contacts (350 pm - 400 pm) only between peripheral sulfur atoms are found. Obviously, the strongly dipolar $(NC)_2C{=}C_{ring}$ moieties in **11** increase the ability of planar dithiolene metal complexes to form aggregated structures.

Magnetic measurements

The small intermolecular distances in **11** make a magnetic ordering of the anions (S = 1/2) likely. The plot of the molar susceptibiliy χ_{exp} versus temperature T (Figure 3) shows a typical deviation from simple paramagnetic behaviour indicative of an antiferromagnetic coupling within the dimers (cf., theoretical treatment of magnetically coupled dimers[24]). There are two contributions to the paramagnetism. At very low temperature Curie type defects dominate the magnetic susceptibility, whereas at higher temperatures the magnetic susceptibility reflects the behaviour of a singlet-triplet system with the singlet as the low lying state. The room temperature value of μ_{eff} = 1.71 μ_B per molecule corresponds with the calculated moment μ = 1.73 μ_B per molecule for an unpaired electron.

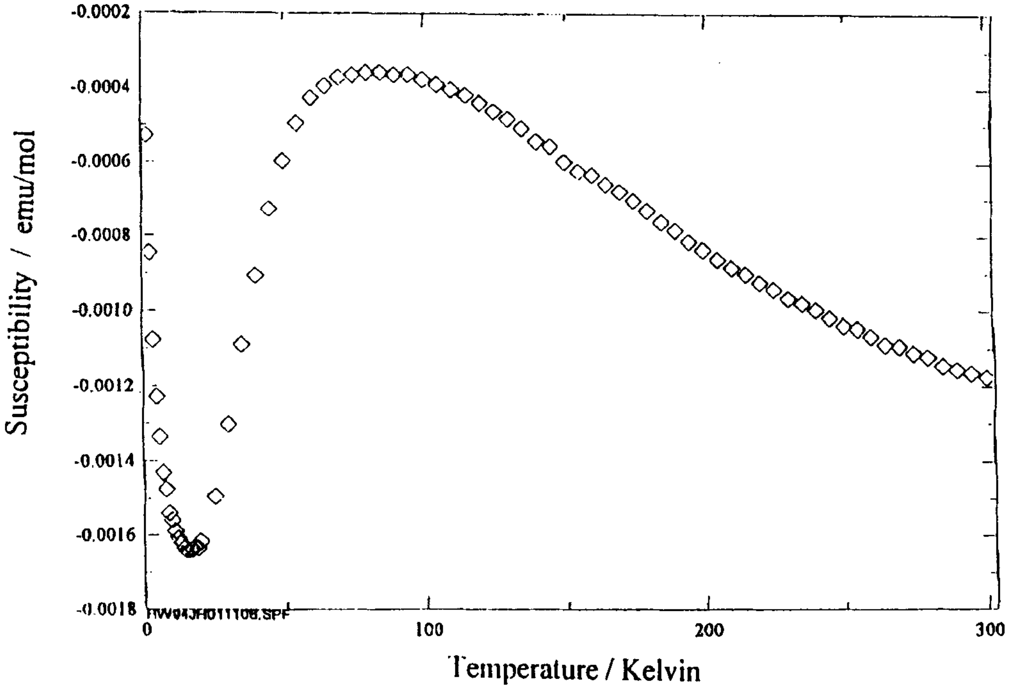


FIGURE 3 Temperature dependence of the magnetic susceptibility $\chi(T)$ of **11** as determined with a SQUID magnetometer

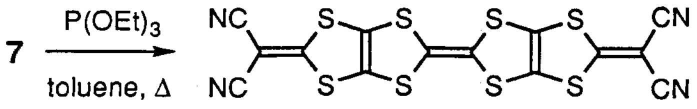
Although $[Ni(mnt)_2]^-$ salts are known to crystallize in alternating stacks and exhibit strong antiferromagnetic coupling, the structurally more related $[Ni(dmit)_2]^-$ and $[Ni(DDDT)_2]^-$ complexes do not show magnetic ordering phenomena of a size comparable to that of **11**.The dianionic Cu dithiolene complex **8b** is an almost perfect paramagnet. The molar susceptibility of **8b** obeys the Curie-Weiss law $\chi_{mol} = C\,(T - \Theta)^{-1}$ with Θ = 2.1 ± 3.0 K. In the temperature range from 300 to 13 K a constant magnetic moment μ_{eff} = 1.75 ± 0.01 μ_B per molecule is observed.

In order to increase magnetic interactions in compounds derived from $[Ni(DCDD)_2]^-$ the salt **12** containing the open-shell ferricinium cation was prepared by reacting a solution of **11** in acetonitrile with a solution of $[Fc^*]^+$ $[BF_4]^-$ [8a] (Fc^* = decamethylferrocene). The IR spectrum of **12** shows typical bands of the $[Ni(DCDD)_2]^-$ anion (ν_{CN} = 2203 cm^{-1}, $\nu_{C=C}$ = 1442 cm^{-1}).The low solubility of **12** did not allow the growth of single crystals.

Preliminary magnetic measurements with a Faraday balance show considerable deviations from the Curie-Weiss law below 120 K whereas above 120 K it is obeyed with $\Theta = -131 \pm 4$ K indicative of strong antiferromagnetic interactions between the radical ions. The temperature dependence of the magnetic moment μ_{eff} supports this view. Starting from $\mu_{eff} = 2.88\ \mu_B$ at room temperature the moment decreases upon cooling. Below 27 K, however, an increase of μ_{eff} is observed (a similar behaviour has been predicted for an alternating chain of antiferomagnetically coupled spins[25]). Lack of structural data precludes a detailed analysis of the magnetic properties of **12** at the moment. The corresponding dmit complex $Fc^*[Ni(dmit)_2]$ has been shown to behave completely different.[7a] Our own measurements confirm the reported data which characterize this compound as a typical paramagnet in the temperature range between 300 and 40 K ($\Theta = -0.3 \pm 3.9$ K) with signs of ferromagnetic interactions below 40 K.

Tetrathiafulvalenes

The reaction of **6** with triethyl phosphite in boiling toluene yields the brick-red tetrathiafulvalene derivative **13**. In accord with the symmetrical structure of **13** the IR spectrum contains only two strong bands (ν_{CN}) = 2211 cm^{-1}, $\nu_{C=C}$ = 1436 cm^{-1}). The mass spectrum shows the parent ion with 74 % relative intensity. **13** belongs to a new group of TTF derivatives containing fused 1,3-dithiole-2-ylidene moieties. Alkyl derivatives of this type have recently been described as donor molecules in electrical conducting CT complexes.[26] Due to the extremely low solubility of **13** the electrochemical properties in solution could not be studied up to now.



13

EXPERIMENTAL

2-Thioxo-1,3-dithiole-4,5-diyl-bis(thio-S-benzoate)[5] (**3**), oxiranetetracarbonitrile[18b] (**5**), 5-thioxo-1,3-dithiolo[4,5-d]-1,3-dithiole-2-one,[15] and decamethylferrocenium tetrafluoroborate[8a] [Fc*][BF_4] were prepared according to literature procedures; other reagents were commercially available. Solvents were purified by standard procedures and degassed. All experiments were carried out under a nitrogen atmosphere. Analyses were performed by Mikroanalytisches Labor of the Institut für Organische Chemie der Universität München. - IR: Bruker IFS 45. - UV/VIS/NIR: Zeiss DMR 10, Zeiss PQM II. - NMR: Varian VXR 400 S, internal standard TMS. - MS: Finnigan MAT 90.

Susceptibility measurements: Magnetic susceptibility data were measured with a SQUID magnetometer (magnetic flux densities up to 55 kG in the temperature range 2 to 300 K) and a Faraday balance (temperature range from 8 to 300 K at magnetic fields from 0.1 T to 0.9 T). Diamagnetic corrections were taken from the literature (Fc*[8a]) or estimated using Pascal constants.[27]

2-Dicyanomethylene-1,3-dithiole-4,5-diyl-bis(thio-S-benzoate) (6)

2.02 g (5.00 mmol) of **3** were dissolved in 90 ml of toluene. The solution was cooled to 0 °C after a drop of water had been added. Then a solution of 0.74 g (5.00 mmol) of **5** in 5 ml acetonitrile was added quickly. The mixture was allowed to warm to 20 °C and stirred for 18 h. The resulting precipitate was collected by filtration, washed with ether, and recrystallized from ethyl acetate. Yield 1.34 g (61%), pale yellow needles, m.p. 171 °C. IR(KBr): ν = 2215 cm^{-1} (CN), 1691 (CO), 1447 (C=C), 1206, 886, 677. - UV ($CHCl_3$): λ_{max} (lg ε) = 251 nm (4.581), 270 (4.382) sh, 347 (4.253) sh, 362 (4.394), 371 (4.390). - ^1H NMR ($CDCl_3$): δ = 7.53 (t, ^3J = 7.5 Hz, 4 H, H-3'), 7.70 (t, ^3J = 7.5 Hz, 2 H, H-4'), 7.95 (d, ^3J = 7.5 Hz, 4 H, H-2'). - ^{13}C NMR ($CDCl_3$): δ = 64.39 (s, $C(CN)_2$), 112.59 (s, CN), 128.12 (d, C-2'/6'), 129.32 (d, C-3'/5'), 130.51 (s, C-4/5), 134.40 (s, C-1'), 135.33 (d, C-4'), 180.76 (s, C-2), 184.57 (s, C=O). - MS (70 eV), m/z (%): 438 (2) [$M^{+\cdot}$], 105 (100) [$PhCO^+$]. $C_{20}H_{10}N_2O_2S_4$ Calcd. C 54.78 H 2.30 N 6.39 S 29.24 (438.6) Found C 54.59 H 2.29 N 6.39 S 29.34.

2-(5-Oxo-1,3-dithiolo[4,5-d]-1,3-dithiole-2-ylidene)-malononitrile (7)

1.12 g (5.00 mmol) of 5-thioxo-1,3-dithiolo[4,5-d]-1,3-dithiole-2-one[15] were dissolved in 200 ml of toluene. The solution was filtered and cooled to 0 °C after a drop of water had been added. Then a solution of 0.74 g (5.00 mmol) of oxiranetetracarbonitrile (**5**) in 5 ml of acetonitrile was added quickly. The mixture was allowed to warm to 20 °C and stirred for 2 d. The resulting precipitate was collected by filtration, washed with ether, and recrystallized from acetic acid. Yield 0.37 g (29%), pale yellow needles, m.p. 214 °C. IR(KBr): ν = 2215 cm^{-1} (CN), 1696 (C=O), 1442 (C=C). - UV (DMF): λ_{max} (lg ε) = 331 nm (3.950), 394 (4.194), 478 (3.281). - MS (70 eV), m/z (%): 256 (71) [$M^{+\cdot}$], 228 (100) [$M^{+\cdot}$ – CO], 152 (43) [$C_2S_4^{+\cdot}$]. $C_7N_2OS_4$ Calcd. C 32.79 H 0.00 N 10.93 S 50.04 (256.4), Found C 32.98 H 0.29 N 10.73 S 50.04.

Bis(tetrabutylammonium)-[bis{2-(1,3-dithiole-2-ylidene)-malononitrile-4',5'-dithiolato}nickelate(II)] (**8a**). General Procedure for **8**.

To a suspension of 0.54 g (1.20 mmol) of **7** in 5 ml of methanol 1.23 ml of a 2 M solution of sodium methanolate in methanol were added. The resulting deep violet solution was stirred for 30 min. Then 0.36 g (1.12 mmol) of tetrabutylammonium bromide were added, followed by adding dropwise a solution of 0.14 g (0.55 mmol) of nickel(II) acetate tetrahydrate in 6 ml of methanol. After stirring for 1 h at room temp. a dark green precipitate was collected by filtration and washed with methanol. Further purification was achieved by dissolving the product in acetone, adding the same volume of isopropanol, and cooling overnight. Yield 0.28 g (47%), dark green needles, m.p. 233 °C. IR(KBr): ν = 2962 cm^{-1} (CH), 2198 (CN), 1401 (C=C), 1390. - UV ($CHCl_3$): λ_{max} (lg ε) = 292 nm (4.411), 313 (4.432), 406 (4.383), 576 (4.024). - UV (acetone): λ_{max} (lg ε) = 420 nm (4.367), 624 (4.019). - UV (MeOH): λ_{max} (qual.) = 290 nm, 312, 400, 565. - ^{13}C NMR ([D_6]DMSO): δ = 13.40 (q, CH_3), 19.14 (t, CH_2-CH_3), 23.04 (t, CH_2-CH_2-CH_2), 55.95 (s, $C(CN)_2$), 57.55 (t, N-CH_2), 114.46 (s, CN), 132.49 (s, C-4'/5'), 189.69 (s, C-2'). $C_{44}H_{72}N_6NiS_8$ Calcd. C 52.83 H 7.26 N 8.40 S 25.65 (1000.3) Found C 52.95 H 7.26 N 8.30 S 25.62.

Bis(tetrabutylammonium)-[bis{2-(1,3-dithiole-2-ylidene)-malononitrile-4',5'-dithiolato}cuprate(II)] (**8b**)

With 0.11 g (0.55 mmol) of copper(II)-acetate-hydrate in 10 ml of methanol (16 h). Yield 0.37 g (60%), red-brown platelets, m.p. 205 °C. IR(KBr): ν = 2961 cm^{-1} (CH), 2198 (CN), 1400 (C=C) sh, 1386. - UV ($CHCl_3$): λ_{max} (lg ε) = 309 nm (4.414), 398 (4.080), 518 (4.332). - UV (acetone): λ_{max} (qual.) = 296 nm, 551. $C_{44}H_{72}CuN_6S_8$ Calcd. C 52.57 H 7.22 N 8.36 S 25.52 (1005.1) Found C 52.49 H 7.43 N 8.16 S 25.43.

Bis(tetrabutylammonium)-[bis{2-(1,3-dithiole-2-ylidene)-malononitrile-4',5'-dithiolato}zincate(II)] (**8c**)

With 1.21 g (2.76 mmol) of **7** in 25 ml of methanol , 2.80 ml of a 2 M solution of sodium methanolate in methanol, 0.97 g (3.01 mmol) of tetrabutylammonium bromide in 5 ml of methanol, and a solution of 0.18 g (1.32 mmol) of zinc(II)-chloride and 2 ml of concentrated ammonia in 8 ml of methanol. After stirring for 18 h at room temp. the mixture was filtered. 10 ml of isopropanol were added to the filtrate and the resulting solution was evaporated to half of its volume. Upon cooling overnight a red product crystallized. By dissolving it in a small amont of acetone, adding the same volume of isopropanol, and cooling a pure sample was prepared. Yield 0.56 g (40%), wine-red cuboids, m.p. 188 °C. IR(KBr): ν = 2970 cm^{-1} (CH), 2200 (CN), 1380. - UV ($CHCl_3$): λ_{max} (lg ε) = 312 nm (4.650), 496 (4.442). - UV (acetone): λ_{max} (lg ε) = 517 nm (4.291). - ^{13}C NMR ($CDCl_3$): δ = 13.40 (CH_3), 19.15 (CH_2-CH_3), 23.01 (CH_2-CH_2-CH_2), 54.90 ($C(CN)_2$), 57.51 (N-CH_2), 114.79 (CN), 129.01 (C-4/5), 177.78 (C-2). $C_{44}H_{72}N_6S_8Zn$ Calcd. N 8.35 S 25.52 (1006.9) Found. N 8.24 S 25.48.

[1,2-Bis(diphenylphosphino)ethane]nickel(II)-[2-(1,3-dithiole-2-ylidene)-malononitrile-4',5'-dithiolate] (**9**)

To a suspension of 0.44 g (1.00 mmol) of **7** in 20 ml of methanol was added 1.00 ml of a 2 M solution of sodium methanolate in methanol. The resulting deep violet solution was stirred for 30 min. After adding a suspension of 0.53 g (1.00 mmol) of [1,2-bis(diphenylphosphino)ethane]nickel(II)-chloride in 20 ml of methanol the mixture was heated for 6 h under reflux. A greenish precipitate was collected by filtration and washed with water, methanol and ether. Further purification was achieved by dissolving the product in chloroform, filtering the solution, and slowly adding pentane. Yield 0.50 g (73%), green-yellow needles, m.p. > 280 °C. IR(KBr): ν = 3052 cm^{-1} (CH), 2938 (CH), 2198 (CN), 1618, 1435 (C=C). - UV ($CHCl_3$): λ_{max} (lg ε) = 280 nm (4.558), 304 (4.513), 446 (4.323), 655 (2.618). - MS (70 eV), m/z (%): 716 (2) [$M^{+\cdot}$ + MeOH], 684 (62) [$M^{+\cdot}$], 428 (29), 183 (100) [$(C_6H_4)_2P^+$]. $C_{32}H_{24}N_2NiP_2S_4 \times MeOH$ Calcd. C 55.24 H 3.93 N 3.90 S 17.87 (685.4) Found. C 55.26 H 3.94 N 4.07 S 17.80.

Tetrabutylammonium-[bis{2-(1,3-dithiole-2-ylidene)-malononitrile-4',5'-dithiolato}nickelate(III)] (**11**)

A filtered solution of 0.21 g (0.80 mol) iodine und 0.35 g (2.08 mmol) potassium iodide in 55 ml of acetone was added dropwise to a solution of 1.63 g

(1.63 mmol) **8a** in 150 ml of acetone. After stirring for 1 h at room temp. the precipitate was collected by filtration and washed with methanol and ether. Yield 0.88 g (71%), dark olive-green needles, m.p. 257 °C. IR(KBr): ν = 2963 cm^{-1} (CH), 2203 (CN), 1442 (C=C), 1363. - UV (acetone): λ_{max} (lg ε) = 385 nm (4.209), 425 (4.461), 447 (4.340) sh, 573 (3.634), 590 (3.603) sh, 1135 (4.344). $C_{28}H_{36}N_5NiS_8$ Calcd. C 44.37 H 4.79 N 9.24 S 33.85 (757.8) Found C 44.62 H 4.96 N 9.27 S 33.75.

Decamethylferrocenium-[bis{2-(1,3-dithiole-2-ylidene)-malononitrile-4',5'-dithiolato}nickelate(III)] (**12**)

A solution of 0.11 g (0.27 mmol) of Fc*[BF$_4$]^{8a} in 100 ml of acetonitrile was added dropwise to a stirred solution of 0.20 g (0.27 mmol) of **11** in 100 ml of acetonitrile. After standing overnight the precipitate was isolated by filtration and washed with acetonitrile. Yield 0.08 g (35%), olive-grey microcrystals, dec. > 240 °C. IR(KBr): ν = 2962 cm^{-1} (CHal), 2874, 2203 (CN), 1442 (C=C), 1388, 1363, 1266 br. - MS (70 eV), m/z (%): 326 (100) [Fe(C$_5$Me$_5$)$^+$]. $C_{32}H_{30}FeN_4NiS_8 \times 2\ H_2O$ Calcd. C 43.79 H 3.90 N 6.38 (841.6) Found C 43.47 H 3.63 N 6.79.

2-[5-(5-Dicyanomethylene-1,3-dithiolo[4,5-d]-1,3-dithiole-2-ylidene)-1,3-dithiolo[4,5-d]-1,3-dithiole-2-ylidene]-malononitrile (**13**)

1.50 g (5.85 mmol) of **6** and 5.14 ml (30 mmol) of freshly distilled triethyl phosphite were heated under reflux in 140 ml of toluene for 18 h. The red precipitate was isolated by filtration, washed with toluene, ether and boiling chloroform. Yield 0.59 g (42%), brick-red powder, m.p. > 310 °C. IR(KBr): ν = 2211 cm^{-1} (CN), 1436 (C=C). - UV (1,2,4-trichlorobenzene): λ_{max} = 358 nm sh, 371, 395 sh. - MS (70 eV), m/z (%): 480 (74) [M$^+$], 296 (62), 76 (100) [CS$_2^+$]. $C_{14}N_4S_8$ Calcd. C 34.98 H 0.00 N 11.66 S 53.37 (480.7) Found. C 35.24 H 0.36 N 11.42 S 53.36.

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REFERENCES

1. a) J. A. McCleverty, Prog. Inorg. Chem. 10, 49 (1969); b) R. P. Burns, C. A. McAuliffe, Adv. Inorg. Chem. Radiochem. 22, 303 (1979); c) U. T. Müller-Westerhoff, B. Vance in Comprehensive Coordination Chemistry (Ed.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Vol. 2, Pergamon Press, Oxford, 1987, p. 595.
2. S. Alvarez, R. Vicente, R. Hoffmann, J. Am. Chem. Soc. 107, 6253 (1985).
3. a) P. I. Clemenson, Coord. Chem. Rev. 106, 171 (1990); b) P. Cassoux, L. V. Interrante, Comments Inorg. Chem. 12, 47 (1991).
4. P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, A. E. Underhill, Coord. Chem. Rev. 110, 115 (1991).
5. G. Steimecke, H.-J. Sieler, R. Kirmse, E.Hoyer, Phosph. Sulfur 7, 49 (1979).
6. N. Venkatalashmi, B. Varghese, S. Lalitha, R. F. X. Williams, P. T. Manoharan, J. Am. Chem. Soc. 111, 5748 (1989).
7. a) W. E Broderick, J. A. Thompson, M. R. Godfrey, M. Sabat, B. M. Hoffman, J. Am. Chem. Soc. 111, 7656 (1989); b) J. S. Miller, J. C. Calabrese, A. J. Epstein, Inorg. Chem. 28, 4230 (1989); c) W. E Broderick, J. A. Thompson, B. M. Hoffman, Inorg. Chem. 30, 2958 (1991).
8. a) J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff, A. J. Epstein, J. Am. Chem. Soc. 109, 769 (1987); b) J. S. Miller, A. J. Epstein, W. M. Reiff, Chem. Rev. 88, 201 (1988); c) J. S. Miller, Science 252, 1415 (1991); d) J. S. Miller, J. C. Callabrese, R. S. McLean, A. J. Epstein, Adv. Mater. 4, 498 (1992).
9. a) A. E. Underhill, J. Hawkins, J. Chem. Soc., Chem. Commun. 1990, 1593; b) O. A. Dyachenko, S. V. Konovalikhim, G. V. Shilov, E. B. Yagubskii, C. Faulmann, P. Cassoux, J. Chem. Soc., Chem. Commun. 1993, 508.
10. a) G. C. Papavassiliou, G. A. Mousdis, V. Grionis, J. S. Zambounis, S. Y. Yiannopoulos, Z. Naturforsch. 42b, 1050 (1987).; b) D. Mentzafos, A. Terzis, Acta Cryst. C45, 818 (1989).
11. a) R. D. Bereman, C. T. Vance, J. Bardner, W. E. Hatfield, J. H. Helms, Inorg. Chem. 24, 2905 (1985); b) A. J. Schultz, H. H. Wang, L. C. Soderholm, T. L. Sifter, J. M. Williams, K. Bechgaard, M.-H. Whangbo, Inorg. Chem. 26, 3757 (1987); c) J. H. Welch, R. D. Bereman, P. Singh, Inorg. Chem. 27, 3680 (1988); d) J. H. Welch, R. D. Bereman, P. Singh, D. Haase, W. E. Hatfield, M. L. Kirk, Inorg. Chim. Acta 162, 89 (1989).
12. a) R. Vicente, J. Ribas, P. Cassoux, N. J. Chem. 8, 653 (1984); b) R.-M. Olk, W. Dietsch, K. Köhler, R. Kirmse, J. Reinhold, E. Hoyer, Z. anorg. allg. Chem. 567, 131 (1988); c) S. Ikegawa, T. Nogami, Y. Shirota, Bull. Chem. Soc. Jpn. 63, 262 (1990).
13. a) J. P. Cornelissen, D. Reefman, J. G. Haasnoot, L. Spek, J. Reedijk, Recl. Trav. Chim. Pays-Bas 110, 345 (1991); b) H. Poleschner, R. Radeglia, J. Fuchs, J. Organomet. Chem. 427, 213 (1992); c) R.-M. Olk, B. Olk, J. Rohloff, J. Reinhold, J. Sieler, K. Trübenbach, R. Kirmse, E. Hoyer, Z. anorg. allg. Chem. 609, 103 (1992).
14. a) W. J. Middleton, V. A. Engelhardt, J. Am. Chem. Soc. 80, 2788 (1958); b) K. Wallenfels, K. Friedrich, J. Rieser, W. Ertel, H. K. Thieme, Angew. Chem. 88, 311 (1976); Angew. Chem. Int. Ed. Engl. 15, 299 (1976).
15. a) H. Poleschner, W. John, F. Hoppe und E. Fanghänel, J. prakt. Chem. 325, 957 (1983); b) U. Pelzer, Ph. D. Thesis, Universität München, 1990.

16. a) R. Gompper, E. Kutter, Chem. Ber. 98, 1365 (1965); b) K. Ohta, H. Hasebe, H. Ema, T. Fujimoto, I. Yamamoto, J. Chem. Soc., Chem. Commun. 1989, 1610.
17. a) U. Pelzer, Ph. D. Thesis, Universität München, 1990; b) J.-G. Hansel, Ph. D. Thesis, Universität München, 1993.
18. a) W. J. Linn, J. Am. Chem. Soc. 87, 3651 (1965); b) W. J. Linn in Organic Syntheses (Ed.: H. E. Baumgarten), Coll. Vol. 5, John Wiley & Sons, New York, 1973, p. 1007.
19. a) A. Rouessac, J. Vialle, Bull. Soc. Chim. Fr. 5, 2054 (1968); b) W. J. Linn, E. Ciganek, J. Org. Chem. 34, 2146 (1969); c) J. W. Lown, K. Matsumoto, Can. J. Chem. 50, 534 (1972); d) Y. Tominaga, Y. Matsuoka, Y. Uchimura, H. Komiya, M. Hirayama, S. Kohra, A. Hosomi, J. Heterocycl. Chem. 27, 647 (1990).
20. C. Reichhardt, E. Harbusch-Görnert, Liebigs Ann. Chem. 1983, 721.
21. U. T. Müller-Westerhoff, B. Vance, D. I. Yoon, Tetrahedron 47, 909 (1991).
22. Crystal structure determination: Enraf Nonius diffractometer, Mo-K_α radiation, $\lambda = 71.069$ pm, $T = 296$ K, $C_{28}H_{36}N_5NiS_8$, $M_r = 757.8$, crystal size $0.13 \times 0.23 \times 0.53$ mm^3, triclinic, space group $P\bar{1}$, $a = 975.1(2)$, $b = 1350.4(5)$, $c = 1392.5(5)$ pm, $\alpha = 99.58(2)$, $\beta = 100.96(2)$, $\gamma = 94.41(2)$ °, $V = 1.7640$ nm^3, $Z = 2$, $\rho_{calc} = 1.427$ g cm^{-1}, $\mu = 10.337$ cm^{-1}, data collec tion: ω-scan $0.50 + 0.30 \tan \Theta$, reflexions ±h, ±k, +l, $2\Theta_{max} = 45°$, number of reflexions 4986, independent reflexions 4747, observed reflexions $I > 3\sigma(I)$ 3970, parameters 379. Structure solution SHELXS-86, refinement MolEN, $w = 1/\sigma^2(F_o)$, $R = 0.0299$, $R_w = 0.0466$, residual electron density +0.440/-0.074 e pm^{-3} 10^6. Supplementary material on the X-ray structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-58707, the names of the authors and the journal citation.
23. a) O. Lindqvist, L. Andersen, J. Sieler, G. Steimecke, E. Hoyer, Acta Chem. Scand. A36, 855 (1982); b) D. Mentzafos, A. Hountas, A. Terzis, Acta Cryst. C44, 1550 (1988); c) L. R. Groenveld, B. Schuller, G. J. Kramer, J. G. Haasnoot, J. Reedijk, Rec. Trav. Chim. Pay-Bas 105, 507 (1986).
24. O. Kahn, Angew. Chem. 97, 837 (1985); Angew. Chem. Int. Ed. Engl. 24, 799 (1985).
25. M. Verdaguer, M. Julve, A. Michalowicz, O. Kahn, Inorg. Chem. 22, 2624 (1983).
26. a) Y. Misaki, H. Nishikawa, K. Kawakami, T. Uehara, T. Yamabe, Tetrahedron Lett. 33, 4321 (1992); b) Y. Misaki, H. Nishikawa, H. Fujiwara, K. Kawakami, T. Yamabe, H. Yamochi, G. Saito, J. Chem. Soc., Chem. Commun. 1992, 1408.
27. E. König, G. König in Landoldt-Börnstein (Neue Serie), Bd. 12 (ED.: K.-H. Hellwege, A. M. Hellwege), Springer, Berlin, Heidelberg, New York, 1984, p. 29.