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# Ferromagnetic Ordering in Bis(benzene)chromium(+) Bis(4,5-dimethoxybenzene-1,2-dithiolato)nickel(–)

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The compound bis(benzene)chromium(+) bis(4,5-dimethoxy-1,2-benzenedithiolato)nickel(–), $[Cr(bz)_2]^+[Ni(dmox)_2]^-$, was prepared as well-defined crystals by a metathesis reaction. X-ray single-crystal structure confirms the expected symmetries of the cations ($D_{6h}$) and anions ($D_{2h}$). The Ni–S bond length is typical for a monoanionic bis(arene)-1,2-dithiolato nickel complex thus confirming the ascribed charges. The structure reveals interpenetrating cation and anion sublattices where all ions are well separated from other ions of the same charge and with almost perpendicular symmetry planes of cations and anions. Above ca. 10 K the compound is paramagnetic and follows the Curie–Weiss law for $S = 1/2$ on each ion with a Weiss temperature of 8.5 K. Magnetic susceptibility and magnetization studies reveal the transition to a ferromagnetically ordered phase at 3.4 K. The ferromagnetic interaction is likely to occur through short contacts between anion heteroatoms (O and Ni) and cation H atoms, forming a 2-D network. A third dimension is possible through somewhat longer interionic S–H contacts. The Curie–Weiss law behavior can be modeled for 1-D chains with a ferromagnetic interaction of $J = 11.6$ K.

## Introduction

In 1986 Miller et al. reported a ferromagnetic ordering in the charge-transfer salt decamethylferrocenium tetracyanoethenide, $[Fe(Cp^*)_2]TCNE$.[1,2] This was the first example of ferromagnetic ordering in an organometallic compound, and one of the first ferromagnetically ordered molecular based materials at all.

Their discovery strongly stimulated the interest in molecular magnetic materials in general and contributed to a lengthy debate on the possible mechanisms for ferromagnetic ordering.[3−8] The preparation of a number of related compounds soon followed, and several were found to have interesting magnetochemical properties. The analogous $[M(Cp^*)_2]TCNE$ (M = Cr,[9] Mn[10]) and $[M(Cp^*)_2]TCNQ$ (M = Cr,[11] Mn;[12] TCNQ = tetracyanoquinodimethane) were all found to order ferromagnetically at low temperatures. Although no magnetic ordering was observed in $[Fe(Cp^*)_2][Ni(dmit)_2]$[13] (dmit = 2,5-dithiacyclopent-3-en-thione-3,4-dithiolate) down to 2 K, the compound is dominated by ferromagnetic interactions. Metamagnetic behavior was observed in $[Fe(Cp^*)_2]TCNQ$[14] and $[Mn(Cp^*)_2][M(tfd)_2]$[15]

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(1) Miller, J. S.; Calabrese, J. C.; Epstein, A. J.; Bigelow, R. W.; Zhang, J. H.; Reiff, W. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1026.
(2) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.
(3) Miller, J. S.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3850.
(4) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Science* **1988**, *240*, 40.
(5) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201.
(6) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21*, 114.
(7) Kollmar, C.; Couty, M.; Kahn, O. *J. Am. Chem. Soc.* **1991**, *113*, 7994.
(8) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385.
(9) Eichorn, D. M.; Skee, D. C.; Broderick, W. E.; Hoffman, B. M. *Inorg. Chem.* **1993**, *32*, 491.
(10) Yee, G. T.; Manriquez, J. M.; Dixon, D. A.; McLean, R. S.; Groski, D. M.; Flippen, R. B.; Narayan, K. S.; Epstein, A. J.; Miller, J. S. *Adv. Mater.* **1991**, 309.
(11) Broderick, W. E.; Hoffman, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 6334.
(12) Broderick, W. E.; Thompson, J. A.; Day, E. P.; Hoffman, B. M. *Science* **1990**, *249*, 401.
(13) Rabaca, S.; Gama, V.; Belo, D.; Santos, I. C.; Duarte, M. T. *Synth. Met.* **1999**, *103*, 2302.
(14) Candela, G. A.; Swartzendruber, L. J.; Miller, J. S.; Rice, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2755.
(15) Broderick, W. E.; Thompson, J. A.; Hoffman, B. M. *Inorg. Chem.* **1991**, *30*, 2958.

10.1021/ic034610m CCC: $27.50

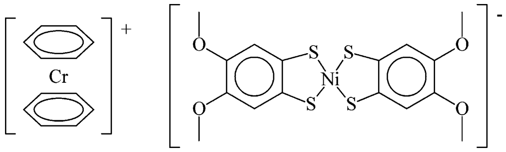

**Figure 1.** Chemical drawing of the title compound $[Cr(bz)_2]^+[Ni(dmox)_2]^-$.

(M = Ni, Pd, Pt; tfd = bis(trifluoromethyl)ethylenedithiolate) and more recently in $[Fe(Cp^*)_2][Ni(dmio)_2]^*THF$[16] (dmio = 2,5-dithiacyclopent-3-enone-3,4-dithiolate). The dmit, dmio, and tfd ligands are examples of the so-called dithiolene ligands. Due to the noninnocent character of these ligands, metal dithiolene complexes are often stable in a wide range of oxidation states. In combination with the many possible structural motifs of metal dithiolene complexes and the way to control the electronic and sterical properties of the ligand by means of the substituents, they offer a valuable building unit within molecular materials chemistry.[17] An example of a hybrid metallocene/dithiolene complex has been reported.[18]

Apart from the metallocenium salts and the Prussian blue magnets,[19] very few reports exist on ferromagnetic ordering in organometallic compounds. $[Cr(C_6(CH_3)_6)_2]$TCNE displayed a field-dependent magnetization at low temperature indicative of a 1-D ferromagnetic ordering,[20] while $[Cr(C_6H_6)_2]$TCNQ has ordinary paramagnetic behavior.[21] More recent examples of magnetochemical investigations of materials containing the bis(benzene)chromium(+) ion include attempts of structural engineering with squarate and cyclohexane-1,3-dionate[22,23] and the possible formation of bis(arene) nanowires in a mesoporous niobium oxide host.[24]

We wish to report on the magnetic and structural characteristics of the novel compound bis(benzene)chromium(+) bis(4,5-dimethoxy-1,2-benzenedithiolato)nickel(−), $[Cr(bz)_2]^+[Ni(dmox)_2]^-$, which to our knowledge represents the first example of a ferromagnetically ordering metal bis(arene) complex. A chemical drawing is shown in Figure 1.

## Experimental Section

**Materials.** The title compound bis(benzene)chromium bis(4,5-dimethoxybenzene-1,2-dithiolato)nickel was prepared as follows. Bis(benzene)chromium(I) iodide, $[Cr(C_6H_6)_2]I$ (0.20 mmol, 67 mg), was dissolved in 50 mL of acetone. Tetrabutylammonium bis(4,5-dimethoxybenzene-1,2-dithiolato)nickel(III), $Bu_4N[Ni(dmox)_2]$ (0.20 mmol, 140 mg), was dissolved in 20 mL of acetone. The two solutions were transferred to an H-shaped diffusion cell with two compartments separated by a porous glass fritt. The volumes of the compartments were 60 and 25 mL, respectively. The cell was closed and left undisturbed in a dark closet at room temperature for 2 weeks. Black crystals growing from the glass frit were collected on a sintered glass funnel, washed with acetone (50 mL), and dried in the air. The crystals were of sufficient quality for X-ray structure determination. The yield was 65 mg = 50%. Anal. Found (calcd for $C_{28}H_{28}CrNiO_4S_4$): C, 50.25 (50.38); H, 4.25 (4.23). The title compound may also be obtained in good purity by simply combining the two solutions in a stoppered flask and leaving the flask for a few days in the dark. $[Cr(C_6H_6)_2]I$ was prepared according to *Inorganic Syntheses*.[25] $Bu_4N[Ni(dmox)_2]$ was prepared as described elsewhere.[26−27]

**Table 1.** Crystallographic Data for Compound $[Cr(bz)_2]^+[Ni(dmox)_2]^-$

| | |
|---|---|
| formula | $C_{28}H_{28}CrNiO_4S_4$ |
| fw | 667.45 |
| cryst system | monoclinic |
| space group | $P2_1/c$ |
| Z | 2 |
| $a$, Å | 7.843(2) |
| $b$, Å | 21.670(4) |
| $c$, Å | 8.547(2) |
| α, deg | 90 |
| $\beta$, deg | 101.52(3) |
| $\gamma$, deg | 90 |
| $V$, Å$^3$ | 1423.4(5) |
| $\rho$, g cm$^{-3}$ | 1.557 |
| cryst dimens, mm | 0.35 × 0.23 × 0.075 |
| type of radiation | Mo Kα |
| $\mu$, cm$^{-1}$ | 1.370 |
| $T$, K | 293(2) |
| no. of reflcns | 14 978 |
| no. unique reflcns ($I > 2\sigma(I)$) | 2915 |
| $^R(F)$, $R_w(F^2)$ all data | 0.0339, 0.0970 |

**Magnetic Measurements.** Polycrystalline powder of the title compound were used to measure the magnetic properties by using a Cryogenic S600 SQUID magnetometer also equipped to measure the ac magnetic susceptibility. The magnetization in the paramagnetic region was measured by using a static field of 1.0. kOe and 10 Oe. The diamagnetic contribution of our sample holder is negligible (<0.1% of the signal) while the diamagnetic contribution of the compound was estimated by using the Pascal constants. The phase transition was evidenced by using a field of 10 Oe while the ac susceptibility was measured in zero static field at 2.3, 8.1, and 23 Hz. Microcrystalline powder EPR spectra were recorded at the X-band frequency using a Varian E9 spectrometer with a liquid-helium continuous-flow cryostat.

**X-ray Structure Analysis.** General crystallographic data can be found in Table 1. The crystal was mounted on a glass fiber using epoxy glue and transferred to the diffractometer (Siemens SMART CCD Platform). An almost complete sphere of reciprocal space was covered by a combination of several sets of exposure frames, each set with a different $\varphi$ angle for the crystal and each frame covering a scan of 0.3° in $\omega$.

Data collection, integration of frame data, and conversion to intensities corrected for Lorenz, polarization, and absorption effects were performed using the programs SMART,[28] SAINT,[28] and SADABS.[29] Structure solution, refinement of the structures, structure analysis, and production of crystallographic illustrations was carried out using the programs SHELXS97,[30] SHELXL97,[30]

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(16) Rabaca, S.; Santos, I. C.; Duarte, M. T.; Gama, V. *Synth. Met.* **2003**, *135−136*, 695.

(17) Robertson, N.; Cronin, L. *Coord. Chem. Rev.* **2002**, *227*, 93.

(18) Clérac, R.; Formigué, M.; Coulon, C. *J. Solid State Chem.* **2001**, *159*, 413.

(19) Mallah, T. *Science* **1993**, 1554.

(20) O'Hare, D.; Miller, J. S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 381.

(21) Zvarykina, A. V.; Karimov, Yu. S.; Ljubovsky, R. B.; Makova, M. K.; Khidekel, M. L.; Shchegolev, I. F.; Yagubsky, E. B. *Mol. Cryst. Liq. Cryst.* **1970**, *11*, 217.

(22) Braga, D.; Grepioni, F.; Byrne, J. J.; Wolf, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1023.

(23) Braga, D.; Maini, L.; Prodi, L.; Caneschi, A.; Sessoli, R.; Grepioni, F. *Chem.*—*Eur. J.* **2000**, *6*, 1310.

(24) He, X.; Trudeau, M.; Antonelli, D. *Adv. Mater.* **2000**, *12*, 1036.

(25) Fischer, E. O. *Inorg. Synth.* **1960**, *6*, 132.

(26) Schiødt, N. C.; Sommer-Larsen, P.; Bjørnholm, T.; Folmer Nielsen, M.; Larsen, J.; Bechgaard, K. *Inorg. Chem.* **1995**, *34*, 3688.

(27) Bjørnholm, T.; Geisler, T.; Petersen, J. C.; Greve, D. R.; Schiødt, N. C. *Nonlinear Opt.* **1995**, *10*, 129.

(28) *Siemens SMART and SAINT. Area-Detector Control and Integration Software*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995.

(29) Empirical absorption program (SADABS) written by George Sheldrick for the Siemens SMART platform.

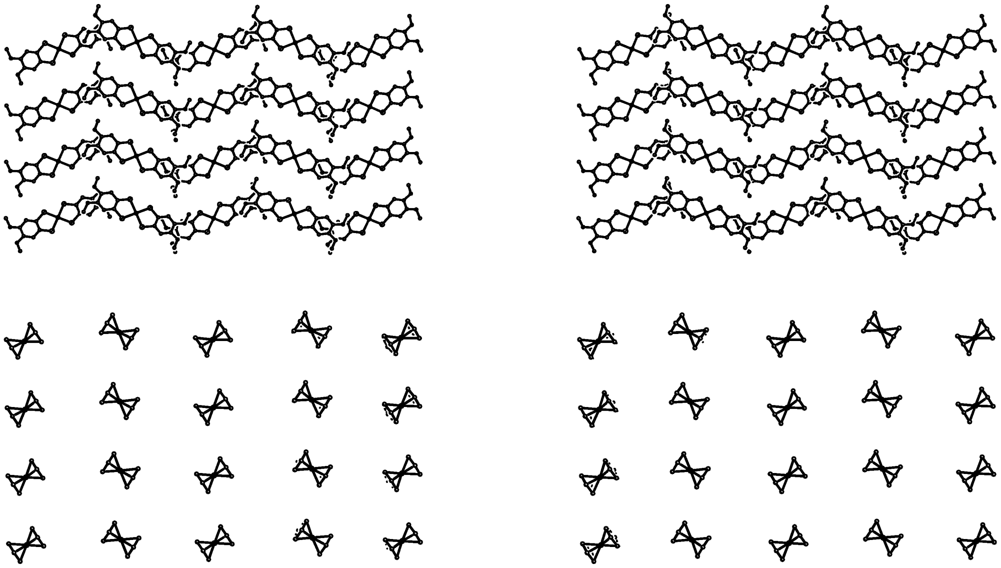

**Figure 2.** Anion (above) and cation (below) sublattices shown as stereoviews.

and SHELXTL.[31] The structures were checked for higher symmetry, and none was found.[32] H atoms were included with their calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 205004. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (+44)1223-336-033; E-mail deposit@ccdc.cam.ac.uk).

## Results and Discussion

**Molecular Crystal Structure of [Cr($C_6H_6$)$_2$][Ni(dmox)$_2$].** The crystal structure determination revealed that the molecular structure of both the cation and the anion (as shown in Figure 1) exhibit a typical geometry when compared to crystal structures having a similar molecular substructure.

In principle [Cr($C_6H_6$)$_2$][Ni(dmox)$_2$] may be a salt comprised by ions with charge ±1 or it may be a molecular complex between uncharged [Cr($C_6H_6$)$_2$] donors and [Ni(dmox)$_2$] acceptors. Therefore, we wished to compare metal−ligand bond lengths of [Cr($C_6H_6$)$_2$][Ni(dmox)$_2$] with those of other bis(arene)chromium and nickel dithiolene compounds (see Supporting Information).

While there are no examples in the literature on any Ni(dmox)$_2$ compounds, there are currently 20 known structures with various other (benzene-1,2-dithiolato)nickel species. The Ni−S bond distance depends as expected on the charge of the nickel-containing species with a decrease in bond length with increase in charge. Dianionic and monoanionic species fall in distinct groups with average Ni−S bond lengths of 2.16−2.18 and 2.13−2.16 Å, respectively. There is only one documented example of a neutral Ni(dithiolene) species, but this exhibits the shortest Ni−S bond lengths (2.12−2.13 Å) as expected.[33]

In the case of [Cr($C_6H_6$)$_2$][Ni(dmox)$_2$] we found Ni−S distances of 2.1453(8) and 2.1584(8) Å, in perfect agreement with the formulation as a monoanionic species. The nickel atom of the title compound is situated on an inversion center, and the molecular geometry is planar with near $D_{2h}$ symmetry as commonly observed for nickel dithiolene complexes.

The Cr(bz)$_2^+$ cations are close to the ideal $D_{6h}$ symmetry with Cr−C distances of between 2.130(3) and 2.140(3) Å. The chromium atom is situated on an inversion center. The Cr−C bond distances fall in the range of 2.10−2.14 Å, which is typical for bis(benzene)chromium compounds. Although existing crystallographic data indicate the expected Cr−C bond shortening with increase in charge as an overall trend, the actual Cr−C bond length seems to be more dependent on the temperature of the crystallographic data collection than on the charge of the bis(benzene)chromium species.

To summarize on the molecular crystal structure of [Cr($C_6H_6$)$_2$][Ni(dmox)$_2$], the anion and cation geometries are as expected, and the Ni−S bond distance indicates that the overall charge of the anion is −1 and thus in accordance with the magnetic behavior. It also fits the straightforward observation that while bis(benzene)chromium is very air sensitive, the $Bu_4N^+$ salt of [Ni(dmox)$_2$]$^-$ is infinitely stable in air both in solution and in the solid state.

**Crystal structure of [Cr($C_6H_6$)$_2$][Ni(dmox)$_2$].** A common structural feature of the magnetically ordering [M(Cp*)$_2$] compounds with TCNE and other planar counterions mentioned in the Introduction is that the planes defined by the Cp* rings and the planes of the anions are parallel or very closely so. In the case of [Cr($C_6H_6$)$_2$][Ni(dmox)$_2$], the planes defined by the benzene rings of the arene complex and the anion are almost perpendicular. The crystal structure reveals packing of the anions and cations in an interpenetrating network. There are no significant cation−cation or anion−anion contacts. The anion and cation sublattices are shown in Figure 2.

There are at least two significant anion−cation interactions that might be linked to the magnetic ordering. These

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(30) SHELX-97, program for structure solution and refinement written by George M. Sheldrick, 1997.

(31) Sheldrick, G. M. *SHELXTL95*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995.

(32) Spek, A. L. *Acta Crystallogr*. **1990**, *A46*, C-34.

(33) Sellmann, D.; Binder, H.; Haussinger, D.; Heinemann, F. W.; Sutter, J. *Inorg. Chim. Acta* **2000**, *300*, 829.

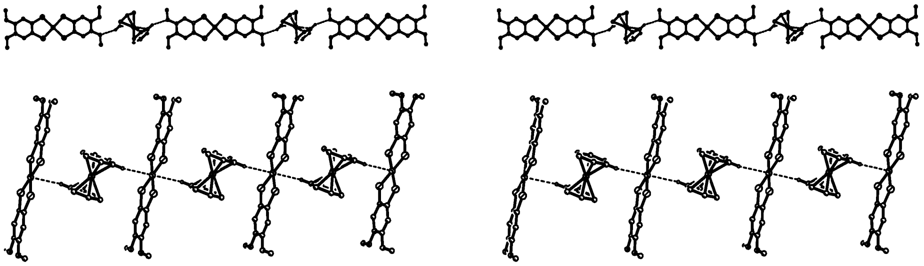

**Figure 3.** Two different anion−cation interactions as they run in infinite chains through the crystal lattice shown in stereoviews.

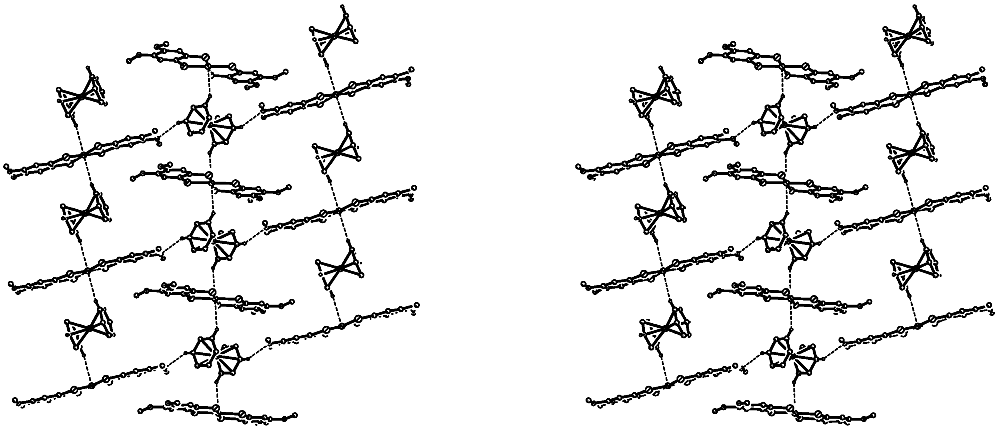

**Figure 4.** Stereoview of the 2-dimensional network of anion−cation interactions.

interactions can be viewed as infinite anion−cation chains as shown in Figure 3.

One interaction is between an oxygen atom of $[Ni(dmox)_2]$ and a hydrogen atom on $[Cr(bz)_2]$, and the other is formed between the Ni atom and another hydrogen atom of $[Cr(bz)_2]$. The hydrogen atoms through which the interactions take place are *meta* to each other. The combination of the anion−cation chains of interaction gives rise to a 2-dimensional network as shown in Figure 4.

A third possible interaction can be identified between the two sulfur atoms at one side of the $[Ni(dmox)_2]$ anion and a hydrogen atom on the benzene rings of the $[Cr(bz)_2]$ cation (*meta* to the two other interacting hydrogen atoms). The approximate distances are however quite long (S−H = 3.148 and 3.260 Å) as compared to the above-mentioned interactions (O−H = 2.437 Å and Ni−H = 2.908 Å), and therefore, the interaction is not ascribed to as high a significance while it would make the network of interactions fully 3-dimensional.

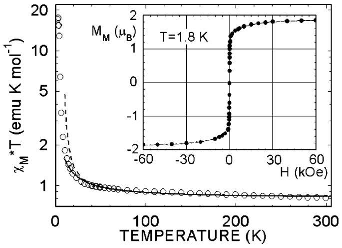

**Figure 5.** Temperature dependence of the product of temperature and magnetic susceptibility of $[Cr(bz)_2][Ni(dmox)_2]$. The solid and broken lines correspond to the calculated value using the 1-D model and the Curie−Weiss law, respectively. In the inset is the magnetization vs applied field at $T = 1.8$ K.

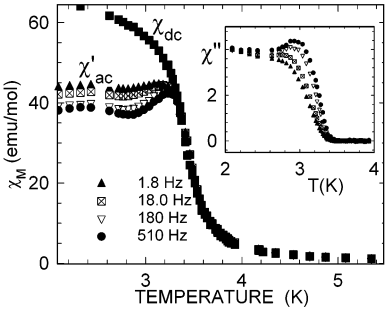

**Figure 6.** Low-temperature magnetic susceptibility of the title compound in dc and ac magnetic fields. In the inset is the imaginary component of ac susceptibility at four frequencies.

**Magnetic Measurements.** The room-temperature value of the magnetic susceptibility (note: actually what is measured is the ratio between the magnetization and the applied magnetic field) multiplied by the temperature is 0.81 emu K mol$^{-1}$, slightly higher than the value expected for two uncorrelated spins $S = 1/2$ with $g = 2.00$ (0.75 emu K mol$^{-1}$). On decrease of the temperature, the $\chi T$ value increases steadily, and below 10 K, the increase is quite sharp reaching the value of ca. 20 emu K mol$^{-1}$ in an applied field of 1.0 kOe (see Figure 5). Such a rapid increase of the susceptibility at low temperature suggests the presence of a magnetic phase transition, which has been evidenced by measuring the static susceptibility in low field (10 Oe) and the ac susceptibility at four different frequencies in the range 1.8−510 Hz; see Figure 6. The magnetic susceptibility shows a divergence at $T = 3.4$ K, and at this temperature the real component of the ac susceptibility, $\chi'$, becomes different from the static one and a small imaginary component, $\chi''$, appears. The onset of $\chi''$ is practically frequency independent, as expected in the case of phase transition to magnetic order.

The isofield magnetizations measured by cooling the sample in zero field and then applying the measuring field, or measured by cooling directly the sample in the magnetic field, are superimposable down to 1.8 K. The reversible movement of the domain walls is also responsible for the lack of a sizable opening of the hysteresis cycle. The magnetization curve shows a very rapid increase in low field, and a value of 1.93 $\mu_B$/formula unit is attained at the maximum field (60 kOe) as shown in the inset of Figure 5. This value is in good agreement with that expected for a parallel alignment of the $S = 1/2$ of the $[Cr(bz)_2]^+$ cation and of the $[Ni(dmox)_2]^-$ anion, confirming a genuine ferromagnetism of the compound.

The irreversibility of domain walls is directly related to magnetic anisotropy. Even if single-crystal magnetic data are not available, the polycrystalline EPR spectra (not shown) confirm that the magnetic anisotropy is small. At 40 K an almost isotropic line is observed centered at $g = 2.02$. On reduction of the temperature down to 4.2 K the line width gradually increases but no significant deviations from $g = 2$ are observed. A quantitative analysis of the temperature dependence of the magnetic susceptibility has been performed by using the Curie–Weiss law in a molecular field approximation. This analysis gives a Curie constant of 0.81 emu mol$^{-1}$, compatible with two $S = 1/2$ spins with average $g = 2.07$ and a ferromagnetic Weiss temperature of 8.5 K (broken line of Figure 5). A similar agreement with the experimental values in the high-temperature range and a significant improvement for the low-temperature data can be achieved using a model in which the ferromagnetic interactions are confined in a chain as suggested by the short contacts between the Ni atoms and a hydrogen of the benzene ring of $[Cr(bz)_2]^+$. The nearest-neighbor exchange interaction was estimated using the Baker formula[34] for ferromagnetically quantum $S = 1/2$ spin chains through a best-fit procedure and found to be 11.6 K with average $g = 2.06$ (solid line Figure 5). However, the onset of magnetic ordering at temperatures comparable to the intrachain interaction suggests that the magnetic interaction is not restricted along the chain. Indeed other short H contacts are observed describing a plane (or 3-dimensional structure if the very long S–H interactions are considered).

The $[Ni(dmox)_2]^-$ anions are almost completely planar when neglecting the methyl groups. According to previous analysis of nickel dithiolene complexes and of the $dmoxH_2$ and related ligands,[26] the singly occupied molecular orbital (SOMO) is of $b_{2g}$ symmetry. This SOMO is a weakly antibonding $\pi$-orbital with the largest contribution from the two dithiolene ligand HOMO's (highest occupied molecular orbitals) and some contribution from the Ni $3d_{zx}$ orbital.

With respect to the $[Cr(bz)_2]^+$ cation, the SOMO is $a_{1g}$.[33,34] It may be described as an antibonding combination of a ligand group orbital consisting of two $a_{2u}$ benzene $\pi$-orbitals and the Cr $3d_{z^2}$ and Cr 4s orbitals. The SOMO's are shown in Figure 7.

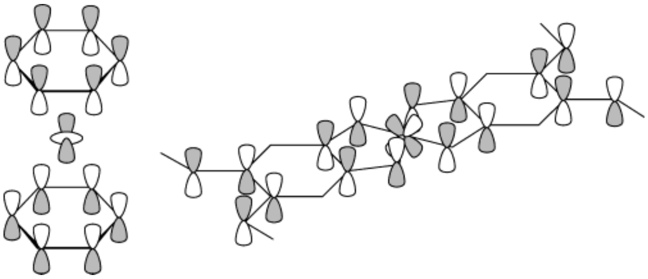

**Figure 7.** Left: $a_{1g}$ SOMO of $[Cr(bz)_2]^+$. Right: $b_{2g}$ SOMO of $[Ni(dmox)_2]^-$.

As discussed above, the crystal structure reveals that the closest interionic distance (2.44 Å) is between one of the H atoms on a benzene ring in $[Cr(bz)_2]^+$ and one of the O atoms in $[Ni(dmox)_2]^-$. The interionic O–H contacts define a chain structure along the *b*-axis. The second shortest interionic distance is that between Ni and another benzene H atom, defining another chain structure along the *c*-axis. These interionic contacts may be viewed upon as hydrogen bonds, since the hydrogen atoms are covalently bound to the cation while the receptor atoms belong to the anion. This leads to the question wether these hydrogen bonds are mediating the interionic magnetic coupling responsible for the observed ferromagnetic ordering. Hydrogen bonds as a magnetic exchange path are considered by several authors,[35–38] but an argument against it is that the spin population on hydrogen atoms is usually negligibly small.[39,40] However, the spatial overlap between the benzene C–H $\sigma$-bonds in the $[Cr(bz)_2]^+$ cations and the SOMO in the $[Ni(dmox)_2]^-$ anions would lead to a weak interionic ferromagnetic coupling due to the strict orthogonality between the benzene C–H $\sigma$-bonds and the $\pi$-symmetry SOMO in the $[Cr(bz)_2]^+$ cations. For the same reason the possible third interionic contact S–H would also give rise to a ferromagnetic coupling. A through-space interaction, on the other hand, would result in antiferromagnetic coupling due to the nonorthogonality between the cation and anion SOMO's. A similar argument has been used in a recent experimental and computational study of H-bonded nitroxide dimers.[40] In this case the observed intradimer interaction was AFM and this was interpreted as the through-space exchange pathway being dominant. These arguments favor that the magnetic couplings in the present case are mediated through the H-contacts, but this cannot be conclusively established on the basis of the present data.

## Conclusion

The crystalline compound $[Cr(C_6H_6)_2][Ni(dmox)_2]$ is comprised by singly charged cations and anions, each with spin $S = 1/2$. At room temperature the salt shows ordinary

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(34) Baker, G. A., Jr.; Rushbrooke, J. S.; Gilbert H. E. *Phys. Rev.* **1964**, *135*, A1272.

(35) Okamura, T.; Takano, Y.; Yoshika, Y.; Ueyama, N.; Nakamura, A.; Yamaguchi, K. *J. Organomet. Chem.* **1998**, *569*, 177.

(36) Akita, T.; Mazaki, Y.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1861.

(37) Sugawara, T.; Matsushita, M. M.; Izuoka, A.; Wada, N.; Takeda, N.; Ishikawa, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1723.

(38) Zhang, J.; Baumgarten, M. *Chem. Phys.* **1997**, *214*, 291.

(39) Deumal, M.; Robb, M. A.; Novoa, J. J. *Polyhedron* **2003**, *22*, 1935 and references therein.

(40) Ferrer, J. F.; Lahti, P. M.; George, C.; Oliete, P.; Julier, M.; Palacio, F. *Chem. Mater.* **2001**, *13*, 2447.

paramagnetic behavior with a value of $\chi T = 0.81$ emu K mol$^{-1}$, corresponding to the value for two uncorrelated spins with $g = 2.07$. On decrease of the temperature $\chi T$ increases to a maximum of approximately 20 emu K mol$^{-1}$ with a Weiss temperature of $\Theta = 8.5$ K. The compound shows frequency independent ac susceptibility at low temperature (below 5 K), demonstrating the presence of a ferromagnetic phase. The maximum magnetization gives a value of $M = 1.93$ $\mu_B$/formula unit corresponding to the value for two aligned $S = 1/2$ spins as expected. Isofield magnetization demonstrates the absence of hysteresis of this compound.

The crystal structure of $[Cr(C_6H_6)_2][Ni(dmox)_2]$ is defined by interionic hydrogen bonds forming chains along the crystallographic directions, so as to form a 3-D network. Ions of the same kind are well separated from each other so that all close contacts are between ions of different charge. There are three closest contacts in the structure, each involving a hydrogen atom on one of the aromatic rings of the cations. These contacts are O−H (2.437 Å), Ni−H (2.908 Å), and S−H (3.148 and 3.260 Å) with O, Ni, and S belonging to the anions and the three hydrogens being in positions 1, 3, and 5 to each other. It is suggested that the structural motif of hydrogen bonds may also be responsible for mediating the interionic magnetic communication. On the basis of molecular orbital considerations, this would give rise to interionic ferromagnetic coupling as opposed to a through-space exchange pathway. A phenomenological 1-dimensional model for the ferromagnetic interaction gives a nearest-neighbor exchange parameter of $J = 11.6$ K.

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**Note Added after ASAP:** There was an error in the second paragraph of the Introduction of the version of this paper posted ASAP on December 19, 2003. The corrected version appeared on January 23, 2004.

**Supporting Information Available:** Tables of fractional coordinates, equivalent isotropic and anisotropic thermal parameters, bond lengths, bond angles, and unit cell parameters, an ORTEP plot of the molecular crystal structure of $[Cr(bz)_2][Ni(dmox)_2]$, a diagram of frequency of reported Ni−S bond lengths in nickel dithiolene complexes, and a diagram of frequency of reported Cr−C bond lengths in bis(benzene)chromium compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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