

Coordination Modes of the 1,3-Dithiosquarate (1,3-dtsq) Ligand. Syntheses, Crystal Structures, and Magnetic Properties of [Ni(tren)(1,3-dtsq)(H₂O)] and [Ni₂(tren)₂(1,3-dtsq)](ClO₄)₂ [tren = Tris(2-aminoethyl)amine]

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The first X-ray crystallographic structure determinations of metal complexes of the 1,3-dithiosquarate (1,3-dtsq, dianion of 3-hydroxy-4-mercapto-2-thioxo-3-cyclobuten-1-one) are reported herein. Compounds [Ni(tren)(1,3-dtsq)(H₂O)] (C₁₀H₂₀N₄NiO₃S) (**1**) and [Ni₂(tren)₂(1,3-dtsq)](ClO₄)₂ (C₁₆H₃₆Cl₂N₈Ni₂O₁₀S₂) (**2**) (where tren is tris(2-aminoethyl)amine) both crystallize in the monoclinic system, space group *P*2₁/*c*, with *a* = 8.519(1) Å, *b* = 13.931(1) Å, *c* = 13.587(3) Å, β = 106.705(8)°, and *Z* = 4 for **1** and *a* = 8.663(1) Å, *b* = 14.496(2) Å, *c* = 11.617(2) Å, β = 98.135(9)°, and *Z* = 2 for **2**. The structure of **1** consists of mononuclear, neutral [Ni(tren)(1,3-dtsq)(H₂O)] complex units, whereas that of **2** is made up of dinuclear dithiosquarate-bridged cations, [Ni₂(tren)₂(1,3-dtsq)]²⁺, and uncoordinated perchlorate anions. The nickel environment is distorted octahedral in both cases, the tren group acting as a tetradentate ligand through its four nitrogen atoms and the dithiosquarate being monodentately coordinated through one of the sulfur atoms in **1** and bridging bis-bidentate in **2**. A water molecule which is hydrogen bonded to the neighboring carbonyl-oxygen atom of the dithiosquarate completes the octahedron around the metal atom in **1**. The intradimer metal–metal separation in **2** is 7.096(1) Å. Variable-temperature magnetic susceptibility measurements of complex **2** reveal the occurrence of a weak intramolecular antiferromagnetic coupling. The ability of the 1,3-dithiosquarate ligand to transmit electronic effects between metal ions has been analyzed through extended Hückel calculations. The theoretical influence of the position (1,2-dithiosquarate versus 1,3-dithiosquarate) and the number of sulfur (1,2,3,4-tetrathiosquarate) atoms on the exchange coupling through bis-bidentate thiosquarates is also considered.

Introduction

Much work has been devoted to the organic chemistry of the planar dianions of general formula C_{*n*}O_{*n*}²⁻ [*n* = 3 (deltate), 4 (squarate), 5 (croconate), and 6 (rhodizonate)], which are named oxocarbons.^{2,3} The substitution of one or more of the oxygen atoms by heteroatoms like sulfur or nitrogen has led to the so-called pseudooxocarbons whose syntheses, reactivity, and applications were reviewed very recently.⁴

This systematic and exhaustive research work dealing with the organic chemistry of oxocarbons and related pseudooxo-

carbons has opened vast perspectives in coordination chemistry because of their potential use as ligands. Concerning the oxocarbon series, the coordination modes of croconate and squarate are now well-known. Chelating,⁵ bischelating,^{5,6} and simultaneous chelating and monodentate⁷ coordination modes are normally adopted by the former, whereas monodentate,⁸ bimonodentate,^{8,9} and even tetramonodentate¹⁰ binding modes are the most frequent ones in the metal complexes of the latter. The large bite distance of the squarate ligand accounts for the absence of the chelating and bischelating coordination modes in its complexes with first-row transition-metal ions.^{8b} However, the reduction of the bite parameter (bite distance/M–O(squarate) bond length)^{8b,11} by using heavier metal ions (alkaline- and rare-earth cations)^{12,13} renders possible these coordination modes as shown by X-ray diffraction studies. The replacement of two adjacent oxygen atoms of squarate by a larger substituent such as sulfur also reduces the bite parameter, and the resulting 1,2-dithiosquarate group is able to act as a chelating ligand through its two sulfur atoms to 3d and heavier metal ions.^{14–19} If the substitution of squarate oxygen atoms by sulfur atoms is carried

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out on two nonadjacent positions, the resulting 1,3-dithiosquarate anion (dianion of 3-hydroxy-4-mercapto-2-thioxo-3-cyclobuten-1-one, hereafter noted 1,3-dtsq)²⁰ could exhibit both chelating and bischelating coordination modes. To our knowledge, no crystallographic report concerning metal complexes with 1,3-dtsq has been published thus far.

In the present work we report the synthesis, structural, and spectroscopic characterization of the compounds of formula [Ni(tren)(1,3-dtsq)(H₂O)] (**1**) and [Ni₂(tren)₂(1,3-dtsq)](ClO₄)₂ (**2**). The investigation of the magnetic properties of **2** and theoretical calculations to analyze the ability of this type of sulfur multiaetal ligands to mediate exchange coupling are also included.

Experimental Section

Materials. Tren, nickel(II) perchlorate hexahydrate, and lithium perchlorate trihydrate were purchased from commercial sources and used as received. Potassium 1,3-dithiosquarate dihydrate was prepared according to the literature.²¹ Elemental analysis (C, H, N, S) was conducted by the Microanalytical Service of the Universidad Autónoma de Madrid.

Synthesis. *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

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Preparation of Compounds. [Ni(tren)(1,3-dtsq)(H₂O)] (**1**). This complex was prepared by adding 0.120 g of K₂C₄O₂S₂·2H₂O (0.5 mmol) dissolved in a minimum amount of water to an aqueous solution (70 mL) of Ni(tren)(NO₃)₂ [0.291 g of Ni(NO₃)₂·6H₂O (1 mmol) and 0.146 g of tren (2 mmol)]. The addition of the thiosquarate ligand was accompanied by a color change from blue to brown and by the formation of a small amount of brown powder that was filtered off and discarded. Polyhedral brown crystals of **1** separate from the mother liquid by standing at room temperature for a few hours. They were collected, washed with water, and stored over calcium chloride. Anal. Calcd for C₁₀H₂₀NiN₄O₃S₂ (**1**): C, 32.73; H, 5.45; N, 15.26; S, 17.48. Found: C, 32.59; H, 5.38; N, 15.0; S, 17.24.

[Ni₂(tren)₂(1,3-dtsq)](ClO₄)₂ (**2**). This compound was obtained as a green polycrystalline powder by mixing aqueous solutions of [Ni(tren)]²⁺ [0.582 g of Ni(NO₃)₂·6H₂O (2 mmol) and 0.292 g of tren (2 mmol) in 30 mL of water] and Li₂C₄O₂S₂ [0.120 g of K₂C₄O₂S₂·2H₂O (0.5 mmol) and 1.063 g of LiClO₄·3H₂O (10 mmol) in the minimum amount of water and removal of the subsequent precipitate of KClO₄]. The yield is nearly quantitative under these conditions. Yellow-greenish arrow-shaped crystals of **2** which were suitable for X-ray diffraction analysis were grown from the mother liquid by slow evaporation at room temperature. Anal. Calcd for C₁₆H₃₆Cl₂Ni₂N₈O₁₀S₂ (**2**): C, 25.53; H, 4.78; N, 14.88; S, 8.52. Found: C, 25.65; H, 5.13; N, 14.84; S, 8.41.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 300–4000 cm⁻¹ region, and electronic spectra in solution and as Nujol mull samples were measured on a Perkin-Elmer Lambda 9 spectrophotometer. The magnetic susceptibility of a polycrystalline sample of **2** was measured over the temperature range 4.2–300 K with a fully automatized pendulum-type susceptometer equipped with a TBT continuous-flow cryostat and a Brüker BE15 electromagnet, operating at 1.8 T. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Diamagnetic corrections of the constituent atoms were calculated from Pascal's constants²² and found to be -374 × 10⁻⁶ cm³ mol⁻¹. The value 120 × 10⁻⁶ cm³ mol⁻¹ was used for the temperature-independent paramagnetism of the nickel(II) ion.

Crystallographic Data Collection and Structure Determination. Crystals of dimensions 0.31 × 0.25 × 0.18 mm (**1**) and 0.28 × 0.28 × 0.20 mm (**2**) were selected, and X-ray diffraction data were collected at 21 °C with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo K α radiation (λ = 0.710 73 Å). Unit cell parameters were determined from least-squares fits of the 2θ angles of 25 reflections in the 2θ ranges 28–44 and 20–42° for **1** and **2**, respectively. Totals of 3512 (**1**) and 2526 (**2**) unique reflections were recorded within $2\theta < 55^\circ$ (**1**) and $2\theta < 50^\circ$ (**2**) using the ω (**1**) and $\omega/2\theta$ (**2**) scan techniques. The intensities of three reference reflections monitored throughout each data collection showed no signs of crystal deterioration. Space groups were in each case unambiguously determined from systematic extinctions to be $P2_1/c$. The data were corrected for Lorentz and polarization effects. In each case an empirical absorption correction based on ψ -scans was carried out, the maximum and minimum transmissions being 99.89 and 87.20% in **1** (μ = 15.315 cm⁻¹) and 99.97 and 90.83% in **2** (μ = 16.962 cm⁻¹).

The structures were solved by direct methods and successive structure factor calculations and Fourier syntheses. All non-hydrogen atoms were anisotropically refined. Thermal parameters as well as bond distances involving carbon atom C(1) in compound **2** indicate the presence of a slight disorder in this part of the molecule. An attempted refinement of a disordered model was not successful, however. Hydrogen atoms, except those in the disordered region of **2**, were located in difference Fourier maps and were isotropically refined. The full-matrix least-squares refinements converged at $R = 0.028$, $R_w = 0.027$, $S = 1.452$ (**1**) and $R = 0.039$, $R_w = 0.039$, $S = 1.318$ (**2**). The refinements were based on 2881 (**1**) and 2159 (**2**) reflections with $I > 2\sigma(I)$, varying 262 (**1**) and 237 (**2**) parameters, and minimizing $\sum_w(|F_o| - |F_c|)^2$. The final difference Fourier map showed residual densities between +0.37 and -0.11 e Å⁻³ in **1** and between +0.70 and -0.65 e Å⁻³ in **2**. The higher values in compound **2** are found in the disordered region of the

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Table 1. Crystallographic Data for [Ni(tren)(1,3-dtsq)(H₂O)] (**1**) and [Ni₂(tren)₂(1,3-dtsq)](ClO₄)₂ (**2**)

	1	2
chem formula	C ₁₀ H ₂₀ N ₄ NiO ₃ S	C ₁₆ H ₃₆ Cl ₂ N ₈ Ni ₂ O ₁₀ S ₂
fw	367.13	752.97
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> /Å	8.519(1)	8.663(1)
<i>b</i> /Å	13.931(1)	14.496(2)
<i>c</i> /Å	13.587(3)	11.617(2)
β/deg	106.705(8)	98.135(9)
<i>V</i> /Å ³	1544.4(8)	1444.2(6)
<i>Z</i>	4	2
ρ(calcd)/(g cm ⁻³)	1.579	1.731
λ/Å	0.710 73	0.710 73
<i>T</i> /°C	21	21
μ/cm ⁻¹	15.315	16.962
<i>R</i> = (Σ <i>F</i> _o - <i>F</i> _c /Σ <i>F</i> _o)	0.028	0.039
<i>R</i> _w = ((Σ(<i>F</i> _o - <i>F</i> _c) ² /Σ <i>w</i> <i>F</i> _o ²) ^{1/2}) ^b	0.027	0.039

^a Cell dimensions are calculated from a least-squares fit of the 2θ angles of 25 reflections (28° < 2θ < 44° in **1**, 20° < 2θ < 42° in **2**). ^b In **1** *w* = 4*F*_o²/[σ_c² + (*kF*_o²)²], where σ_c is the standard deviation in *F*² based on counting statistics alone; in **2** unit weights were used.

Table 2. Final Atomic Fractional Coordinates and Equivalent Isotropic Displacement Parameters^{a,b} for Non-Hydrogen Atoms of [Ni(tren)(1,3-dtsq)(H₂O)] (**1**)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} /Å ²
Ni	0.23738(3)	0.04972(2)	0.22641(2)	2.021(4)
S(1)	0.24386(6)	0.12877(4)	0.06943(4)	3.05(1)
S(2)	0.83778(6)	0.18699(4)	0.01297(4)	2.99(1)
O(1)	0.4163(2)	0.2153(1)	-0.1136(1)	3.49(3)
O(2)	0.6712(2)	0.0808(1)	0.1949(1)	3.96(4)
O(3)	0.4715(2)	0.1071(1)	0.3181(1)	2.99(3)
N(1)	0.0138(2)	-0.0147(1)	0.1518(1)	3.17(4)
N(2)	0.1247(2)	0.1652(1)	0.2773(1)	3.07(4)
N(3)	0.3765(2)	-0.0730(1)	0.2219(1)	3.59(4)
N(4)	0.1984(2)	-0.0193(1)	0.3554(1)	2.75(4)
C(1)	-0.0156(3)	-0.0958(2)	0.2119(2)	3.86(5)
C(2)	0.0420(3)	-0.0747(2)	0.3244(2)	3.97(5)
C(3)	0.0762(3)	0.1381(2)	0.3692(2)	4.07(5)
C(4)	0.1890(3)	0.0598(2)	0.4260(2)	3.67(5)
C(5)	0.3815(3)	-0.1366(2)	0.3103(2)	4.31(6)
C(6)	0.3439(3)	-0.0804(2)	0.3954(2)	3.79(5)
C(7)	0.4298(2)	0.1366(1)	0.0531(1)	2.21(4)
C(8)	0.4857(2)	0.1782(1)	-0.0292(1)	2.37(4)
C(9)	0.6561(2)	0.1608(1)	0.0287(1)	2.28(4)
C(10)	0.6005(2)	0.1169(2)	0.1102(1)	2.56(4)

^a Estimated standard deviations in the last significant digits are given in parentheses. ^b *B*_{eq} = (4/3)Σ_iβ_{ij}*a*_i²*a*_j².

structure, whereas the residual density in other regions of the cell is comparable to that found in **1**. Crystal parameters and refinement results are summarized in Table 1. All calculations were carried out with programs in the MolEN structure determination system.²³ The scattering curves, with anomalous scattering terms included, were those of Cromer and Waber.²⁴

Atomic coordinates and bond lengths and interbond angles are listed in Tables 2–5. Supporting Information comprises crystal data, anisotropic thermal parameters, atomic parameters of hydrogen atoms, complete list of bond lengths and angles, hydrogen bond parameters, least-squares planes, and torsional angles (Tables S1–S13).

Results

Description of Structures. [Ni(tren)(1,3-dtsq)(H₂O)] (**1**). Compound **1** is built of mononuclear, neutral [Ni(tren)(1,3-dtsq)(H₂O)] complex units (Figure 1). The nickel atom, bonded to the four tren nitrogen atoms, a 1,3-dtsq sulfur atom, and a water molecule, has a cis-distorted octahedral coordination geometry. The Ni–N (2.086(2)–2.107(2) Å) bond lengths are in the expected range for N_{amine} groups, while the Ni–O (2.177(2)

Table 3. Final Atomic Fractional Coordinates and Equivalent Isotropic Displacement Parameters^{a,b} for Non-Hydrogen Atoms of [Ni₂(tren)₂(1,3-dtsq)](ClO₄)₂ (**2**)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} /Å ²
Ni	0.30551(5)	0.44140(3)	0.23892(4)	2.246(8)
Cl	-0.3261(1)	0.22889(8)	0.0227(1)	3.73(2)
S	0.5619(1)	0.51345(9)	0.23350(9)	3.39(2)
O(1)	0.2783(3)	0.4345(2)	0.0433(2)	3.18(6)
O(2)	-0.4887(5)	0.2393(5)	-0.0051(4)	9.7(2)
O(3)	-0.2925(5)	0.2499(5)	0.1432(4)	9.0(2)
O(4)	-0.2812(8)	0.1408(3)	0.0088(6)	14.0(2)
O(5)	-0.2445(7)	0.2865(4)	-0.0400(5)	10.5(1)
N(1)	0.3097(4)	0.4425(3)	0.4193(3)	3.69(8)
N(2)	0.3823(4)	0.3058(3)	0.2312(3)	3.36(8)
N(3)	0.1738(4)	0.5624(2)	0.2077(3)	3.36(7)
N(4)	0.0875(4)	0.3807(2)	0.2389(3)	2.98(7)
C(1)	0.1596(8)	0.4203(8)	0.4443(5)	10.8(3)
C(2)	0.0520(6)	0.3736(4)	0.3590(5)	4.9(1)
C(3)	0.2512(6)	0.2428(3)	0.2356(5)	4.7(1)
C(4)	0.1014(6)	0.2893(3)	0.1851(5)	4.3(1)
C(5)	0.0060(5)	0.5412(3)	0.1991(4)	3.7(1)
C(6)	-0.0235(5)	0.4417(3)	0.1661(4)	3.49(9)
C(7)	0.5331(4)	0.5082(3)	0.0892(4)	2.75(8)
C(8)	0.3986(4)	0.4699(3)	0.0156(3)	2.68(8)

^a Estimated standard deviations in the last significant digits are given in parentheses. ^b *B*_{eq} = (4/3)Σ_iβ_{ij}*a*_i²*a*_j².

Å) bond length is slightly longer than those usually found in nickel–aqua complexes and Ni–S (2.415(1) Å) is comparable to bond lengths reported for several thioether, thiourea, and chelating thiocarboxylate compounds, but longer than those typically found in thiolates and dithiocarbamates.²⁵

The 1,3-dithiosquarato ligand is monodentately coordinated through one of the sulfur atoms. The coordination does not introduce a significant difference in the two the S–C bond lengths (1.665(2) and 1.663(2) Å); by comparison, in the uncomplexed 1,3-dtsq dianion the corresponding bonds are slightly longer (1.672(2) Å).²⁰ The external angles at C(7) are markedly different, S(1)–C(7)–C(8) = 131.5(1)° and S(1)–C(7)–C(10) = 139.0(2)°; this distortion is probably related to the accommodation of an intramolecular hydrogen bond between O(2) of the dtsq group and the coordinated water molecule (O(2)⋯O(3) = 2.733(2) Å). The four 1,3-dtsq carbon atoms are coplanar within the limit of error, but the sulfur atoms deviate significantly from the plane (Table S10). The mean plane of the 1,3-dtsq group is tilted 31° relative to the N(1)N(4)O(3)S(1) plane.

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Table 4. Selected Bond Lengths (Å) and Interbond Angles (deg) for [Ni(tren)(1,3-dtsq)(H₂O)] (**1**)

Nickel Chromophore			
Ni–S(1)	2.415(1)	Ni–N(2)	2.091(2)
Ni–O(3)	2.177(2)	Ni–N(3)	2.091(2)
Ni–N(1)	2.086(2)	Ni–N(4)	2.107(2)
S(1)–Ni–O(3)	95.05(5)	O(3)–Ni–N(4)	91.66(6)
S(1)–Ni–N(1)	90.95(6)	N(1)–Ni–N(2)	92.87(9)
S(1)–Ni–N(2)	94.04(6)	N(1)–Ni–N(3)	94.6(1)
S(1)–Ni–N(3)	100.94(6)	N(1)–Ni–N(4)	82.41(7)
S(1)–Ni–N(4)	172.57(5)	N(2)–Ni–N(3)	163.12(8)
O(3)–Ni–N(1)	173.92(7)	N(2)–Ni–N(4)	83.03(8)
O(3)–Ni–N(2)	87.71(8)	N(3)–Ni–N(4)	82.97(8)
O(3)–Ni–N(3)	83.31(8)		
1,3-Dithiosquarato Ligand			
S(1)–C(7)	1.665(2)	C(7)–C(8)	1.455(3)
S(2)–C(9)	1.663(2)	C(7)–C(10)	1.464(3)
O(1)–C(8)	1.242(2)	C(8)–C(9)	1.459(2)
O(2)–C(10)	1.241(2)	C(9)–C(10)	1.459(3)
Ni–S(1)–C(7)	114.31(7)	S(2)–C(9)–C(8)	135.5(2)
S(1)–C(7)–C(8)	131.5(1)	S(2)–C(9)–C(10)	135.0(1)
S(1)–C(7)–C(10)	139.0(2)	C(8)–C(9)–C(10)	89.4(1)
C(8)–C(7)–C(10)	89.3(1)	O(2)–C(10)–C(7)	135.3(2)
O(1)–C(8)–C(7)	134.5(2)	O(2)–C(10)–C(9)	134.1(2)
O(1)–C(8)–C(9)	134.7(2)	C(7)–C(10)–C(9)	90.5(2)
C(7)–C(8)–C(9)	90.8(2)		
Tren Ligand			
N(1)–C(1)	1.457(3)	N(4)–C(6)	1.473(3)
N(2)–C(3)	1.473(3)	C(1)–C(2)	1.495(3)
N(3)–C(5)	1.483(3)	C(3)–C(4)	1.510(4)
N(4)–C(2)	1.492(3)	C(5)–C(6)	1.506(4)
N(4)–C(4)	1.478(3)		
Ni–N(1)–C(1)	110.0(1)	C(4)–N(4)–C(6)	112.9(2)
Ni–N(2)–C(3)	110.5(2)	N(1)–C(1)–C(2)	111.2(2)
Ni–N(3)–C(5)	110.5(2)	N(4)–C(2)–C(1)	113.2(2)
Ni–N(4)–C(2)	110.1(1)	N(2)–C(3)–C(4)	109.0(2)
Ni–N(4)–C(4)	104.5(1)	N(4)–C(4)–C(3)	110.6(2)
Ni–N(4)–C(6)	104.7(1)	N(3)–C(5)–C(6)	110.3(2)
C(2)–N(4)–C(4)	111.0(2)	N(4)–C(6)–C(5)	111.1(2)
C(2)–N(4)–C(6)	113.2(2)		

The molecules are connected through intermolecular hydrogen bonds (Table S8), including two very weak N–H···S contacts. Pairs of molecules related by an inversion center are arranged with parallel, overlapping 1,3-dtsq groups, the interplanar spacing being 4.2 Å. The shortest intermolecular metal–metal separation is Ni···Ni(–x, –y, –z) = 6.467(1) Å.

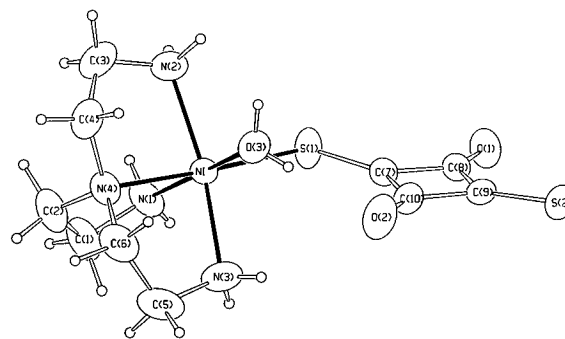
[Ni₂(tren)₂(1,3-dtsq)](ClO₄)₂ (2**).** The structure of compound **2** is built of centrosymmetric, dinuclear dithiosquarato-bridged cations, [Ni₂(tren)₂(1,3-dtsq)]²⁺ (Figure 2) and uncoordinated ClO₄[–] counterions. The nickel atom, bonded to the four tren nitrogen atoms and an oxygen and a sulfur atom from the 1,3-dtsq moiety, has a cis-distorted octahedral coordination geometry with Ni–N bond lengths in the normal range (2.082(4)–2.095(4) Å), and rather long Ni–O (2.253(3) Å) and Ni–S bonds (2.463(1) Å) (see above). In this context it also deserves to be noted that the Ni–S bond lengths in a square planar NiS₄ complex of the 1,2-dtsq ligand, K₂[Ni(1,2-dtsq)]·2H₂O (1,2-dtsq is 1,2-dithiosquarate dianion), are 2.212(1) and 2.234(2) Å.¹⁴

The 1,3-dtsq group acts as a bis-bidentate ligand. To accommodate the chelating coordination mode the S–C(7)–C(8) and O(1)–C(8)–C(7) angles are narrowed down to 127.2(3) and 129.5(4)° as compared to the remaining external angles at the C4 ring, S–C(7)–C(8)ⁱ of 144.1(3)° and O(1)–C(8)–C(7)ⁱ of 139.3(3)°. This allows for a S···O(1) bite distance in this complex of 3.270(3) Å, while the S···O(1)ⁱ distance is 3.754(3) Å. By comparison the S(2)···O(1) distance in **1** (3.530(1) Å), which is not affected by coordination, is also close to

Table 5. Selected Bond Lengths (Å) and Interbond Angles (deg) in [Ni₂(tren)₂(1,3-dtsq)](ClO₄)₂ (**2**)^a

Nickel Chromophore			
Ni–S	2.463(1)	Ni–N(2)	2.082(4)
Ni–O(1)	2.253(3)	Ni–N(3)	2.095(4)
Ni–N(1)	2.090(4)	Ni–N(4)	2.083(3)
S–Ni–O(1)	87.66(7)	O(1)–Ni–N(4)	90.9(1)
S–Ni–N(1)	97.7(1)	N(1)–Ni–N(2)	95.2(1)
S–Ni–N(2)	96.0(1)	N(1)–Ni–N(3)	95.7(1)
S–Ni–N(3)	96.4(1)	N(1)–Ni–N(4)	83.7(1)
S–Ni–N(4)	178.5(1)	N(2)–Ni–N(3)	162.3(1)
O(1)–Ni–N(1)	174.6(1)	N(2)–Ni–N(4)	84.1(1)
O(1)–Ni–N(2)	84.4(1)	N(3)–Ni–N(4)	83.2(1)
O(1)–Ni–N(3)	83.4(1)		
1,3-Dithiosquarato Bridge			
S–C(7)	1.662(4)	C(7)–C(8)	1.454(5)
O(1)–C(8)	1.245(5)	C(7)–C(8) ⁱ	1.462(6)
Ni–S–C(7)	90.0(1)	C(8)–C(7)–C(8) ⁱ	88.8(3)
Ni–O(1)–C(8)	105.7(2)	O(1)–C(8)–C(7)	129.5(4)
S–C(7)–C(8)	127.2(3)	O(1)–C(8)–C(7) ⁱ	139.3(3)
S–C(7)–C(8) ⁱ	144.0(3)	C(7)–C(8)–C(7) ⁱ	91.2(3)
Tren Ligand			
N(1)–C(1)	1.409(8)	N(4)–C(6)	1.480(5)
N(2)–C(3)	1.463(6)	C(1)–C(2)	1.432(9)
N(3)–C(5)	1.476(6)	C(3)–C(4)	1.506(7)
N(4)–C(2)	1.474(6)	C(5)–C(6)	1.504(7)
N(4)–C(4)	1.478(6)		
Ni–N(1)–C(1)	108.7(3)	C(4)–N(4)–C(6)	112.2(3)
Ni–N(2)–C(3)	109.4(3)	N(1)–C(1)–C(2)	119.6(5)
Ni–N(3)–C(5)	110.1(3)	N(4)–C(2)–C(1)	114.8(5)
Ni–N(4)–C(2)	109.9(3)	N(2)–C(3)–C(4)	109.8(4)
Ni–N(4)–C(4)	104.5(3)	N(4)–C(4)–C(3)	110.7(4)
Ni–N(4)–C(6)	105.3(2)	N(3)–C(5)–C(6)	110.3(4)
C(2)–N(4)–C(4)	112.2(4)	N(4)–C(6)–C(5)	110.7(3)
C(2)–N(4)–C(6)	112.2(3)		

^a Symmetry code: (i) 1 – x, 1 – y, –z.

**Figure 1.** Complex molecule [Ni(tren)(1,3-dtsq)(H₂O)] (**1**) with the atomic numbering used. Thermal ellipsoids are plotted at the 50% probability level.

the S···O distances in the squarate dianion in K₂(1,3-dtsq)·2H₂O (3.554(1) and 3.515(1) Å).²⁰ Furthermore the Ni–S–C(7) bond angle in **2** is only 90.0(1)°, while the corresponding angle in **1** is 114.31(7)°. The dithiosquarato group is planar within the limit of errors and is coplanar with the mean plane of O(1)N(1)N(4)S (dihedral angle 1.4(1.6)°).

The intradimer Ni···Ni distance across the 1,3-dtsq bridge is 7.096(1) Å. The shortest intermolecular metal–metal separation is Ni···Ni(1–x, 1–y, 1–z) = 6.727(1) Å. In the crystal there are several weak interactions between perchlorate oxygen atoms and amine nitrogen atoms (Table S9), but only two of these contacts are short enough to be characterized as hydrogen bonds.

Infrared and Electronic Spectra of 1 and 2. The most interesting aspects of the infrared data concerning complexes **1** and **2** are those dealing with the occurrence of monodentate (**1**) and bis-bidentate (**2**) 1,3-dtsq coordination modes. According

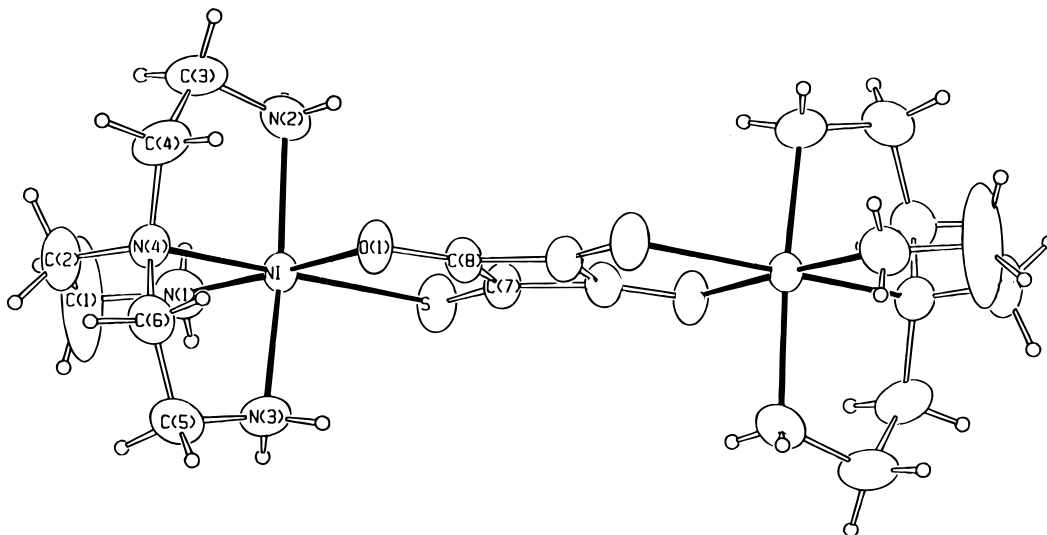


Figure 2. Complex cation $[\text{Ni}_2(1,3\text{-tren})_2(\text{dtsq})]^{2+}$ (**2**) with the atomic numbering used. Thermal ellipsoids are plotted at the 50% probability level.

to the literature,²¹ the IR spectra of the dipotassium salt of 1,3-dithiosquarate consists of a strong and broad feature centered at 1545 cm^{-1} , three strong peaks at 1260 , 1235 , and 1210 cm^{-1} , and a doublet at 800 (strong) and 770 cm^{-1} (sharp and medium intensity), which are attributed to $\nu(\text{OCCO})$, $\nu(\text{CCS})$, and $\nu(\text{CS})$ stretching vibrations, respectively. The IR bands of the 1,3-dithiosquarate ligand in complex **1** are a weak absorption at 1700 cm^{-1} , a strong peak in the $1560\text{--}1600\text{ cm}^{-1}$ region, and two doublets, one with strong absorptions centered at 1265 and 1220 cm^{-1} and the other consisting of a somewhat broad and medium intensity peak at 810 cm^{-1} and a sharp and weak feature at 765 cm^{-1} . The presence of the weak absorption at 1700 cm^{-1} in complex **1** supports the occurrence of localized C=O bonds in this compound in line with the monodentate character of 1,3-dtsq, as shown by the X-ray structure determination. The IR features associated with the 1,3-dtsq bridging ligand in complex **2** are very close to that of complex **1** but sharper. They are as follows: two strong and sharp peaks at 1530 and 1275 cm^{-1} , a medium intensity peak at 1225 cm^{-1} , and a very asymmetric doublet at 810 (strong and sharp) and 765 cm^{-1} (weak and sharp). The most noticeable difference between the IR spectra of the two complexes is the absence of the high-frequency C=O stretching in the spectrum of complex **2** in agreement with the presence of bischelating 1,3-dtsq ligand in it.

The electronic spectra of mull samples of complexes **1** and **2** are typical of octahedral nickel(II) complexes exhibiting a broad maximum at $10\,300$ (**1**) and $10\,150\text{ cm}^{-1}$ (**2**), a shoulder at $15\,950$ (**1**) and $15\,840\text{ cm}^{-1}$ (**2**), and a peak at $18\,320$ (**1**) and $17\,800\text{ cm}^{-1}$ (**2**). The feature at higher wavelengths corresponds to the value of $10Dq$ ($A_{2g}\text{--}T_{2g}$ transition), whereas the shoulder and the remaining peak could be attributed to the spin-forbidden $A_{2g}\text{--}E_g$ and spin-allowed $A_{2g}\text{--}T_{1g}$ transitions, respectively, in O_h symmetry. Very intense 1,3-dithiosquarate internal and metal–ligand charge transfer transitions obscure the region of lower wavelengths and preclude the observation of the third spin-allowed transition for a Ni(II) ion in O_h symmetry. A comparison between the values of $10Dq$ of **1** and **2** reveals that the ligand field strength of the S and O couple from chelating 1,3-dtsq is slightly lower to that from water oxygen and sulfur-bound 1,3-dtsq. This can be accounted for by the fact that the Ni–S [$2.415(1)$ and $2.463(1)\text{ \AA}$ in **1** and **2**, respectively] and Ni–O [$2.177(2)$ (**1**) and $2.253(3)\text{ \AA}$ (**2**)] bonds are significantly longer in the chelate structure.

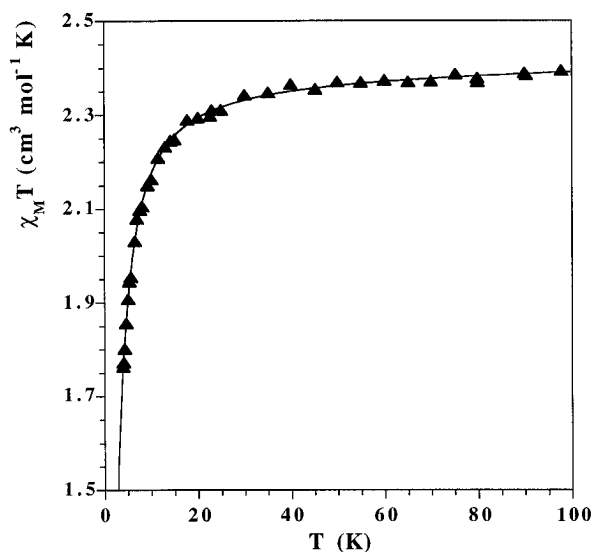


Figure 3. Thermal dependence of $\chi_M T$ for complex **2**: (▲) experimental data; (○) best theoretical fit (see text).

Magnetic Properties of 2. The thermal dependence of $\chi_M T$ (χ_M being the molar magnetic susceptibility) for complex **2** in the temperature range $4.2\text{--}100\text{ K}$ is shown in Figure 3. The value of $\chi_M T$ at room temperature ($2.38\text{ cm}^3\text{ mol}^{-1}\text{ K}$) corresponds to what is expected for two noninteracting single-ion triplet states. This value remains relatively unchanged down to 30 K and then falls rapidly to $1.76\text{ cm}^3\text{ mol}^{-1}\text{ K}$ at 4.2 K . This low-temperature attenuation could be due to weak intramolecular antiferromagnetic coupling, single-ion zero-field interactions (D), or both. It is clear that the ground state of a nickel(II) ion in an octahedral case as in **2** is orbitally nondegenerate, and, therefore, it is possible to represent the intradimer magnetic interaction (J) by the isotropic spin Hamiltonian $\hat{H} = -J\hat{S}_A \cdot \hat{S}_B$ with $S_A = S_B = 1$ and assuming that $g_x = g_y = g_z = g$. In a first approach, the corresponding spin-only formula (J and g as variable parameters) would account for the magnetic behavior of nickel(II) dimers when a relatively strong antiferromagnetic coupling occurs. The effect of D should be considered to describe the magnetic behavior at low temperatures in the cases where the antiferromagnetic coupling is weak. So, in a second step, J was assumed to be zero and D and g were variable parameters. Finally, in a third approach we considered both possibilities (J , g , and D as

variable parameters) by using the Hamiltonian $\hat{H} = -J\hat{S}_A \cdot \hat{S}_B - D(\hat{S}_A^2 + \hat{S}_B^2)$.^{26,27} The results of the least-squares fit through the corresponding theoretical expressions are as follows: $J = -0.5 \text{ cm}^{-1}$, $g = 2.19$, and $R = 3.3 \times 10^{-5}$ for the first, $D = 10.1 \text{ cm}^{-1}$, $g = 2.17$, and $R = 4.2 \times 10^{-5}$ for the second, and $J = -0.4 \text{ cm}^{-1}$, $g = 2.19$, $D = 4.1 \text{ cm}^{-1}$, and $R = 1.8 \times 10^{-5}$ for the third approach, where R is an agreement factor defined as $R = \sum_i [\chi_M^{\text{exptl}}(i) - \chi_M^{\text{calc}}(i)]^2 / \sum_i [\chi_M^{\text{exptl}}(i)]^2$. Very good fits are obtained in the three cases, the quality of the last fit being significantly better than the other two. In addition, the D value of this last fit (4.1 cm^{-1}) is more reasonable than that of the first one (10.1 cm^{-1}), which seems too large.²⁸ Anyway, it is well-known that the determination of D from magnetic susceptibility data on polycrystalline samples cannot be done accurately; anisotropy magnetic measurements on single crystals are required to do that. As far as the exchange coupling is concerned, a very weak antiferromagnetic coupling is obtained, the upper limit being -0.5 cm^{-1} . It is clear that the efficiency of bis-bidentate 1,3-dithiosquarate to mediate antiferromagnetic coupling in dinuclear nickel(II) complexes is much reduced when being compared to other related bis-bidentate ligands such as 2,2'-bipyrimidine ($-J_{\text{Ni}(\text{bpm})\text{Ni}} = 12-14 \text{ cm}^{-1}$)²⁷ and oxalate ($-J_{\text{Ni}(\text{ox})\text{Ni}} = 22-39 \text{ cm}^{-1}$).^{27,29}

Discussion

Preparation of Complexes 1 and 2. The exploration of the coordination chemistry of sulfur-containing ligands such as the thiooxocarbons is difficult due to hydrolytic and redox reactions. For instance, protonation of 1,2-dithiosquarate gives a yellow solid containing S-H bonds which decomposes rapidly with loss of hydrogen sulfide.³⁰ Electrochemical investigations on thiosquarate derivatives $\text{C}_4\text{O}_{4-x}\text{S}_x$ ($x = 1-4$) in acetonitrile have shown they oxidize to yield disulfides by radical condensation.³¹ In Ni(II) and Pd(II) complexes of tetrathiosquarate, partial replacement of sulfur by oxygen has been detected.³² It has also been reported that iron(III) and copper(II) are easily reduced by 1,2-dtsq to iron(II) and copper(I), the resulting complexes being characterized by X-ray diffraction on single crystals.^{15,17b,33} In the preparation of the complexes **1** and **2**, we have not detected any redox reaction accompanying the complex formation. This is not surprising given that with the related 1,2-dtsq ligand a square planar nickel(II) complex of formula $\text{K}_2\text{Ni}(\text{dtsq})_2 \cdot 2\text{H}_2\text{O}$ ¹⁴ was isolated and structurally characterized. The fact that 1,2-dtsq displays an intermediate reducing power toward 3d metal ions may be a consequence of the large chelate bite, which renders 1,2-dtsq a weak field ligand. Our structural and spectroscopic data reveal that 1,3-dtsq can also be classified as a weak sulfur-oxygen chelate, most likely because of the angular strain of its chelating and bis chelating coordination.

Concerning the preparation of complexes **1** and **2**, the main role of the tetradentate tren ligand is to avoid the precipitation of polymeric Ni(II)-1,3-dtsq compounds. Another important aspect is the low solubility of complex **1** which allowed us to obtain single crystals from concentrated aqueous solutions in a few hours at room temperature. However, the synthesis of the dimer was more difficult because of its great solubility in water. It was isolated as a polycrystalline powder from solutions containing a 2:1/2:9 $[\text{Ni}(\text{tren})]^{2+} : 1,3\text{-dtsq}^{2-} : \text{ClO}_4^-$ molar ratio. The presence of an excess of both $[\text{Ni}(\text{tren})]^{2+}$ and ClO_4^- was determinant in the isolation of **2**. Aqueous solutions of **2** lead to the precipitation of **1**. So, single crystals of **2** were obtained from its aqueous solutions only in the presence of an excess of perchlorate. A spectrophotometric study of the complex formation between $[\text{Ni}(\text{tren})]^{2+}$ and 1,3-dtsq in water and dimethyl sulfoxide (DMSO) as solvents revealed the formation of a single 1:1 $[\text{Ni}(\text{tren})]^{2+} : 1,3\text{-dtsq}^{2-}$ species which is nearly totally formed at a 1:1 metal to ligand molar ratio. The formation of the dimeric species was not detected, most likely because its formation requires very concentrated solutions which are not suitable for spectrophotometric investigations.

Coordination Mode of 1,3-dtsq. To our knowledge no metal complex of 1,3-dtsq has been structurally characterized previously. In the present work the ability of this ligand to coordinate in the S-monodentate and in the chelating bis-bidentate coordination modes to a 3d metal ion has been demonstrated. The chelating mode may at a first sight seem surprising considering the fact that a corresponding mode is not found for squarato complexes of 3d metal ions due to the large bite parameter of the latter ligand.^{8b,11} The S...O bite distance in the uncomplexed 1,3-dtsq dianion is 3.53 \AA (average value),²⁰ and considering a complex with a S-M-O angle of 90° would lead to M-X bond distances of approximately 2.50 \AA . In the present case (**2**) the S...O bite distance is reduced to $3.270(3) \text{ \AA}$ through a reduction of the chelate endo S(O)-C-C angles from the idealized 135° to 127.2 and 129.5° , respectively. Furthermore the bond angle at S is only 90.0° . These distortions allow for Ni-S and Ni-O bond distances of 2.463 and 2.253 \AA , respectively. These are clearly rather long bond distances and indicate that the bite distance is in the upper limit of what can be accommodated for a nickel(II) complex. The bite parameter, when the average of the M-S and M-O distances is used, is 1.39 for this complex and is close to the values typically found in oxalato- and hydranilato-type complexes.^{8b}

The 1,2-dtsq ligand has been observed to coordinate in the chelating mode in complexes of 3d-metal ions as well as heavier elements.¹⁴⁻¹⁹ In Table 6, structural parameters of these complexes are compared with those of complex **2**. One may notice that the S...S bite in the 1,2-dtsq ligand in all its chelating complexes ($3.26-3.56 \text{ \AA}$, see Table 6)¹⁴⁻¹⁹ are reduced relative to the corresponding distances ($3.76-3.84 \text{ \AA}$) in the uncomplexed 1,2,3,4-tetrathiosquarate dianion.³⁴ The extent of the reduction of S...S bite in 1,2-dtsq complexes is in some cases appreciably larger than the reduction observed for the S...O bite in compound **2**. In fact, in the 1,2-dtsq nickel(II) complex¹⁴ a S...S bite distance almost identical to the S...O bite distance in **2** is obtained through a considerable further reduction of the endo S-C-C angles. This distortion allows a closer Ni-S approach (2.21 and 2.23 \AA) in the 1,2-dtsq complex without introducing unduly strain in the Ni-S-C angles (99.3 and 99.8°). In an octanuclear Cu(II) complex of 1,2-dtsq the S...S bite is reported to be $3.922(10) \text{ \AA}$.³³ However, in this compound the coordination mode of 1,2-dtsq is bridging, not chelating.

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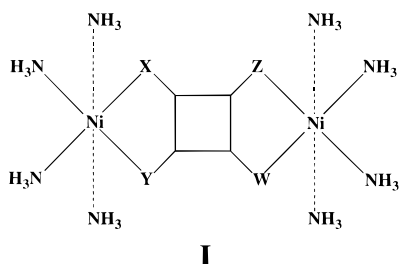
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Table 6. Structural Parameters for Dithiosquarate Ligands^a

compound	$\angle\text{SCC}^b$ ($\angle\text{OCC}$)/deg	$\angle\text{MSC}$ ($\angle\text{MOC}$)/deg	$\angle\text{SMS}$ ($\angle\text{SMO}$)/deg	MS (M–O)/Å	S···S (S···O)/Å	bite param ^c	ref
K ₂ Ni(1,2-dtsq)·2H ₂ O	123.3	99.6	94.2	2.22	3.26	1.47	14
[(C ₆ H ₅) ₄ P] ₂ [Fe(1,2-dtsq) ₂]	129.5	92.1	95.7	2.39	3.54	1.48	15
[Cu(en) ₂][Cu(1,2-dtsq) ₂]	127.0	95.0	95.8	2.30	3.42	1.49	17b
[(C ₆ H ₅) ₄ P] ₂ [Cu(1,2-dtsq) ₂]	126.0	97.4	93.1	2.33	3.38	1.45	17a
[Cu(en) ₂ (H ₂ O) ₂][Cu ₄ (1,2-dtsq) ₄]·2H ₂ O ^d	129.4	93.0	95.1	2.41	3.56	1.48	17b
K ₂ [Pd(1,2-dtsq) ₂]·2H ₂ O	125.6	98.1	92.6	2.33	3.37	1.45	18a
[(C ₄ H ₉) ₄ N] ₂ [Mo ₂ O ₃ S(1,2-dtsq)]	125.0	100.9	84.9	2.49	3.36	1.35	16
(CH ₃) ₂ Sn(1,2-dtsq)· ¹ / ₃ C ₆ H ₆	129.3	96.3	88.8	2.53	3.54	1.40	19
(CH ₃) ₂ Sn(1,2-dtsq)·(CH ₃) ₂ SO	129.4	96.8	87.6	2.55	3.53	1.38	19
[Ni ₂ (tren) ₂ (1,3-dtsq)](ClO ₄) ₂ (2)	127.2 (120.5)	90.0 (105.7)	– (87.7)	2.46 (2.25)	– (3.27)	1.39	this work

^a Bond distances and angles of each structure have been averaged. ^b Endo angle, i.e., angle within the chelate ring. ^c Bite param = (av M–S(O))/(av S···S(O)). ^d A very asymmetric “chelate” with one of the Cu···S distances equal to 3.145 Å, occurring in this structure, has not been included.

Chart 1

Considering the data in Table 6, one may conclude that the radius of the Ni(II) ion is close to the lower limit for permitting the chelating coordination mode of 1,3-dtsq. The fact that the ligand field splitting in **2** is lower than that of **1** also supports this conclusion.

Exchange Pathways through 1,3-dtsq and Related Thiosquarates. The low efficiency of the bis-bidentate 1,3-dtsq ligand to mediate antiferromagnetic coupling between nickel(II) ions contrasts with the remarkable efficiency of oxalato. Although the exchange pathway involved in the former (Ni–S–C–C–O–Ni) is longer than that in the latter (Ni–O–C–O–Ni) the presence of sulfur (atom more diffuse and less electronegative than oxygen)³⁵ would favor the magnetic coupling through 1,3-dtsq. A theoretical analysis dealing with the structural and electronic characteristics of the complex **2** which could account for its magnetic behavior (weak antiferromagnetic coupling) is thus in order. It seems also interesting to consider the influence of the position of the sulfur atoms (1,3- versus 1,2-dithiosquarate) as well as their number (1,2,3,4-tetrathiosquarate, ttsq²⁻), aiming at making predictions on their ability to transmit electronic effects in their metal complexes. To do that, we performed extended Hückel calculations by using the CACAO program.³⁶ Calculations were made on three model compounds (see Chart 1) consisting of octahedral nickel(II) dimers bridged by 1,3-dtsq (X = W = S; Y = Z = O), 1,2-dtsq (X = Z = S; Y = W = O), and ttsq (X = Y = Z = W = S) groups acting as bis-bidentate ligands.³⁷

Atomic parameters used are listed in Table 7.³⁸ The SOMOs containing the unpaired electrons for the three dimeric systems

Table 7. Orbital Exponents (Contraction Coefficients in Double- ζ Expansion Given in Parentheses) and Energies Used in the Extended Hückel Calculations

atom	orbital	ζ_i (c_i)	H_{ii} , eV
Ni	4s	1.825	–9.11
	4p	1.125	–5.15
	3d	5.750 (0.5683)	–13.40
		2.000 (0.6292)	
C	2s	1.625	–21.40
	2p	1.625	–11.40
O	2s	2.275	–32.30
	2p	2.275	–14.80
S	3s	1.817	–20.00
	3p	1.817	–13.30
H	1s	1.300	–13.60
N	2s	1.950	–26.00
	2p	1.950	–13.40

resulting from the interaction between the in-phase and out-of-phase combinations of the $d_{x^2-y^2}$ ($d_{x^2-y^2}^a \pm d_{x^2-y^2}^b$) and d_z^2 ($d_z^{2a} \pm d_z^{2b}$) magnetic orbitals of the two metal centers (a and b) and the HOMOs of the thiosquarate dianions with the appropriate symmetry are shown in Figure 4. In the context of the molecular orbital model introduced by Hay *et al.*,^{38b} the antiferromagnetic part of the exchange interaction (J_{AF}) in the case of two interacting electrons is proportional to the square of the energy gap between the molecular orbitals bearing the unpaired electrons. In the case of octahedral nickel(II) complexes with magnetic orbitals of the $d_{x^2-y^2}$ and d_z^2 type, this model leads to eq 1, where Δ_{12} and Δ_{34} are the energy gaps

$$J_{AF} = -\frac{1}{2}[\Delta_{12}^2/k_{12} + \Delta_{34}^2/k_{34}] \quad (1)$$

between the single occupied molecular orbitals ψ_{ij} (SOMOs) shown in Figure 4 and k_{ij} represents the two-electron terms [$k_{ij} = \frac{1}{2}(J_{aa} - J_{ab})$]. An examination of the values of Δ_{12} and Δ_{34} reveals that they increase when the number of sulfur atoms increases (1,3- and 1,2-dtsq versus ttsq) as expected, due to the smaller electronegativity and more diffuse character of the sulfur atom as compared to oxygen. However, the position of the sulfur atoms (1,3-dtsq versus 1,2-dtsq) have an even larger effect on the energy gaps. These MO calculations allow us to understand the very low efficiency of the 1,3-dtsq bridge to mediate exchange coupling (complex **2**) and to predict a greater efficiency of the 1,2-dtsq and 1,2,3,4-ttsq bridges at this respect. As shown in the Figure 4a, simple symmetry and electron density considerations show that the exchange pathways involving the $d_{x^2-y^2}$ (SOMOs ψ_1 and ψ_2) and the d_z^2 (SOMOs ψ_3 and ψ_4) magnetic orbitals in **2** lead to small overlaps through the S–C–C–C–S and O–C–C–O skeletons, respectively. Although a favorable orbital symmetry is present in the S–C–C–C–S pathway, it involves a long way (five atoms in the

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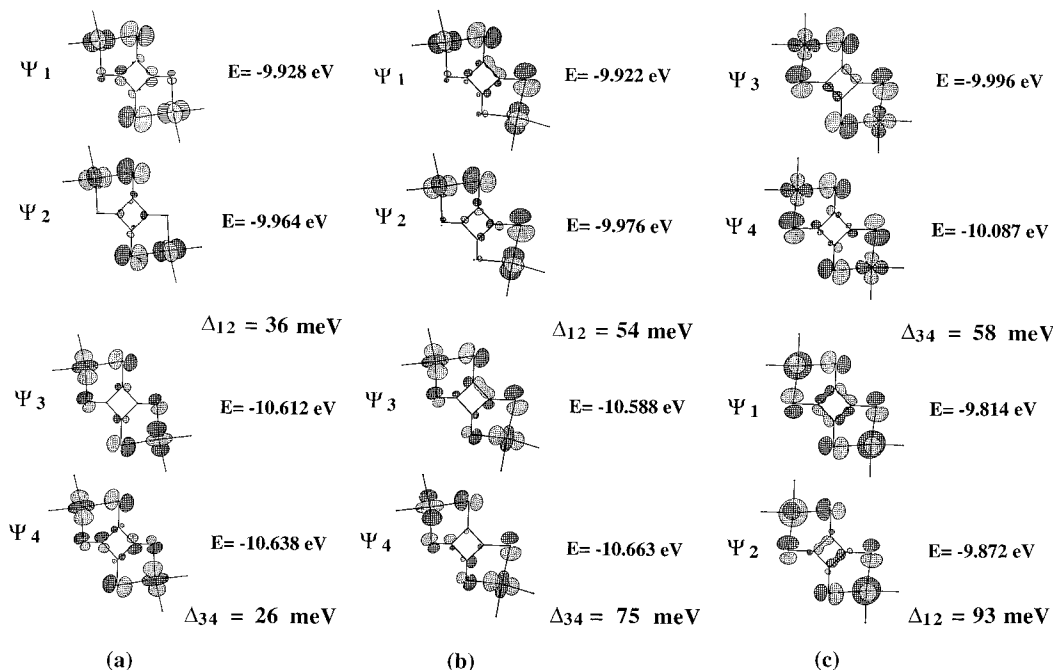


Figure 4. SOMOs resulting from the interaction between two nickel(II) magnetic orbitals through the bis-bidentate 1,3-dtsq (a), 1,2-dtsq (b), and ttsq (c) ligands. In cases a and b the x and z axes are defined by the Ni–S and Ni–O bonds, respectively; in case c the x and y axes correspond to adjacent Ni–S bonds.

bridging unit). This long distance is responsible for the weak antiferromagnetic coupling (-3.6 cm^{-1} for the singlet–triplet energy gap) through the related O–C–C–C–O skeleton in the dimer $[\text{Cu}_2(\text{terpy})_2(\text{H}_2\text{O})_2(\text{sq})](\text{ClO}_4)_2$ (terpy and sq represent 2,2':6',2''-terpyridine and squarate dianion, respectively),^{8b} a feature which is in line with the small antiferromagnetic coupling observed in **2**. The other pathway, (S–C–C–O linking unit), which is shorter, exhibits a less favorable symmetry and could even lead to orthogonality under small structural changes. A comparison of these results with that concerning the $\text{Ni}_2(1,2\text{-dtsq})$ case (Figure 4b) reveals that the bis-bidentate 1,2-dtsq ligand has a greater efficiency to transmit antiferromagnetic coupling because of the larger overlap through S–C–C–S ($d_x^2-y^2$ type orbitals) and O–C–C–O (d_z^2 type orbitals) skeletons. The strongest antiferromagnetic coupling is expected through the bridging 1,2,3,4-ttsq ligand as shown in Figure 4c: the appropriate orientation of the in-plane magnetic orbitals ($d_x^2-y^2$) to interact through both S–C–C–S fragments provides the largest Δ_{12} energy gap of the series; in addition, although the orientation of the d_z^2 magnetic orbitals is not the most adequate, the great diffuseness of the four sulfur atoms of the bis-bidentate tetrathiosquarate leads to a significant Δ_{34} energy gap.

In summary, our theoretical calculations indicate that, firstly, the antiferromagnetic interaction through the 1,3-dtsq is weak as observed (complex **2**) and, secondly, the antiferromagnetic coupling through the bridging ligands should increase significantly when going from the former to the latter in the series 1,3-dtsq, 1,2-dtsq, and 1,2,3,4-ttsq. Unfortunately, the lack of magnetostructural data concerning the two last members of this family does not allow one yet to check our theoretical predictions.

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Supporting Information Available: Tables listing crystal data, anisotropic thermal parameters, hydrogen atom coordinates, intramolecular bond distances and angles, hydrogen bonding parameters, torsion angles, and least-squares planes and two figures showing stereodrawings (14 pages). Ordering information is given on any current masthead page.

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