One-Dimensional S = 1 Ferromagnetic Chain Formed by a Square Ni_2S_2 Motif in $Ni(qt)_2$ (qt = Quinoline-8-thiolate)

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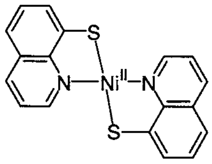
X-ray crystallographic analysis of the title complex reveals that nickel(II) ions are arranged to form a one-dimensional chain structure with double thiolate-bridges. The Ni–S–Ni angle is 94.3°. Magnetic susceptibility measurements indicate that the nickel S = 1 spins are ferromagnetically coupled within a chain.

Considerable attention has been paid to the study of low-dimensional magnetic systems which is characteristic of molecule-based materials. Uniform one-dimensional nickel(II) systems showing antiferromagnetic interaction have been extensively studied in connection with Haldane's conjecture.[1] One-dimensional nickel(II) systems showing ferromagnetic interaction are, however, rather limited in halogen-[2] and pseudohalogen-bridged[3,4] compounds. The azido-bridged nickel complexes is the most investigated, and the coordination modes generally observed for the bridging azido group are end-on (μ-1,1) with ferromagnetic interaction and end-to-end (μ-1,3) with antiferromagnetic one.[3] We report here a uniform one-dimensional structure with double thiolate-bridges in the crystal of nickel(II) bis(quinoline-8-thiolate), abbreviated as $Ni(qt)_2$ hereafter, which exhibits intra-chain ferromagnetic interaction.



$Ni(qt)_2$

Complexation with $NiCl_2 \cdot 6H_2O$ and a two-equiv amount of quinoline-8-thiol hydrochloride in CH_3OH gave $Ni(qt)_2$ as dark brown powder (yield: 81%). Recrystallization of the product from benzonitrile gave black needle-like crystals (mp >300 °C). The elemental analysis (C, H, N) satisfied the formula $Ni(qt)_2$. X-Ray diffraction data were collected on a Rigaku Raxis-Rapid IP diffractometer with a monochromated MoKα radiation. Magnetic properties were measured on a Quantum Design MPMS SQUID magnetometer equipped with a 7 T magnet.

The X-ray crystallographic analysis[5] of $Ni(qt)_2$ reveals a uniform one-dimensional molecular arrangement. As Figure 1(a) shows, every nickel(II) ion is located at an inversion center and surrounded by two nitrogen and two sulfur atoms at *trans* equatorial positions with the bond distances of 2.065(3) and 2.4038(8) Å for Ni–N and Ni–S, respectively. Figure 1(b) shows that the almost planar $Ni(qt)_2$ units are arranged to construct a columnar structure along the a axis; the nearest neighbor is related by the a-translation. The sulfur atom is deviated from the averaged quinoline plane by 0.290(4) Å toward a neighboring Ni ion, in which the axial coordination is found with the Ni–S distance of 2.5992(9) Å. A non-bonded S···N distance is 3.393(3) Å, which is close to the sum of the van der Waals radii. The angles of S–Ni–S and Ni–S–Ni are 85.66(3) and 94.34(3)°, respectively. All of the Ni_2S_2 units are coplanar within a chain. The shortest inter-chain Ni···Ni distance is 9.85 Å, which is much longer than intra-chain one (3.67 Å). There is no appreciable contact between chains. Therefore the crystal of $Ni(qt)_2$ has almost an ideal one-dimensional structure.

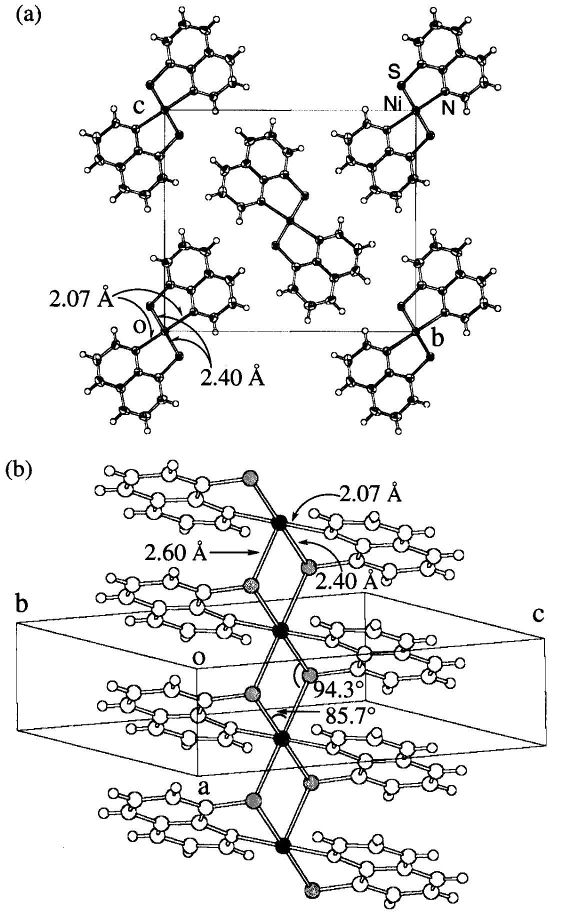


Figure 1. a) Crystal structure of $Ni(qt)_2$ viewed along the a axis with thermal ellipsoids at the 50% level. b) One-dimensional structure of $Ni(qt)_2$. Ni and S atoms are shaded. Selected bond lengths and angles are shown.

Figure 2(a) shows the temperature dependence of the product of magnetic susceptibility and temperature ($\chi_{mol}T$) for $Ni((qt)_2$ measured at 500 Oe. With decreasing temperature, the $\chi_{mol}T$ value monotonically increased and reached 5.07 cm^3 K mol^{-1} at 1.8 K. Figure 2(b) shows the magnetization curve measured at 2.0 K, which is normalized by the magnetization measured at the highest field attained (1.02×10^4 erg Oe^{-1} mol^{-1}).

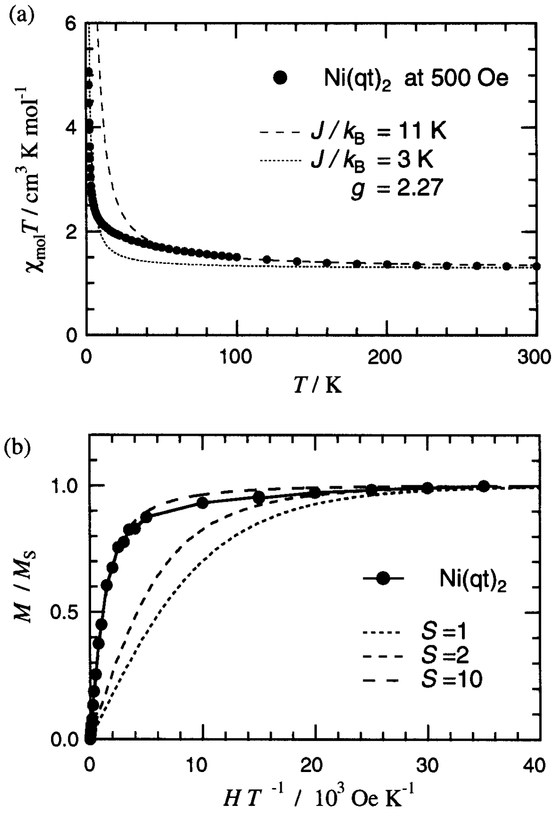


Figure 2. a) Temperature dependence of the product $\chi_{mol}T$ for Ni(qt)$_2$ measured at 500 Oe. The broken lines correspond to the calculated curves by using J/k_B = 11 and 3 K. For the equation, see the text. b) Magnetization curve of Ni(qt)$_2$ measured at 2.0 K. The Brillouin functions of S = 1, 2, and 10 are shown with broken lines.

The magnetization largely exceeded the Brillouin function of S = 1 and the magnetization in a low field region approximately fell on the Brillouin function of S = 10. Thus the presence of ferromagnetic interaction among the nickel(II) spins was confirmed. No magnetic phase transition could be found above 1.8 K, being in agreement with the one-dimensional crystal structure.

The observed ferromagnetic interaction is due to the intrachain interaction. An analytical expression for the magnetic susceptibility of an infinite chain of classical spins has been derived by Fisher.[6,7] The exchange parameter J (defined by the spin Hamiltonian $H = -J\,\Sigma S_i \bullet S_{i+1}$) can be estimated by the following equations.

$$\chi_{mol} = \frac{Ng^2\mu_B^2 S(S+1)}{3\,kT}\,\frac{1+u}{1-u}$$

$$u = \coth\left[\frac{J\,S(S+1)}{kT}\right] - \left[\frac{kT}{J\,S(S+1)}\right]$$

The Landé g factor is estimated to be 2.27 with S = 1 from the $\chi_{mol}T$ value at a high temperature region. A best fit J/k_B is obtained to be ca. +11 K above 40 K, but the calculated curve appears somewhat unsatisfactory in a low temperature region.[8] The calculated curves with J/k_B = +3 and +11 K with a fixed g = 2.27 are shown with broken lines in Figure 2(a). Thus, we can estimate $J/k_B = +7 \pm 4$ K. In this calculation, the contribution of the zero field splitting D of the nickel(II) ion was ignored because of the octahedral coordination geometry of the nickel ions. Below ca. 5 K, the observed $\chi_{mol}T$ values are downward deviated from the calculated line of J/k_B = 3 K. In a region of $T < |D|/k_B$, D may not be neglected. The deviation of $\chi_{mol}T$ below 5 K is attributed to a possible zero field splitting, an antiferromagnetic inter-chain interaction, and/or a saturation effect. The magnetization of Ni(qt)$_2$ was not fully saturated up to 70 kOe at 2.0 K. This finding may be due to single-ion crystal-field anisotropy[2c] or to a canted spin structure.[9]

A superexchange pathway through Ni–X–Ni (X = bridging atom) should be noted. In the present work, the Ni–S–Ni angle is 94.3°, which is close to 90°. The magnetic d orbitals of the S = 1 nickel(II) ion are assigned to be $d_{x^2-y^2}$ and d_{z^2}. The geometry of the Ni$_2$S$_2$ unit shown in Figure 1(b) favors a ferromagnetic superexchange drawn as: $d_{x^2-y^2} \mathbin{//} p_y \perp p_z \mathbin{//} d_{z^2}$. The J value is comparable to those of several oligonuclear nickel(II) complexes containing a cubane-like Ni$_4$O$_4$ core,[10] in which the Ni–O–Ni angles were designed to be a right angle. Although several nickel(II) cluster complexes containing a square Ni$_2$S$_2$ core have been reported, they were diamagnetic in most cases.[11] In conclusion, the complex Ni(qt)$_2$ is the first example of a one-dimensional S = 1 ferromagnetic chain consisting of a Ni$_2$S$_2$-type repeating motif.

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References and Notes

1 F. D. M. Haldane, *Phys. Rev. Lett.*, **50**, 1153 (1983).

2 a) C. Dupas and J.-P. Renard, *J. Chem. Phys.*, **61**, 3871 (1974). b) F. W. Klaaijsen, Z. Dokoupil, and W. J. Huiskamp, *Physica*, **79B**, 547 (1975). c) W. E. Estes, R. R. Weller, and W. E. Hatfield, *Inorg. Chem.*, **19**, 26 (1980).

3 P. Chaudhuri, T. Weyhermuller, E. Bill, and K. Wieghardt, *Inorg. Chim. Acta*, **252**, 195 (1996) and the references cited therein.

4 A. Escuer, R. Vicente, M. S. El Fallah, X. Solans, and M. Font-Bardía, *J. Chem. Soc., Dalton Trans.*, **1996**, 1013.

5 Crystallographic data of Ni(qt)$_2$ are: $C_{18}H_{12}N_2S_2Ni$, monoclinic, $P2_1/c$, a = 3.671(1), b = 14.789(5), c = 13.002(3) Å, β = 91.25(1)°, V = 705.8(3) Å^3, Z = 2, D_{calc} = 1.784 g cm^{-3}, $R(F)$ = 0.039 [$I > 2\sigma(I)$], and $R_w(F^2)$ = 0.139 for all 1422 observed reflections.

6 O. Kahn, “Molecular Magnetism,” VCH Publishers, Inc., New York, Weinheim, and Cambridge (1993), Chap. 11.2, pp. 257–261.

7 M. E. Fisher, *Am. J. Phys.*, **32**, 343 (1964).

8 Smaller S gives rise to a worse classical approximation according to Fisher's treatment. See ref. 6.

9 C. S. Hong and Y. Do, *Angew. Chem., Int. Ed. Engl.*, **38**, 193 (1999).

10 J. A. Barnes and W. E. Hatfield, *Inorg. Chem.*, **10**, 2355 (1971); A. Escuer, M. Font-Bardía, S. B. Kumar, X. Solans, and R. Vicente, *Polyhedron*, **18**, 909 (1999).

11 G. R. Brubaker, J. C. Latta, and D. C. Aquino, *Inorg. Chem.*, **9**, 2608 (1970); T. B. Rauchfuss and D. M. Roundhill, *J. Am. Chem. Soc.*, **97**, 3386 (1975).