

**Ferromagnets Based on Polymeric 2,3,6,7-Tetrachloronaphthalene-1,4,5,8-tetrathiolato Nickel and Cobalt Complexes****E. Fanghänel and A. Ullrich**

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*Dedicated to Prof. Dr. Dr. h.c. mult. F. Aisinger on the Occasion of his 90th Birthday*

**Abstract.** The polymeric nickel complexes **3**, **5**, **7**, **8** and cobalt complexes **4**, **6** were synthesized from the bis(tetrabutylammonium) 2,3,6,7-tetrachloronaphthalene-1,5-dithiol-4,6-dithiolate (**2**) or the tetrathiolate **1** and the corresponding metal ions ( $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ ), using a large excess of tetrabutylammonium bromide for introducing  $\text{NBu}_4^+$  as counter ion. The diamagnetic nickel coordination polymer **3** was oxidized by iodine to the paramagnetic complex **5**. By exchange of the  $\text{NBu}_4^+$  ion by  $\text{Ni}^{2+}$  and the tetrathiafulvalenium ion, respectively, the complexes **7** and **8** are obtained.

The coordination polymer **7** was characterized as ferromagnetic beneath 20 K by investigating the temperature dependence of the magnetic susceptibility and the magnetization behavior. A coercive field of 1200 Oe was determined from the hysteresis loop of **7** at 4.4 K.

The measured heat capacity of **7** in dependence on the temperature is in good accordance with a ferromagnetic spin ordering below 20 K. Magnetic properties comparable with those of **7** were determined for the complexes **4** and **8**.

The extensive use of conventional ferromagnetics has strongly stimulated investigations to synthesize ferromagnetics based on organic and coordination compounds. The advantage of materials based on these molecular magnets might be their synthesis by using common organic methods at low temperature, the ease of fabrication and their tailor made properties, in particular concerning the combination of optical and magnetic properties for applications in new technologies [1].

The research in this field of molecular magnets has had interesting results. Ferromagnetic behavior was observed in pure organic materials such as the 2-(4-nitrophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide ( $\beta$ -*p*- $\text{NO}_2\text{C}_6\text{H}_4\text{NIT}$ ) [2] at  $T_C = 0,6$  K for the first time. Other nitroxides also exhibit ferromagnetic properties, e.g. the 1,3,5,7-tetramethyl-2,6-diazaadamantane-*N,N'*-dioxyl ( $T_C = 1.48$  K [3]).

Besides organic radicals metal compounds are hopeful systems for ferro- or ferrimagnetic spin ordering. The CT-salt formed by the reaction of decamethylferrocene

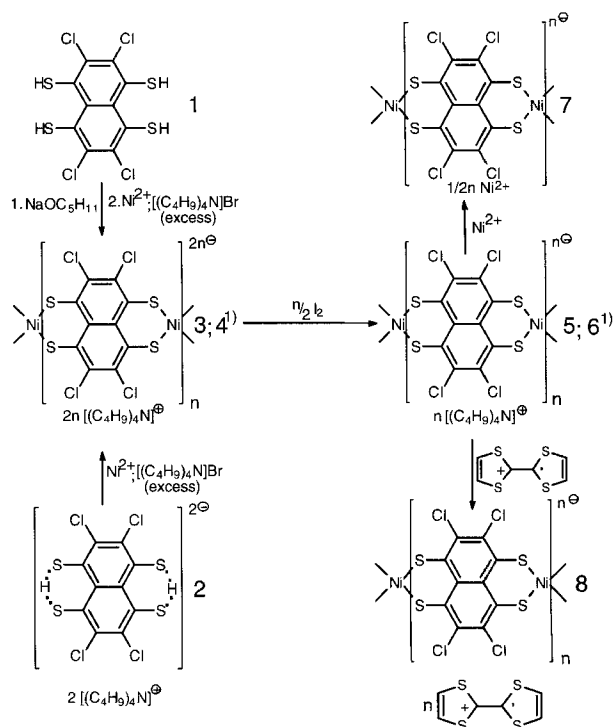
with tetracyanoethylene ( $[\text{Fe}^{\text{III}}(\text{C}_5\text{Me}_5)_2]^+ [\text{TCNE}]^-$ ;  $T_C = 4.8$  K) was the first molecule-based magnet in this field [4]. Replacing iron with manganese or chromium and substitution of TCNE by other acceptors like 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) or 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) led also to a ferromagnetic behavior of the corresponding complexes [5]. The  $\text{MnCp}_2^*$  as donor and dithiolene complexes like  $\text{Pt}[\text{S}_2\text{C}_2(\text{CF}_3)_2]$  ( $T_C = 2.3$  K),  $\text{Pd}[\text{S}_2\text{C}_2(\text{CF}_3)_2]$  ( $T_C = 2.8$  K) or  $\text{Ni}[\text{S}_2\text{C}_2(\text{CF}_3)_2]$  ( $T_C = 2.4$  K) as acceptor led to metamagnetic behavior [6].

Furthermore, metal porphyrines are a class of compounds with well-characterized ferromagnetism, e.g. the *meso*-tetraphenylporphyrinatomanganese(III)-complex ( $[\text{MnTTP}]^+ [\text{TCNE}]^- \cdot 2\text{PhMe}$ ,  $T_C = 18$  K) [7]. Mixed *N,N'*-bis(2-carboxylphenyl)oxamidato-complexes of  $\text{Mn}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  ( $T_C = 14$  K) [8] or dithiooxalate complexes ( $\{\text{NPr}_4[\text{M}(\text{dto})_3]\}_x$ ;  $\text{dto} = \text{dithiooxalato}$ ;  $\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}$ ) and complexes of ethylenetetrathiolate [9] or dithiocarbamate (e.g.  $\text{Fe}^{\text{III}}\text{Cl}(\text{S}_2\text{CNET}_2)_2$ ;

$T_C = 2.46$  K) and analogous compounds are described as molecular magnets [10]. The "polymer" and extremely air-sensitive vanadium-TCNE-complex  $V(\text{TCNE})_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$  has a  $T_C$  of about 400 K (extrapolated; the material decomposes above 350 K) [11] and represents the actual limit of temperature up to which "organic" molecular magnets are known.

With the aim to synthesize linear sulfur containing coordination polymers with ferromagnetic spin ordering we chose the 2,3,6,7-tetrachloronaphthalene-1,4,5,8-tetrathiolate [12] as ligand. Besides the bis(1,3-dithiolate) structure for complexing thiophilic metal ions, this ligand exhibits the extensive  $10\pi$ -system of the naphthalene ring and the chloro-substituents for supramolecular interactions (compare also [13]). The corresponding complexes should exist, analogously to dithiolenes complexes [14], in more than one oxidation state. This property reveals the possibility to influence the spin configuration *via* oxidation. There exist some examples of polymer complexes with the unsubstituted naphthalene-1,4,5,8-tetrathiol as ligand, synthesized by the reaction of naphtho[1,8-c,d; 4,5-c',d']-bis-[1,2]-dithiole with  $\text{Ni}(\text{CO})_4$  or  $\text{Co}_2(\text{CO})_8$  [15]. These complexes are very weakly soluble and have not been characterized as magnetic materials. As precursor for our investigations we have used the 3,4,7,8-tetrachloronaphtho[1,8-c,d; 5,4-c',d']-bis-[1,2]-dithiol [16], from which the corresponding tetrathiolate was obtained by reduction with sodium borohydride. Under inert conditions the isolation and characterization of the air-sensitive ligand was possible both as tetrathiole **1** and tetrabutylammonium-thiol-thiolate **2** [17]. In order to obtain metal complexes of cobalt and nickel which have at least some solubility in common organic solvents the complexation reaction was carried out by using a large excess of the lipophilic tetrabutylammonium ion as counter ion (ligand:  $\text{NBu}_4\text{Br}$  like 1:25, scheme 1).

Unfortunately, the synthesis of complexes containing exclusively this counter ion was not successful. Complexes with both the metal ion and the tetrabutylammonium ion as counter ion were formed, which are bad soluble. The mixed counter ions in the complexes might be one reason that we could not grow single crystals suitable for X-ray diffraction. To provide informations about the composition of the complexes they were characterized by elemental analysis (C, H, N, S, Cl) and by determination of the metal content using AAS. In this way the ratio of tetrabutylammonium and metal ion as counter ion could be fixed. The infrared spectra of all synthesized complexes show four strong bands in regions where the free 3,4,7,8-tetrachloronaphtho[1,8-cd; 5,4-c',d']-bis-[1,2]-dithiole absorbs intensively too ( $1523$  (s),  $1425$  (s),  $1296$  (s) and  $854$  (m)  $\text{cm}^{-1}$ ). Furthermore all complexes exhibit two new bands at  $1296$  (s) and  $970$  (m)  $\text{cm}^{-1}$  which are absent in the starting



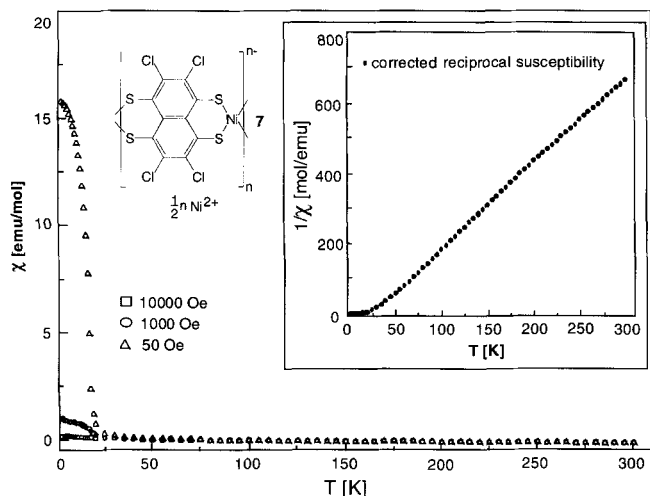
**Scheme 1** Synthesis of the polymeric metal complexes **3–8**. The formulas were simplified for clearness. For the exact composition see experimental part. <sup>1)</sup> Co instead Ni

material. The described i.r. absorptions are considered to be characteristic for linear sulfur containing coordination polymers [14]. Further strong bands are found in the complexes **3**, **4** and **5** at  $2962$ ,  $2933$  and  $2673$   $\text{cm}^{-1}$  resulting from the  $[\text{NBu}_4]^+$  ion. The exchange of this ion by other ions is clearly seen by the absence of this bands in the i.r. spectra of **7** and **8**.

Under exclusion of air the nickel complex **3** was obtained as a diamagnetic solid. This fact indicates the square planar coordination of the nickel atoms. By the oxidation of one complex unit with one equivalent of iodine the nickel complex **3** became paramagnetic (**5**). A diamagnetic compound **6** results by oxidizing the paramagnetic cobalt complex **4**. In the still weakly soluble complexes containing tetrabutylammonium ions we could exchange this bulky and magnetic inert counter ion by spin bearing organic cations, for instance the tetrathiafulvalenium ion ( $\text{TTF}^+$ ), or the nickel ion, which yielded the complexes **7** and **8**.

The ferromagnetic properties of the complex **7** are clearly to be seen in the plot of the magnetic susceptibility versus temperature (fig. 1).

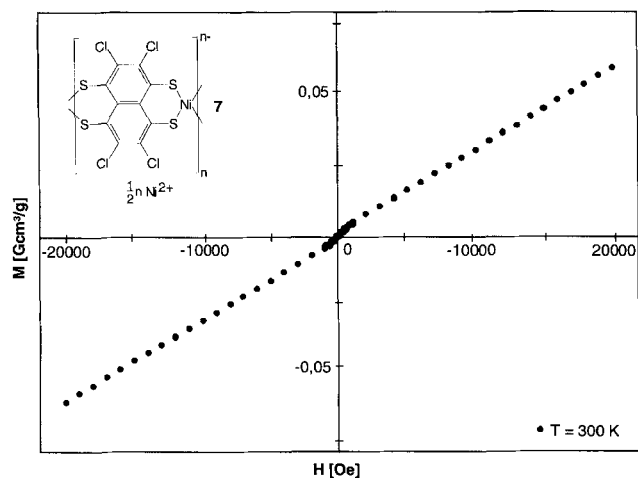
All magnetic data are referred to the molecular mass of one repetition unit of the polymeric complexes. In the range from 300 to 50 K the course for a paramagnetic compound was obtained. At temperatures below 20 K a strong dependence of the susceptibility on the applied magnetic field is obvious. Therefrom the de-



**Fig. 1** Temperature dependence of the susceptibility and corrected reciprocal susceptibility of the Ni/Ni-complex **7**

tected magnetic properties can be referred to a long-range magnetic coupling in the studied material. The plot of the reciprocal susceptibility versus temperature reveals a ferromagnetic spin ordering near 20 K (inset fig. 1) for the Ni/Ni-complex **7**.

Small quantities of ferromagnetic impurities have to be taken into consideration for a detailed characterization of the magnetic properties of the complexes. Using the hysteresis loop at room temperature the quantity of the ferromagnetic impurities could be approximated,



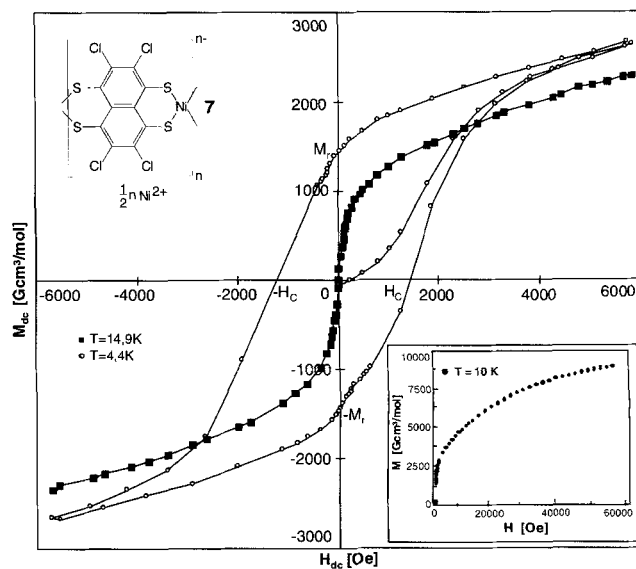
**Fig. 2** Field dependence of the magnetization of the Ni/Ni-complex **7** at room temperature

from the measured remanent magnetizations ( $M_r = 10^{-3}$  to  $10^{-2}$  Gcm<sup>3</sup>/g) (fig. 2). The value indicate very small amounts of ferromagnetic impurities (calculated as metallic iron) in the range of 1 to 6 ppm of the bulk

material. These impurities can not be responsible for the observed ferromagnetic spin ordering at low temperatures.

By correcting the magnetic susceptibility regarding these impurities the following equation was used:  $\chi_{\text{cor}} = \{M(10 \text{ kOe}) - M(1 \text{ kOe})\} / 9 \text{ kOe}$  (corrected susceptibility for **7**) from which the Curie–Weiss-temperature for the Ni/Ni-complex **7** was determined by linear correlation of  $1/\chi$  as function of  $T$  in the range from 300 to 50 K to  $\theta = (23 \pm 2) \text{ K}$ .

The complexes **6**, **7** and **8** exhibit the typical magnetization behavior (hysteresis) – resulting from the domain structure and energy differences for different magnetization directions – characteristic for ferromagnetic compounds (fig. 3).



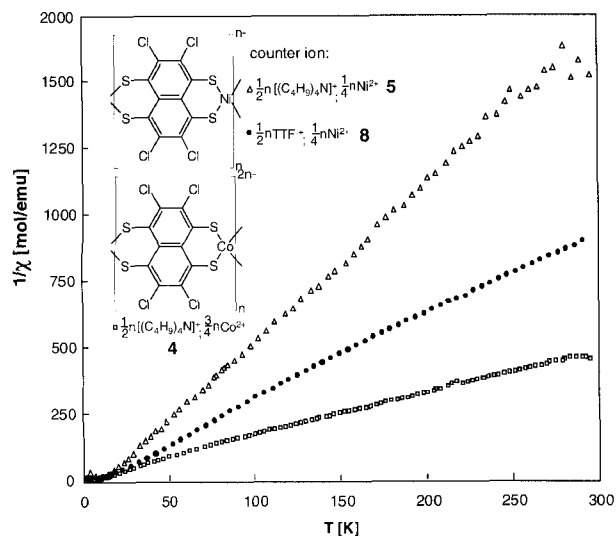
**Fig. 3** Hysteresis and saturation magnetization of the Ni/Ni-complex **7**

The segment of the hysteresis loop, having the highest gradient and broadest splitting, exhibits the part of the sample with ferromagnetic spin ordering. This part of the hysteresis loop of complex **7** at 4.4 K (fig. 3) extends to a magnetization of about  $M = 2040 \text{ Gcm}^3/\text{mol}$  (molecular mass of one repetition unit  $478.5 \text{ g/mol}$ ). This result corresponds to about 37% of the magnetization of one mol of spins with  $s = 1/2$  and  $g = 2$ . Using a stronger magnetic field (60 kOe), the saturation value of the magnetization of about  $8600 \text{ Gcm}^3/\text{mol}$  was estimated (inset fig. 3) and leads to 1.54 mol of spins with  $s = 1/2$  ( $g = 2$ ).

The heat capacity of the sample of the ferromagnetic Ni/Ni complex **7** shows also a characteristic anomaly within the temperature range (12–25 K) in which the spinordering occurs. The maximum of the deviation

corresponds satisfactorily to the ordering temperature found by the magnetic measurements [18].

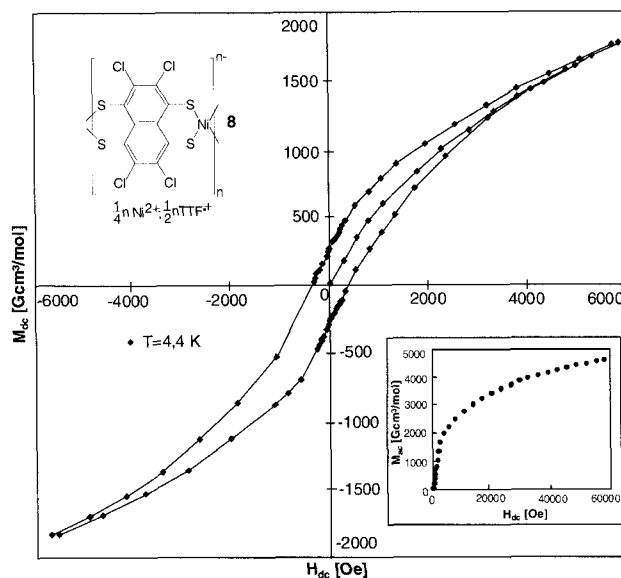
Magnetic properties which were similar to those of **7** were observed for both the nickel complex **8** containing the tetrathiafulvalenium radical cation as counter ion and for the cobalt complex **4** (fig. 4).



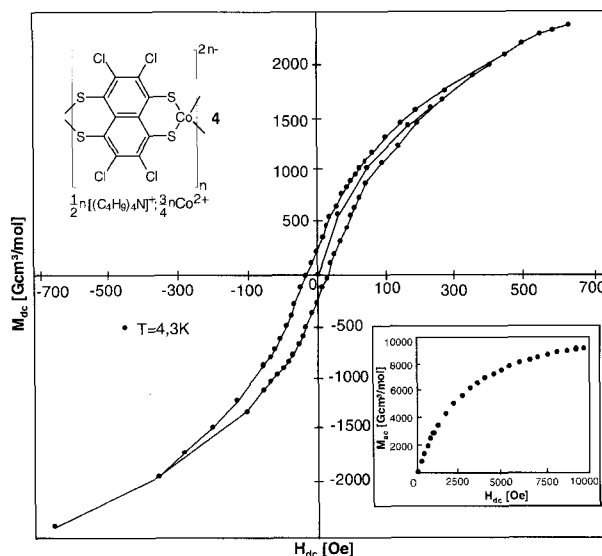
**Fig. 4** Temperature dependence of the reciprocal susceptibility of the Ni<sup>3+</sup>-[NBu<sub>4</sub>]<sup>+</sup>-complex **5**, the Ni/TTF-complex **8** and the Co-complex **4**

The  $T_C$  values for the Ni/TTF-complex **8** ( $T_C \approx 16$  K) and the Co-complex **4** ( $T_C \approx 14$  K) are lower than those for **7**. Both complexes exhibit a significant less splitting off of the hysteresis loop. For the Ni/Ni-system **7** we found a hard magnetic behavior by a coercive field of about 1200 Oe ( $T = 4.4$  K; fig. 3). For the Ni/TTF-complex **8**, the coercive field was determined to about 75 Oe ( $T = 4.5$  K) and the saturation magnetization at 60 kOe to 4960 Gcm<sup>3</sup>/mol (molecular mass of one repetition unit 565.75 g/mol; fig. 5). This value indicates 0.89 mol of spin ( $s = 1/2$ ;  $g = 2$ ). Also the ferromagnetic ordered part of the sample (about 1000 Gcm<sup>3</sup>/mol; 18% of the magnetization of one mol of spins with  $s = 1/2$  and  $g = 2$ ) is smaller than for **7** (both complexes are made from the same charge of the starting material **3**).

The Co-complex **4** exhibits a soft magnetic behavior like **8** by a coercive field of about 35 Oe ( $T = 4.3$  K; fig. 6). The saturation magnetization at strong magnetic field and the ferromagnetic ordered part of a sample of **4** are similar to the Ni/Ni-complex **7**. The saturation magnetization of **4** was determined to about 10000 Gcm<sup>3</sup>/mol (1.79 mol of spin;  $s = 1/2$ ;  $g = 2$ ) and the splitted part of the hysteresis loop extends to a magnetization of about 2000 Gcm<sup>3</sup>/mol (36% of the magnetization of one mol of spins with  $s = 1/2$  and  $g = 2$ ).



**Fig. 5** Hysteresis of the Ni/TTF-complex **8**



**Fig. 6** Hysteresis of the Co-complex **4**

The dependence of the reciprocal susceptibility  $1/\chi$  or the susceptibility  $\chi$ , respectively, of the nickel complex with the tetrabutylammonium ion as counter ion **5** on the temperature (fig. 4), indicates a magnetic spin coupling too ( $T_C = 10$  K), but we did not found a hysteresis effect.

Due to the bulky and spinless tetrabutylammonium ion the spin coupling in solid **5** is not so effective as in complexes with the smaller metal ions **4** (this complex contains only a small part of NBu<sub>4</sub><sup>+</sup>) and **7** (without NBu<sub>4</sub><sup>+</sup>) or **8** with the planar TTF-radical cation (in combination with a share of Ni<sup>2+</sup> ions). Obviously the counter ion influences the strength of the spin interaction.

In conclusion, it has been shown that we were able to synthesize coordination polymers on the base of a tetrafunctional sulfur containing ligand, which exhibit ferromagnetic properties at temperatures below 20 K. All the described compounds were synthesized and analyzed several times. Their magnetic properties were checked in several working groups. In this way we proved the reproducibility of our experimental results and could show that the described magnetic effects are characteristic for the new coordination polymers.

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## Experimental

The magnetic properties of the described compounds were investigated with a AC-susceptometer/DC-magnetometer (Lake Shore Model 7221; AC-susceptibility: frequency 375 Hz, magnetic field strength 3,75 Oe; DC-magnetization: magnetic field strength  $\pm 10000$  Oe) and a commercial SQUID magnetometer, respectively. IR spectra were recorded on a Philips PU 9426 FTIR spectrometer as KBr (Fluka Chemical Co.) pellets.

The 3,4,7,8-tetrachloro-naphtho[1,8-c,d; 5,4-c',d']-bis-[1,2]-dithiole [15], the 2,3,6,7-tetrachloronaphthalene-1,4,5,8-tetrathiol (**1**) [16] and the 2,3,6,7-tetrachloro-naphthalene-1,4,5,8-thiol-thiolate (**2**) [16] were synthesized as described in literature.

All steps of the synthesis of the metal complexes were carried out in an argon atmosphere

## Synthesis of the complexes

The tetra-*n*-butylammonium salt of 2,3,6,7-tetrachloronaphthalene-1,4,5,8-thiol-thiolate (**2**) (0,5 g; 0,57 mmol) was dissolved in 200 ml ethanol. (Tetrachloro-naphthalene-tetrathiol **1**, must be converted prior into the corresponding tetrathiolate with sodium amylate in ethanol.) 5 g (15 mmol) tetra-*n*-butylammonium bromide was added. To this solution the metal salt (0,35 mmol), dissolved in 100 ml ethanol, was added within 2 h. The mixture was stirred for 10 h and the black precipitate was filtered off. The product was washed with water, methanol and ether and dried under vacuum. The yield was about 90% (related to the amount of metal salt).

### *Ni*<sup>2+</sup>-[NBu<sub>4</sub>]<sup>+</sup>-complex **3**

(C<sub>10</sub>Cl<sub>4</sub>S<sub>4</sub>Ni)Ni<sub>0,5</sub> [N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>] (molecular mass of one repetition unit : 720.50 g/mol). Found (calcd.): C 44.97 (43,30), H 5.75 (4,99), N 1.99 (1,94), Cl 21.43 (19,71), S 17.88 (17,76), Ni 12.2 (12,30).<sup>1)</sup>

<sup>1)</sup> determined after destroying the complex with HNO<sub>3</sub>/HClO<sub>4</sub> by titration using EDTA and murexide indication.

### *Co*<sup>2+</sup>-[NBu<sub>4</sub>]<sup>+</sup>-complex **4**

(C<sub>10</sub>Cl<sub>4</sub>S<sub>4</sub>Co)Co<sub>0,75</sub> [N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>]<sub>0,5</sub> (molecular mass of one repetition unit : 614.25 g/mol). Found (calcd.): C 35.23 (35,16), H 2.71 (2,93), N 0.91 (1,13), Cl 25.30 (23,17), S 22.94 (20,83), Co 16.43 (16,81).

## Oxidation of the complexes with I<sub>2</sub>

40 mg (0.15 mmol) I<sub>2</sub>, dissolved in 50 ml ethanol, were added to the reaction mixture for synthesizing **3** (after stirring for 1 h). Then, the solution was stirred for 10 h. The precipitate was filtered off and washed with water, methanol and ether and dried under vacuum. The yield was nearly quantitative.

### *Ni*<sup>3+</sup>-[NBu<sub>4</sub>]<sup>+</sup>-complex **5**

(C<sub>10</sub>Cl<sub>4</sub>S<sub>4</sub>Ni)Ni<sub>0,25</sub> [N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>]<sub>0,5</sub> (molecular mass of one repetition unit: 584.75 g/mol). Found (calcd.): C 36.35 (36,94), H 3.40 (3,08), N 1.04 (1,19), Cl 23.90 (24,28), S 21.15 (21,89), Ni 13.1<sup>1)</sup> (12,62)

### *Co*<sup>3+</sup>-*Co*<sup>3+</sup>-complex **6**

(C<sub>10</sub>Cl<sub>4</sub>S<sub>4</sub>Co)Co<sub>0,33</sub> (molecular mass of one repetition unit: 468.74 g/mol). Found (calcd.): C 24.85 (25,62), H 0.41 (0), N 0.11 (0), Cl 29.90 (30,25), S 26.75 (27,36), Co 17.21 (16,76).

## Exchange of the counter ion of the nickel complex **5**

100 mg of the Ni<sup>2+</sup>-[NBu<sub>4</sub>]<sup>+</sup>-complex **5** were suspended in 30 ml acetonitrile and equivalent amounts of NiCl<sub>2</sub> · 6 H<sub>2</sub>O (resp. of (TTF)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>) dissolved in 50 ml acetonitrile were added. The mixture was stirred for 2 h. After this time the precipitate was filtered off and washed with water, acetonitrile and ether and dried under vacuum. The yield is nearly quantitative.

### *Ni*<sup>3+</sup>-*Ni*<sup>2+</sup>-complex **7**

(C<sub>10</sub>Cl<sub>4</sub>S<sub>4</sub>Ni)Ni<sub>0,5</sub> (molecular mass of one repetition unit: 478.50 g/mol). Found (calcd.): C 24.83 (25,08), H 0.05 (0), N 0.04 (0), Cl 29.81 (29,67), S 26.15 (26,75), Ni 18.79 (18,50)

### *Ni*<sup>3+</sup>-[TTF]<sup>+</sup>-complex **8**

(C<sub>10</sub>Cl<sub>4</sub>S<sub>4</sub>Ni)Ni<sub>0,25</sub> [C<sub>6</sub>H<sub>4</sub>S<sub>4</sub>]<sub>0,5</sub> (molecular mass of one repetition unit: 565.75 g/mol). Found (calcd.): C 29.23 (27,57), H 0.49 (0,35), N 0.14 (0), Cl 24.23 (25,09), S 31.86 (33,94), Ni 13.21 (13,05)

## References

- [1] a) J. S. Miller, A. J. Epstein, *Angew. Chem.* **106** (1994) 399  
b) D. Gatteschi, "Molecular Magnets : A Basis for New Material", *Adv. Mat.* **6** (1994) 635;  
c) O. Kahn, "Molecular Magnetism": VCH Publishers Inc. New York 1993
- [2] M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hoskoshi, M. Ishikawa, M. Takashi, M. Kinoshita, *Chem. Phys. Lett.* **186** (1991) 401
- [3] a) R. Chiarelli, A. Rassat, P. Rey, *J. Chem. Soc. Chem. Commun.* **1992**, 1081;  
b) R. Chiarelli, M. A. Novak, A. Rassat, J. L. Tholence, *Nature*, **363** (1993) 147
- [4] J. S. Miller, J. C. Calabrese, H. Rommelmann, S. Chit-

- tapeddi, J. H. Zhang, W. M. Reiff, A. J. Epstein, *J. Am. Chem. Soc.*, **109** (1987)769
- [5] a) G. A. Candela, L. Swartzendruber, J. S. Miller, M. J. Rice, *J. Am. Chem. Soc.*, **101** (1979) 2755;  
b) E. Gerbert, A. H. Reis, J. S. Miller, H. Rommelmann, A. J. Epstein, *J. Am. Chem. Soc.*, **104** (1982) 4403
- [6] W. E. Broderick, J. A. Thompson, B. M. Hoffman, *Inorg. Chem.*, **30** (1991) 2960
- [7] J. S. Miller, J. C. Calabrese, R. S. McLean, A. J. Epstein, *Adv. Mater.*, **4** (1992) 498
- [8] a) F. Nakatani, J. Y. Carriat, Y. Journaux, O. Kahn, F. Lloret, J. P. Renard, Y. Pei, J. Sletten, M. Verdaguer, *J. Am. Chem. Soc.*, **111** (1989) 5739;  
b) O. Kahn, Y. Pei, M. Verdaguer, J. P. Renard, J. Sletten, *J. Am. Chem.*, **110** (1988) 782;  
c) F. Nakatani, P. Bergerat, E. Codjovi, C. Mathoniere, Y. Pei, O. Kahn, *Inorg. Chem.*, **30** (1991) 3977
- [9] a) H. Okawa, M. Mitsumi, M. Ohaba, M. Kodera, N. Matsumoto, *Bull. Chem. Soc. Jpn.* **67** (1994) 2139;  
b) D. G. Xenikos, H. Müller, C. Jouan, A. Sulpice, J. L. Tholence, *Solid State Commun.* **102** (1997) 681
- [10] a) H. H. Wickman, A. M. Trozzolo, H. J. Williams, G. W. Hull, F. R. Merritt, *Phys. Rev.* **155** (1967) 563  
b) H. H. Wickman, *J. Chem. Phys.*, **56** (1972) 976;  
c) G. C. DeFotis, F. Palacio, C. J. O'Conner, S. N. Bhaatia, R. L. Carlin, *J. Am. Chem. Soc.*, **99** (1977) 8314;  
d) N. Araj, M. Sorai, H. Suga, S. Seki, *J. Phys. Chem. Solids*, **36** (1977) 1231
- [11] a) J. M. Manriquez, G. T. Yee, R. S. McLean, A. J. Epstein, J. S. Miller, *Science* **252** (1991) 1415;  
b) J. S. Miller, A. J. Epstein, *Mol. Cryst. Liq. Cryst.*, **233** (1993)133
- [12] a) E. Fanghänel, I. Alsleben, B. Gebler, A. Herrmann, R. Herrmann, T. Palmer, K. Strunk, A. Ullrich, K. Lüders, H. Mahdjour, Proceedings of the 17th International Symposium on the Organic Chemistry of Sulfur (ISOCS), Tsukuba, Japan, 1996, Phosphorus, Sulfur, Silicon, in press  
b) H. Möhwald, E. Dormann, E. Fanghänel, R. Gompfer, S. Hünig, K. Lüders, M. Schwoerer, Proceedings of the research project: "Polymere mit außergewöhnlichen Eigenschaften im Hinblick auf Ferromagnetismus" supported by the BASF/BMFT, 03 M 4067 6, Dec. 1996
- [13] G. R. Desiraju, *Angew. Chem.*, **107** (1995) 2541
- [14] J. A. McCleverty, *Progr. Inorg. Chem.*, **10** (1968) 49
- [15] Boon-Keng Teo, F. Wudl, J. J. Hauser, A. Kruger, *J. Am. Chem. Soc.*, **99** (1977) 4862
- [16] E. Klingsberg, *Tetrahedron*, **28** (1972) 963
- [17] E. Fanghänel, J. Bierwisch, K. Strunk and A. Ullrich, *Sulfur Letters*, **18** (3), (1995) 129
- [18] Personal information given by Prof. E. Dormann, Karlsruhe.

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