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New Family of Thiocyanate-Bridged Re(IV)-SCN-M(II) (M = Ni, Co, Fe, and Mn) Heterobimetallic Compounds: Synthesis, Crystal Structure, and Magnetic Properties

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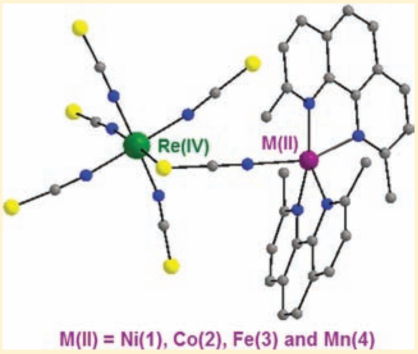
S *Supporting Information*

ABSTRACT: The heterobimetallic complexes of formula $[(Me_2phen)_2M(\mu\text{-}NCS)\text{-}Re(NCS)_5]\cdot CH_3CN$ [Me_2phen = 2,9-dimethyl-1,10-phenanthroline and M = Ni (**1**), Co (**2**), Fe (**3**), and Mn (**4**)] have been prepared, and their crystal structures have been determined by X-ray diffraction on single crystals. Compounds **1**−**4** crystallize in the monoclinic *C*2/*c* space group, and their structure consists of neutral $[(Me_2phen)_2M(\mu\text{-}NCS)Re(NCS)_5]$ heterodinuclear units with a Re-SCN-M bridge. Each Re(IV) ion in this series is six-coordinated with one sulfur and five nitrogen atoms from six thiocyanate groups building a somewhat distorted octahedral environment, whereas the M(II) metal ions are five-coordinated with four nitrogen atoms from two bidentate Me_2phen molecules and a nitrogen atom from the bridging thiocyanate describing distorted trigonal bipyramidal surroundings. The values of the Re···M separation through the thiocyanate bridge in **1**−**4** vary in the range 5.903(1)−6.117(3) Å. The magnetic properties of **1**−**4** as well as those of the parent mononuclear Re(IV) compounds $(NBu_4)_2[Re(NCS)_6]$ (**A1**) (NBu_4^+ = tetra-*n*-butylammonium cation) and $[Zn(NO_3)(Me_2phen)_2]_2[Re(NCS)_5(SCN)]$ (**A2**) were investigated in the temperature range 1.9−300 K. Weak antiferromagnetic interactions between the Re(IV) and M(II) ions across the bridging thiocyanate were found in **1**−**4** [$J = -4.3$ (**1**), −2.4 (**2**), −1.8 (**3**), and -1.2 cm^{-1} (**4**), the Hamiltonian being defined as $\hat{H} = -J\hat{S}_{Re}\cdot\hat{S}_M$]. The magnetic behavior of **A2** is that of a magnetically diluted Re(IV) complex with a large and positive value of the zero-field splitting for the ground level (D_{Re} = +37.0 cm^{-1}). In the case of **A1**, although its magnetic behavior is similar to that of **A2** in the high-temperature range (D_{Re} being +19.0 cm^{-1}), it exhibits a weak ferromagnetism below 3.0 K with a canting angle of 1.3°.



Although magneto-structural studies with second and third row transition metal ions have comparatively received less attention than those of 3d−3d and 3d−4f mixed systems,[1] there is an increasing interest in the magnetic properties of polynuclear compounds with the heavier elements for both fundamental and practical reasons.[2−19] Because of the more diffuse character of the 4d and 5d orbitals versus the 3d ones, a strengthening of the exchange coupling between the paramagnetic centers through the bridging ligands is expected by substitution of 3d ions by 4d or 5d ones. This enhancing of the magnetic interaction together with the larger spin anisotropy and higher spin−orbit coupling values that they exhibit are also important factors when thinking at the preparation of smart systems in molecular magnetism such as single molecule magnets (SMMs) and single chain magnets (SCMs).[20,21]

Among the paramagnetic heavy metal ions to be used with these ideas in mind, the Re(IV) seems to be an excellent candidate for several reasons: (i) the $S = 3/2$ spin ground state (a $5d^3$ metal ion) and relative redox stability that it exhibits in its six-coordinated complexes; (ii) the reluctance to the ligand exchange of these species, a point of special relevance in their use as ligands for metal assembling; (iii) its large magnetic anisotropy arising from spin−orbit coupling (λ ca. 1000 cm^{-1} in the free ion) with values of the zero-field splitting as large as ca. 60 cm^{-1} in some mononuclear compounds;[22] and (iv) the greater spin delocalization on its peripheral ligands, a feature that causes a strengthening of the magnetic coupling through a given bridging ligand in comparison to the related compounds with chromium(III) (a $3d^3$ metal ion) or even through space (intermolecular magnetic interactions).[23−26]

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Table 1. Crystal Data and Structure Refinement for $[M(Me_2phen)_2(\mu\text{-NCS})Re(NCS)_5]\cdot CH_3CN$ with M = Ni (1), Co (2), Fe (3), and Mn (4)[a]

	1	2	3	4
chem formula	$C_{36}H_{27}N_{11}NiReS_6$	$C_{36}H_{27}N_{11}CoReS_6$	$C_{36}H_{27}N_{11}FeReS_6$	$C_{36}H_{27}N_{11}MnReS_6$
M	1050.96	1051.18	1048.10	1047.22
a, Å	23.261(5)	23.105(5)	23.280(3)	23.140(4)
b, Å	12.169(2)	12.151(2)	12.091(1)	12.069(3)
c, Å	31.791(6)	32.372(7)	32.407(3)	32.482(7)
γ, deg	107.36(3)	106.21(3)	105.83(6)	106.21(2)
V, Å^3	8589(3)	8727(3)	8776(2)	8711(3)
D_c/Mg m^{-3}	1.625	1.600	1.587	1.646
$F(000)$	4152	4144	4136	4256
μ(Mo K), cm^{-1}	35.87	34.79	34.12	34.00
refln unique/obs	7622/4866	7722/4453	2319/1918	7733/2903
R^b	0.053	0.114	0.077	0.061
$R_w{}^{c,d}$	0.121	0.256	0.0212	0.120

[a] Details in common: $T = 293(2)$ K, space group $C2/c$, and $Z = 8$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/[\sum(w(F_o{}^2)^2]\}^{1/2}$. [d] $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$ with $P = [F_o{}^2 + 2F_c{}^2]/3$, a = 0.0751 (**1**), 0.1000 (**2**), 0.1346 (**3**), and 0.0579 (**4**) and b = 0 (**1**, **2**, and **4**) and 245.0783 (**3**).

Focusing on the relevant role played by the Re(IV) complexes in molecular magnetism, illustrative examples are the diversity of structures and magnetic behaviors observed through the use of the mononuclear species $[ReX_4(ox)]^{2-}$ (X = Cl and Br; ox = oxalate),[22a,b,27] $[ReX_4(mal)]^{2-}$ (mal = malonate),[28] $[ReCl_5(pyz)]^-$ (pyz = pyrazine),[29] (Hpyzc = 2-pyrazinecarboxylic acid),[30] *trans*-$[ReCl_4(CN)_2]^{2-}$,[31] and $[Re(CN)_7]^{3-}$[see refs 4c, d, and 32] as ligands toward either fully solvated metal ions of partially blocked complexes, some of them exhibiting slow relaxation of the magnetization.

Considering the aforementioned concepts and as a way to extend our previous studies on the chemistry and magnetic studies in rhenium(IV)-based compounds, we have focused on the study of thiocyanate as a bridging ligand between rhenium(IV) and 3d metal ions. The simultaneous presence of N and S donor atoms in the thiocyanate ligand would facilitate the development of a rich heteropolynuclear chemistry when acting as a bridge and also would involve an enhancement of the magnetic coupling due to the diffuse character of the valence orbitals of the sulfur atom. This idea has been materialized in a recent communication where the authors reported a value of the magnetic interaction of $J = -51$ cm^{-1} (the spin Hamiltonian being defined as $\hat{H} = -J\hat{S}_1\cdot\hat{S}_2$) for the thiocyanate-bridged Mo^{III}-NCS-Ni^{II} unit, a value which is twice as large as for the homologous Cr^{III}-NCS-Ni^{II} derivative.[6g]

At that respect, some of us have shown that the reaction of $[ReBr_6]^{2-}$ with an excess of thiocyanate in DMF affords the equimolar mixture of the linkage isomers (**A**) $[Re(NCS)_6]^{2-}$ and $[Re(NCS)_5(SCN)]^{2-}$ as tetra-*n*-butylammonium salts. After some workup both isomers could be selectively isolated as the compounds $(NBu_4)_2[Re(NCS)_6]$ (**A1**) and $[Zn(NO_3)(Me_2phen)_2]_2[Re(NCS)_5(SCN)]$ (**A2**) [$NBu_4{}^+$ = tetra-*n*-butylammonium and Me$_2$phen = 2,9-dimethyl-1,10-phenanthroline].[33] The use of **A** as a ligand toward $[M(Me_2dmphen)_2]^{2+}$ [M = Ni (**1**), Co (**2**), Fe (**3**), and Mn (**4**)] yielded the isostructural complexes of formula $[(Me_2phen)_2M(\mu\text{-NCS})Re(NCS)_5]\cdot CH_3CN$. Their synthesis, crystal structure, and variable-temperature magnetic study are presented in this work.

■ EXPERIMENTAL SECTION

Materials. All chemicals and solvents were purchased from commercial sources and used as received. The equimolar mixture of $[Re(NCS)_6]^{2-}$ and $[Re(NCS)_5(SCN)]^{2-}$ as $NBu_4{}^+$ salts (**A**) and the compounds $(NBu_4)_2[Re(NCS)_6]$ (**A1**) and $[Zn(NO_3)(Me_2phen)_2]_2[Re(NCS)_5(SCN)]$ (**A2**) were synthesized according to published methods.[33]

Synthesis of the Compounds $[M(Me_2phen)_2(\mu\text{-NCS})Re(NCS)_5]\cdot CH_3CN$ [M = Ni (1), Co (2), Fe (3), and Mn (4)]. Complexes **1**−**4** were prepared by using a common synthetic procedure: 0.025 mmol of **A** were added to an acetonitrile solution (15 mL) containing 0.150 mmol of $M(ClO_4)_2\cdot 6H_2O$ and 0.300 mmol of Me$_2$phen under continuous stirring at room temperature. The resulting solution was allowed to evaporate slowly in a hood under ambient conditions. X-ray quality crystals as dark red-brown irregular polyhedrons (**1**−**4**) were grown from the mother liquor after a few days. They were collected by filtration, washed with a small amount of acetonitrile and diethyl ether, and dried over filter paper. Yield (based on Re): ca. 40 (**1**), 50 (**2**), 25% (**3** and **4**). Anal. Calcd for $C_{36}H_{27}N_{11}S_6ReNi$ (**1**): C, 41.14; N, 14,66; H, 2.59; S, 18.31. Found: C, 41.76; N, 14.91; H, 2.34; S, 18.87. Anal. Calcd for $C_{36}H_{27}N_{11}S_6ReCo$ (**2**): C, 41.13; N, 14.66; H, 2.59; S, 18.30. Found: C, 41.35; N, 14.54; H, 1.87; S, 18.43. Anal. Calcd for $C_{36}H_{27}N_{11}S_6ReFe$ (**3**): C, 41.25; N, 14.70; H, 2.60; S, 18.36. Found: C, 40.92; N, 15.11; H, 2.34; S, 17.75. Anal. Calcd for $C_{36}H_{27}N_{11}S_6ReMn$ (**4**): C, 41.29; N, 14.71; H, 2.60; S, 18.37. Found: C, 41.85; N, 15.00; H, 2.33; S, 18.04. IR/cm^{-1}: bands associated with the thiocyanate ligand are located at 2019s, 2088w and 2159w (**1**); 2024s, 2088w, and 2156w (**2**); 2017s, 2091w, and 2150w (**3**); and 2016s, 2091w, and 2150w (**4**).

Physical Measurements. Elemental analyses (C, H, N, S) were performed on a Carlo Erba model 1108 elemental analyzer. The IR spectra were recorded with a Bomen MB-102 FTIR spectrometer as KBr pellets in the 4000−200 cm^{-1} range. Magnetic measurements on polycrystalline samples of **1**−**4**, **A1**, and **A2** were carried out with a Quantum Design SQUID magnetometer in the temperature range 1.9−300 K and under applied dc magnetic fields of 1 T ($T \geq 50$ K) and 100 G ($T < 50$ K) in order to avoid any problem of magnetic saturation. Diamagnetic contributions of the constituent atoms were estimated from Pascal's constants[34] as -556×10^{-6} (**1** and **2**), -557×10^{-6} (**3**), and -558×10^{-6} cm^3 mol^{-1} (**4**) [per Re(IV)-M(II) unit] and -628×10^{-6} (**A1**) and -889×10^{-6} cm^3 mol^{-1} (**A2**) [per Re(IV) ion]. Corrections for the sample holder (plastic bags of ca. 5.0 mg each one) were also applied.

X-ray Data Collection and Structure Refinement. Single crystals were mounted on a Bruker-Nonius X8-APEXII CCD area detector system (**3**) and on a Siemens $R3m$/V automatic four-circle diffactometer (**1**, **2**, and **4**) and the diffraction data were collected at room temperature by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A total of 1236 frames of data were collected for compound **3** through a narrow-frame method with scan widths of 0.3°

in ω and ϕ, exposure times of 30 s per frame and a crystal-to-detector distance of 40 mm. These data were processed through the SAINT[35] reduction and SADABS[36] absorption software to yield a total of 12841 reflections. The unit cell parameters for **3** were based upon least-squares refinement of 2823 reflections. Concerning compounds **1**, **2**, and **4**, a total of 7827 (**1**), 7928 (**2**), and 7932 (**4**) reflections were collected with the ω-2θ scan method and their unit cell parameters were determined from least-squares refinement of the setting angles of 25 reflections in the 2θ range of 15−30°. Information concerning crystallographic data collection and structure refinements of the four compounds is summarized in Table 1. Examination of two standard reflections monitored after every 50 reflections showed no sign of crystal deterioration. Lorentz-polarization and absorption correction through ψ-scan[37] (**1**) and XABS program[38] (**2** and **4**) were applied to the intensity data, maximum and minimum transmission factors being 0.4125 and 0.2952 for **1**. The structures were solved by standard Patterson methods through the SHELXTL structure determination package[39] and subsequently completed by Fourier recycling. In the refinement of the structure of compounds **1**, **2**, and **4**, the solvent molecules of acetonitrile were located on a ΔF map but their atoms have a large thermal motion because of the disorder. For this reason, their atomic coordinates were refined with restrains and a 0.5 occupancy factor. The atomic coordinates and the isotropic displacement parameter of the carbon atom of the methyl group from the solvent molecule were not refined in **4**. A reasonable model for the disordered solvent in the refinement of the structure of compound **3** could not be achieved. All non-hydrogen atoms (except those of the acetonitrile molecule in **1**, **2**, and **4** and the carbon and nitrogen atoms of the thiocyanate and Me_2phen ligands in **3**) were refined anisotropically. The hydrogen atoms from the solvent molecule were not defined. The other hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropically thermal parameter. Full-matrix least-squares refinements on F^2, carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, reached convergence with values of the discrepancy indices given in Table 1. The final geometrical calculations were carried out with the PARST program.[40] The graphical manipulations were performed using the XP utility of the SHELXTL structure determination package and WinGX and POV-Ray software.[41] The main interatomic bond distances and angles for **1**−**4** are listed in Table 2. Crystallographic data for the structures reported in this contribution have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 860884 (**1**), 860885 (**2**), 860886 (**3**), and 860887 (**4**). Copies of the data can be obtained free of charge on application to the CCDC, Cambridge, U.K. (http://www.ccdc.cam.ac.uk/).

■ RESULTS AND DISCUSSION

Syntheses and IR Spectroscopy. The use of the hexathiocyanaterhenate(IV) linkage isomers (mixture noted A) as a ligand toward first-row transition ions whose coordination sphere is partially blocked yielded heterobimetallic compounds where the Re(IV)-(μ-SCN)-M(II) bridging unit occurs [M = Ni (**1**), Co (**2**), Fe (**3**), and Mn (**4**)] (see structural discussion). This result shows that, under our experimental conditions, only the $[Re(NCS)_5(SCN)]^{2-}$ isomer is effective for the preparation and isolation of polynuclear species, being active as a ligand toward the investigated 3d metal ions. The preference of the divalent first-row transition metal ions to coordinate to the thiocyanate-N atom instead of the S atom is largely documented and has been generally explained in terms of their hard (N)/soft (S) character. Finally, it deserves to be noted that although the $[Re(NCS)_5(SCN)]^{2-}$ isomer was isolated as $[Zn(NO_3)(Me_2phen)_2]_2[Re(NCS)_5(SCN)]$ (**A2**),[33] its low solubility in acetonitrile precludes its use to prepare the heterobimetallic complexes **1**−**4**.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 1−4

	1	2	3	4
Re(1)−S(1)	2.473(3)	2.432(9)	2.438(12)	2.420(4)
Re(1)−N(2)	1.995(7)	1.98(2)	1.91(2)	2.020(13)
Re(1)−N(3)	2.018(8)	2.02(2)	2.12(3)	1.943(13)
Re(1)−N(4)	1.983(8)	1.99(2)	1.94(3)	1.932(14)
Re(1)−N(5)	2.002(7)	1.97(2)	1.92(3)	1.995(14)
Re(1)−N(6)	2.030(8)	1.99(2)	2.13(3)	1.969(14)
M(1)−N(1)	2.037(7)	2.12(3)	2.02(4)	2.108(14)
M(1)−N(7)	2.056(7)	2.15(2)	2.24(3)	2.241(14)
M(1)−N(8)	2.047(7)	2.03(2)	2.12(2)	2.192(13)
M(1)−N(9)	2.071(7)	2.08(1)	2.20(2)	2.216(12)
M(1)−N(10)	2.061(6)	2.02(2)	2.06(2)	2.183(11)
N(2)−Re(1)−S(1)	91.8(2)	90.5(5)	93.1(7)	92.5(4)
N(2)−Re(1)−N(3)	89.4(3)	90.8(7)	90.1(9)	90.6(5)
N(2)−Re(1)−N(5)	177.1(3)	177.6(7)	178.4(9)	177.6(5)
N(2)−Re(1)−N(6)	92.2(3)	89.8(7)	90.9(9)	90.7(5)
N(3)−Re(1)−S(1)	89.4(2)	87.9(5)	89.6(7)	89.6(4)
N(4)−Re(1)−S(1)	176.6(2)	175.1(5)	175.4(7)	175.1(4)
N(4)−Re(1)−N(2)	91.6(3)	94.4(7)	91.3(9)	92.4(5)
N(4)−Re(1)−N(3)	90.6(3)	91.6(7)	89.3(9)	90.5(5)
N(4)−Re(1)−N(5)	90.7(3)	87.8(7)	90.1(9)	89.4(5)
N(4)−Re(1)−N(6)	89.0(3)	86.7(7)	89.6(10)	89.7(5)
N(5)−Re(1)−N(3)	88.8(3)	88.2(7)	89.0(9)	87.8(5)
N(5)−Re(1)−S(1)	85.9(2)	87.3(6)	85.5(7)	85.7(4)
N(5)−Re(1)−N(6)	89.6(3)	91.3(7)	90.0(10)	90.9(5)
N(6)−Re(1)−S(1)	90.9(2)	93.7(5)	91.3(7)	90.1(4)
N(1)−M(1)−N(7)	81.7(3)	76.6(8)	81.5(11)	80.2(6)
N(1)−M(1)−N(8)	99.0(3)	107.7(8)	110.3(11)	108.2(6)
N(1)−M(1)−N(9)	89.9(3)	85.1(8)	85.3(11)	86.1(6)
N(1)−M(1)−N(10)	151.2(3)	135.1(8)	133.4(11)	132.5(6)
N(7)−M(1)−N(8)	82.0(3)	80.2(9)	75.5(1)	76.3(5)
N(7)−M(1)−N(9)	164.7(3)	159.4(7)	166.0(9)	165.5(5)
N(7)−M(1)−N(10)	100.5(3)	106.3(7)	110.5(9)	110.1(5)
N(8)−M(1)−N(9)	112.1(3)	114.9(8)	113.8(9)	112.9(5)
N(8)−M(1)−N(10)	109.7(3)	117.0(7)	116.3(9)	119.3(4)
N(9)−M(1)−N(10)	80.9(3)	80.2(6)	75.6(9)	76.0(4)
N(4)−Re(1)−S(1)	176.6(2)	175.1(5)	175.4(7)	175.1(4)
N(4)−Re(1)−N(2)	91.6(3)	94.4(7)	91.3(9)	92.4(5)
N(4)−Re(1)−N(3)	90.6(3)	91.6(7)	89.3(9)	90.5(5)
N(4)−Re(1)−N(5)	90.7(3)	87.8(7)	90.1(9)	89.4(5)
N(4)−Re(1)−N(6)	89.0(3)	86.7(7)	89.6(10)	89.7(5)
N(5)−Re(1)−N(3)	88.8(3)	88.2(7)	89.0(9)	87.8(5)
N(5)−Re(1)−S(1)	85.9(2)	87.3(6)	85.5(7)	85.7(4)
N(5)−Re(1)−N(6)	89.6(3)	91.3(7)	90.0(10)	90.9(5)
N(6)−Re(1)−S(1)	90.9(2)	93.7(5)	91.3(7)	90.1(4)
N(1)−M(1)−N(7)	81.7(3)	76.6(8)	81.5(11)	80.2(6)
N(1)−M(1)−N(8)	99.0(3)	107.7(8)	110.3(11)	108.2(6)
N(1)−M(1)−N(9)	89.9(3)	85.1(8)	85.3(11)	86.1(6)
N(1)−M(1)−N(10)	151.2(3)	135.1(8)	133.4(11)	132.5(6)
N(7)−M(1)−N(8)	82.0(3)	80.2(9)	75.5(1)	76.3(5)
N(7)−M(1)−N(9)	164.7(3)	159.4(7)	166.0(9)	165.5(5)
N(7)−M(1)−N(10)	100.5(3)	106.3(7)	110.5(9)	110.1(5)
N(8)−M(1)−N(9)	112.1(3)	114.9(8)	113.8(9)	112.9(5)
N(8)−M(1)−N(10)	109.7(3)	117.0(7)	116.3(9)	119.3(4)
N(9)−M(1)−N(10)	80.9(3)	80.2(6)	75.6(9)	76.0(4)
N(3)−Re(1)−N(6)	178.3(3)	178.2(7)	178.6(9)	178.7(5)

A weak intensity peak at ca. 2150 cm^{-1} in the IR spectra of **1**−**4** is assigned to the stretching vibration of the C≡N bond of the uncoordinated acetonitrile molecule.[19a] The presence of Me_2phen as a ligand in **1**−**4** is supported by the occurrence of several medium to weak intensity peaks in the range 3100−2800 cm^{-1} and around 1380 cm^{-1} which are attributed to the vibration of the aromatic and aliphatic C−H bonds. Anyway the more relevant aspect in the IR spectra of **1**−**4** concerns the possibility to detect the simultaneous presence of bridging and terminal thiocyanate ligands in them. In this respect, we will focus on the strong v(CN) absorption of the thiocyanate which appears in the high-frequency range 2100−2000 cm^{-1}. This band is located at 2019 (**1**), 2024 (**2**), 2017 (**3**), and 2016 cm^{-1} (**4**), being accompanied of two weak peaks at 2088 and 2159 cm^{-1} (**1**), 2088 and 2156 cm^{-1} (**2**), 2091 and 2150 cm^{-1} (**3**), and 2091 and 2150 cm^{-1} (**4**). Given that the IR spectra in this region of the structurally characterized compounds $(NBu_4)_2[Re(NCS)_6]$ (**A1**) and $[Zn(NO_3)(Me_2phen)_2]_2$ [Re(NCS)$_5$(SCN)] (**A2**) exhibit a strong absorption at 2032 (**A1**) and 2027 cm^{-1} (**A2**) and two weak peaks at 2087 and 2128 cm^{-1} (**A2**),[33] one can conclude that the peak around 2150 cm^{-1} in **1**−**4** is most likely due to the presence of the end-to-end thiocyanate bridge.

Description of the Structure of [M(Me$_2$phen)$_2$(μ-NCS)Re(NCS)$_5$]·CH$_3$CN [M = Ni (1), Co (2), Fe (3), and Mn (4)]. Compounds **1**−**4** are isostructural species and their structure consists of neutral [(Me$_2$phen)$_2$M(μ-NCS)Re(NCS)$_5$] [M = Ni (**1**), Co (**2**), Fe (**3**), and Mn (**4**)] heterodinuclear units (Figure 1) and uncoordinated acetonitrile molecules. Within each herobimetallic unit, five of the six thiocyanate groups act as terminal ligands being coordinated to the Re(IV) ion though the nitrogen atom whereas the remaining thiocyanate adopts the end-to-end bridging mode with its nitrogen atom bound to the M(II) ion.

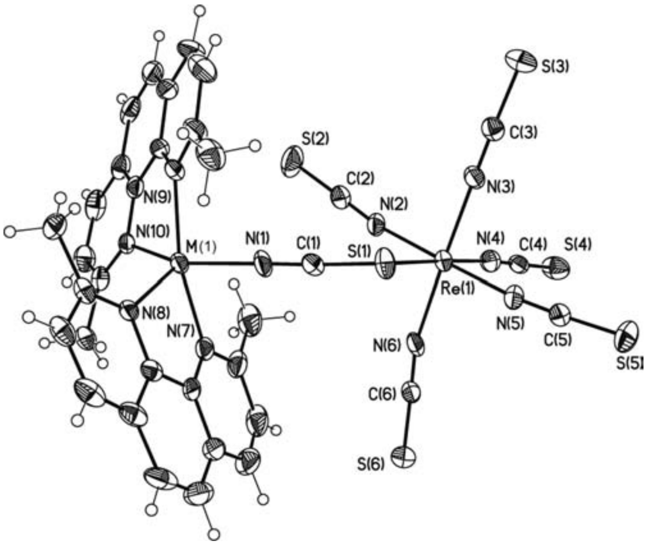


Figure 1. Perspective drawing of the [(Me$_2$phen)$_2$M(μ-NCS)Re(NCS)$_5$] heterobimetallic unit [M = Ni (**1**), Co (**2**), Fe (**3**), and Mn (**4**)] showing the atom numbering. Thermal ellipsoids are plotted at 30% probability level. The labels of the carbon atoms of the Me$_2$phen ligand have been omitted for clarity.

The Re(IV) ion is surrounded by five thiocyanate-*N* and one thiocyanate-*S* atoms in a distorted octahedral geometry. Both Re−N [mean values are 2.006(8) (**1**), 1.99(2) (**2**), 2.00(3) (**3**), and 1.97(1) Å (**4**)] and Re−S [2.473(3) (**1**), 2.432(9) (**2**), 2.438 (**3**), and 2.420(4) Å (**4**) Å] bond lengths are in agreement with those found in **A1** and **A2**[33] and in other thiocyanate-containing rhenium(IV) complexes.[42] The S(1)-N(2)N(4)N(5) set of atoms around the rhenium atom defines the equatorial plane [largest deviations from the mean plane are 0.017(4) (**1**), 0.005(9) (**2**), 0.002(11) (**3**), and 0.017(6) Å (**4**) at the N(4) atom], and the metal center lies in this plane in all four compounds. The M(II) atoms are five-coordinated with one thiocyanate-nitrogen and four nitrogen atoms from two bidentate Me$_2$phen ligands describing a highly distorted trigonal bipyramidal surrounding around the metal atoms. The τ values, defining the index of the degree of trigonality, are 0.23, 0.41, 0.54, and 0.55 for **1**−**4**.[43] The reduced values of the angle subtended at the metal atom by the chelating Me$_2$phen groups [mean values 81.0 (**1**), 80.2 (**4**), 75.6 (**3**), and 76.2°(**5**)] are the main factor for this distortion. The values of the M−N bond lengths [average values 2.054(7) (**1**), 2.08(2) (**2**), 2.13(2) (**3**), and 2.19(2) Å (**4**)] are in agreement with those observed in other thiocyanate-*N* bound metal complexes.[44] The equatorial plane in **1**−**4** is defined by the N(1)N(8)N(10) set of atoms, the metal center being practically in this plane. The two Me$_2$phen ligands are planar and the values of the dihedral angle between them are 62.2(1) (**1**), 64.6(3) (**2**), 62.8(4) (**3**), and 62.6(2)° (**4**). The thiocyanate ligands are quasi linear [the values of the N−C−S angle vary in the range 169(4)−179.5(9) °] and the bond lengths and angles within them are as expected in all compounds. A large bending at the S(1) atom is observed in **1**−**4**, the values of the Re(1)−S(1)−C(1) angle being 102.8(3) (**1**), 103.8(11) (**2**), 106.9(13) (**3**), and 103.9(7)° (**4**). The depart from the strict linearity of the M(1)−N(1)−C(1) fragment is small for **1** but more important for **2**−**4** [M(1)−N(1)−C(1) = 177.1(8) (**1**), 174(2) (**2**), 162(3) (**3**), and 168(2)° (**4**)]. The values of the Re···M separation through the bridging thiocyanato [5.903(1) (**1**), 6.117(3) (**2**), 6.082(5) (**3**), and 6.097(2) Å (**4**)] are shorter than the intermolecular Re···M(1a) distances [7.652(2) (**1**), 7.435(4) (**2**), 7.524(5) (**3**), 7.447(3) (**4**) Å; symmetry code: (a) = $x - {}^1/_2$, $y + {}^1/_2$, z]. Very weak intermolecular sulfur−sulfur contacts are observed in the crystal packing along the crystallographic *a* axis with S(3)···S(6b) distances of 3.846(5) (**1**), 3.76(1) (**2**), 3.758(2) (**3**), and 3.808(8) Å (**4**) Å [see Figure 2; symmetry code: (b) = $x - {}^1/_2$, $y - {}^1/_2$, z] leading to a supramolecular chain of neutral heterobimetallic units. Furthermore, these chains are interconnected by weak π−π offset interactions between the aromatic rings of the Me$_2$phen molecules to afford a supramolecuar layered structure growing in the crystallographic *ab* plane (Figure. 2).

Magnetic Study. This section will be organized as follows: (i) We will present first the magnetic properties of the mononuclear compound **A2** in order to visualize the magnetic behavior of the [Re(NCS)$_5$(SCN)]$^{2-}$ unit which is also present in the complexes **1**−**4**. (ii) In a second step, we will focus on the magnetic properties of the parent mononuclear compound **A1**, for which its original magnetic behavior (weak ferromagnetism through spin canting), moved us to discuss its magnetic properties separately. (iii) Finally, the magnetic properties of the heterobimetallic compounds **1**−**4** will be described and discussed together given that they exhibit a similar antiferromagnetic coupling.

*(i) Magnetic Behavior of [Zn(NO$_3$)(Me$_2$phen)$_2$]$_2$[Re(NCS)$_5$(SCN)] (**A2**).* The magnetic properties of **A2** in the form of $\chi_M T$ versus T [χ_M being the magnetic susceptibility per one Re(IV) ion] are shown in Figure 3. At room temperature, $\chi_M T$ is 1.55 cm^3 mol^{-1} K, a value which is as expected for a

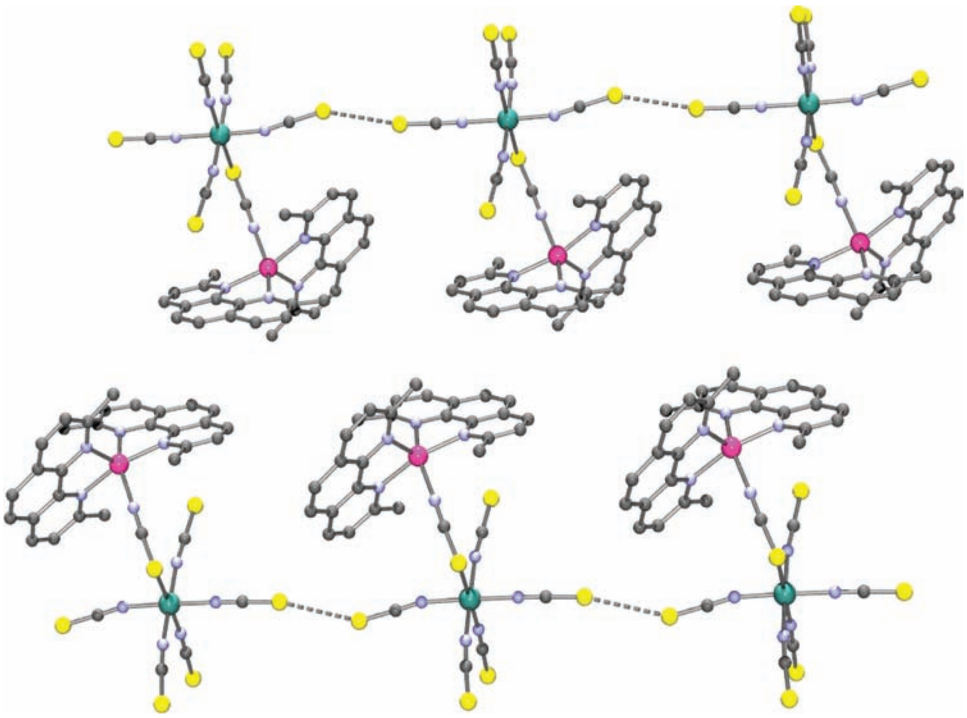


Figure 2. View of the packing showing the π–π staking interactions together with the shortest S···S contacts (broken lines) between the $[(Me_2phen)_2Ni(\mu\text{-}NCS)Re(NCS)_5]$ (**1**) heterobimetallic units. The same holds for the isostructural compounds. Color code: green (Re), magenta (Ni), yellow (S), light blue (N) and gray (C).

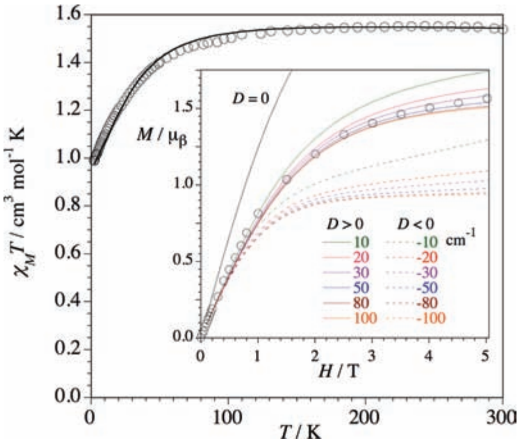


Figure 3. Thermal variation of $\chi_M T$ for **A2**: (○) experimental; (—) best-fit curve through eq 2 (see text). (inset) Magnetization versus H plot for **A2** at 2.0 K: (○) experimental; (—) and (---) calculated curves for $D > 0$ and $D < 0$, respectively.

magnetically isolated mononuclear Re(IV) compound ($S = 3/2$, $g \approx 1.8$–1.9). This value remains practically constant upon cooling until 150 K, and it decreases at lower temperatures tending to a finite value close to 1.0 cm^3 mol^{-1} K at 1.9 K. This magnetic behavior corresponds to that of a magnetically isolated mononuclear rhenium(IV) complex, the magnetic dilution of the paramagnetic $[Re(NCS)_5(SCN)]^{2-}$ units being ensured by the bulky diamagnetic $[Zn(phen)_2(NO_3)]^+$ cations which most likely maximizes the S···S separation between adjacent anions (the shortest S···S contact is ca. 3.98 Å). The observed decrease of $\chi_M T$ for **A2** is due to zero-field splitting effects of the six-coordinated Re(IV) ion, as discussed in previous reports.[22a−c,23b,27e,g,h,28c] These effects also account for the low value of the magnetization (M) at 5 T, the largest value of the applied dc field in our device: $M = 1.47$ μ_β for **A2** at 2.0 K (see inset of Figure 3), a value to be compared with the expected one for the saturation magnetization ($M_S = 2.7$ μ_β for a $S = 3/2$ ion with $g = 1.8$).

Having these features in mind, the magnetic data of **A2** were analyzed through the Hamiltonian of eq 1 and its derived theoretical expression for the magnetic susceptibility [eq 2]

$$\hat{H} = D[\hat{S}_z^{\,2} - S(S+1)/3] + g_{\|}\beta H_z\hat{S}_z + g_{\perp}\beta(H_x\hat{S}_x + H_y\hat{S}_y) \tag{1}$$

$$\chi_{\|} = \frac{N\mu_B^{\,2}g_{\|}^{\,2}}{4k(T-\theta)}\,\frac{1 + 9\exp(-2D/kT)}{1 + \exp(-2D/kT)}$$

$$\chi_{\perp} = \frac{N\mu_B^{\,2}g_{\perp}^{\,2}}{k(T-\theta)}\,\frac{1 + (3kT/4D)[1 - \exp(-2D/kT)]}{1 + \exp(-2D/kT)}$$

$$\chi_m = \frac{\chi_{\|} + 2\chi_{\perp}}{3} \tag{2}$$

The first term in eq 1 accounts for the zero-field splitting of the Re(IV) center ($2D$ is the energy gap between the two $M_S = \pm 3/2$ and $M_S = \pm 1/2$ Kramers doublets), and the last two terms correspond to the Zeeman effects. A θ parameter was included in eq 2 to account for the intermolecular interactions. Although they are very small in **A2** (if any), they are present in the related **A1** compound (see below). Given that it is not possible to get reliable and unique values for $g_{\|}$ and $g_{\perp}$ from magnetic susceptibility measurements on polycrystalline samples and to avoid overparametrization, we assumed that $g_{\|} = g_{\perp} = g$ (average Landé factor). Best-least-squares parameters through the analysis of the $\chi_M T$ data for **A2** are

Table 3. Best Fit Parameters for A1, A2, and 1−4

compound	J/cm^{-1}	D_{Re}/cm^{-1}	D_M/cm^{-1}	g_{Re}	g_M	θ/K
A1		19.0(2)		1.81(1)		1.30(2)
A2		37.0(3)		1.82(1)		
1 (ReNi)	−4.3(1)	27.0(5)	2.0(2)	1.80(1)	2.21(1)	
2 (ReCo)	−2.4(1)	34.0(5)	1.8(1)	1.81(1)	2.30(1)	
3 (ReFe)	−1.80(3)	34.5(5)	12.5(2)	1.89(1)	2.24(1)	
4 (ReMn)	−1.30(2)	38.0(5)	0[a]	1.80(1)	2.00[a]	

[a] Fixed values.

listed in Table 3 together with those for **A1** and the heterobimetallic compounds **1**−**4**. The calculated curve (solid line in Figure 3) reproduces well the magnetic data in the whole temperature range investigated. Although the magnitude of the absolute value of the D_{Re} can be determined quite accurately from the magnetic susceptibility measurements on powder samples, this is not the case for its sign. At this respect, the magnetization measurements (M vs H plot) at low temperature are very sensitive to the sign of D_{Re}, but not to its size when D_{Re} is large ($|D_{Re}| > 20$ cm^{-1}). This is illustrated by the inset of Figure 3 where theoretical M vs H curves at 2.0 K for different values of D_{Re} both positive (solid lines) and negative (dashed lines) are plotted. One can see therein that the experimental data are in the region of the positive values and well above from that of the negative ones. Moreover, the experimental data closely follow the calculated plots in the range of 30−50 cm^{-1} for D_{Re}, according to the obtained one from the $\chi_M T$ data ($D_{Re} = 37.0$ cm^{-1}).

(ii) (NBu$_4$)$_2$[Re(NCS)$_6$] ***(A1)***. The magnetic properties of **A1** in the form of $\chi_M T$ versus T [χ_M being the magnetic susceptibility per one Re(IV) ion] are shown in Figure 4. The shape of the $\chi_M T$ versus T plot in the high temperature region is similar to that observed for **A2**. At room temperature, $\chi_M T$ is 1.53 cm^3 mol^{-1} K, a value as expected for a magnetically diluted Re(IV) compound. At lower temperatures, it decreases to reach a minimum value of 0.8 cm^3 mol^{-1} K at ca. 4.0 K (see Supporting Information Figure S1) and below this temperature an abrupt increase of $\chi_M T$ occurs and it becomes field dependent. Two conclusions can be extracted from these features: (i) first, the presence of a significant intermolecular antiferromagnetic coupling supported by the fact that the value of $\chi_M T$ at the minimum (ca. 0.8 cm^3 mol^{-1} K) is well below 1.0 cm^3 mol^{-1} K, being this value the limit one for $\chi_M T$ in a magnetically isolated Re(IV) when $T \to 0$ ($\lim_{T\to 0} \chi_M T = 9 g_{av}^2/32 \approx 1$ with $g_{av} = 1.85$ and $kT \ll |D|$)[22a,28b] and (ii) second, the occurrence of a spin canting which is responsible for the increase of $\chi_M T$ at very low temperatures, the value of the magnetic ordering ($T_c = 3.0$ K) being given by the position of the frequency-independent maximum of the out-of-phase signal (Figure 5), as well as the field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves (inset of Figure 4).

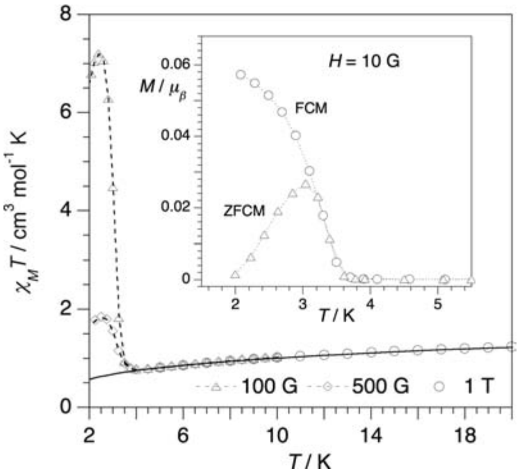


Figure 4. Thermal variation of $\chi_M T$ for **A1** under applied dc fields of 100 G (Δ), 500 G (◊), and 1 T (○): (—) best-fit curve through eq 2 (see text); (---) eye-guide lines. (inset) Field-cooled (FCM) and zero-field cooled (ZFCM) magnetizations under 10 G.

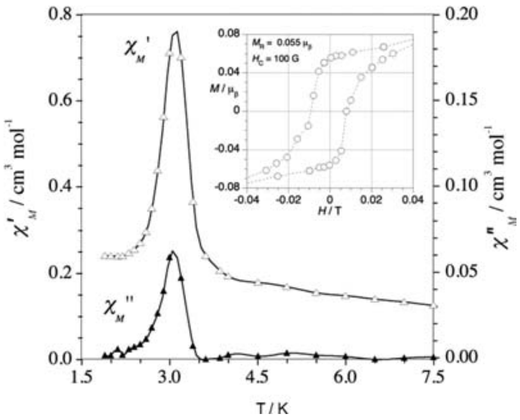


Figure 5. In-fase (χ_M') and out-of-phase (χ_M'') ac susceptibility for **A1** at a frequency of 100 Hz and under an oscillating field of 1 G. The inset shows the hysteresis loop of **A1** at 2.0 K.

Compound **A1** behaves as a soft magnet as evidenced by the magnetic hysteresis loop at 2.0 K (see inset of Figure 5) with values of the coercive field (H_c) and remnant magnetization (M_r) of 100 G and 0.055 μ_β, respectively. The evaluation of the canting angle (α) in **A1** can be done through the expression sin $\alpha = M_{cant}/M_{Re}$ where M_{cant} is the magnetic moment of the canting and M_{Re} is the magnetic moment of the magnetically isolated Re(IV).[45] A value of $\alpha = 1.3°$ can be roughly estimated by assuming that $M_{Re} = g M_s \mu_\beta = 2.72\ \mu_\beta$ (using $g = 1.81$ and $M_s = 3/2$) and that $M_{cant} \approx 0.062\ \mu_\beta$ which can be obtained from the saturation value of the FC magnetization curve (inset of Figure 4). This last value is very close to that obtained for the remnant magnetization at 2.0 K ($M_r = 0.055\ \mu_\beta$; see inset of Figure 5). The magnetic anisotropy of the Re(IV) cation has to be at the origin of the observed spin canting in **A1**, a phenomenon that we observed previously in other structurally characterized mononuclear Re(IV) species[26a,g] as well as in three-dimensional complexes containing six-coordinate high-spin Co(II)[46] or iron(II) ions.[47]

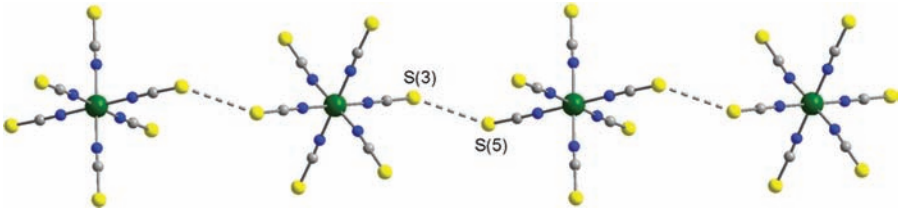


Figure 6. View of a fragment of the intermolecular chain arrangement of the $[Re(NCS)_6]^{2-}$ unit in **A1** through weak S···S contacts (cif file CCDC 661361 retrieved from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif). Color code: green (Re), yellow (S), blue (N), and gray (C).

The analysis of the magnetic data of **A1** from room temperature until 4.0 K through eq 2 leads to the θ, D, and g values listed in Table 3. The calculated curve (solid line in Figures 4 and Supporting Information S1) matches well the magnetic data down to 4.0 K. As far the weak intermolecular antiferromagnetic coupling is concerned ($\theta = -1.3$ K), a detailed inspection of the crystal packing in **A1** shows that the possible exchange pathway involved would be provided by the chain arrangement of the $[Re(NCS)_6]^{2-}$ units through weak intermolecular S···S contacts[48] of ca. 3.848 Å (see Figure 6) which are shorter than the corresponding ones for **A2** (S···S contacts of ca. 3.98 Å). This intermolecular AF interaction can be also observed on the M versus H plot for **A1** at 2.0 K (Supporting Information Figure S2), the experimental magnetization values at low fields are below those of the expected values for magnetically noninteracting Re(IV) ions. Moreover, a positive value for D_{Re} is inferred looking at the high field region where the experimental data reach the expected values for $D_{Re} > 0$.

The value of $D_{Re} = +19.0\ cm^{-1}$ for **A1** is similar to those observed for other mononuclear Re(IV) complexes (values of D_{Re} in the range 9–25 cm^{-1} were obtained for magnetically isolated $[ReX_6]^{2-}$ units being X = Cl, Br, and I).[22a,b] However, it is smaller than the observed one for **A2** ($D_{Re} = +37.0\ cm^{-1}$) due to the larger axial distortion of this last compound caused by the sulfur coordination of one of the six thiocyanato groups (ReN_5S and ReN_6 chromophores in **A1** and **A2**, respectively). In this respect, the greater distortion of six coordinated Re(IV) ion in the mononuclear $[Re(Cl_4(ox)]^{2-}$ complex ($ReCl_4O_2$ chromophore) accounts for the even larger D_{Re} (ca. 60 cm^{-1}).[22a,b]

(iii) Heterodinuclear Compounds ***1–4***. The magnetic properties of the complexes **1–4** under the form of $\chi_M T$ versus T plot [χ_M being the magnetic susceptibility per Re(IV)M(II) heterobimetallic unit with M = Ni (**1**), Co (**2**), Fe (**3**), and Mn (**4**)] are shown in Figure 7. The shape of these curves are qualitatively very similar: a quasi Curie law behavior in the high temperature domain which is followed by a decrease in the low temperature range. At room temperature, the values of $\chi_M T$ are 2.7 (**1**), 4.0 (**2**), 5.4 (**3**), and 5.8 $cm^3\ mol^{-1}$ K (**4**). They are as expected for magnetically noninteracting Re(IV)-M(II) pairs with $S_M = 1$ (**1**), 3/2 (**2**), 2 (**3**), and 5/2 (**4**).

Having in mind the large value of the zero-field splitting of the Re(IV) (**1–4**) and that of the five-coordinated high-spin Ni(II) (**1**), Co(II) (**2**), and Fe(II) (**3**) ions, the observed decrease of $\chi_M T$ in the low temperature region for **1–4** would be mainly governed by these splitting effects together with the possible weak magnetic interactions. In this respect, because of the values of $\chi_M T$ when $T \to 0$ for magnetically isolated Re(IV)-M(II) pairs (assuming a zero-field splitting for the metal ions)[28b] are greater than the respective experimental ones of **1–4** at 1.9 K [0.40 (**1**), 1.50 (**2**), 1.80 (**3**), and 2.20 $cm^3\ mol^{-1}$ K (**4**)], a weak intramolecular antiferromagnetic interactions occurs in the present family of complexes.

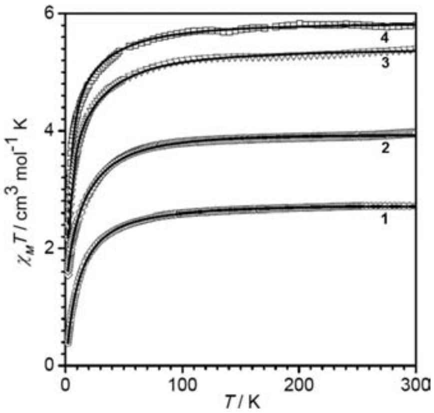


Figure 7. Thermal variation of the $\chi_M T$ product for **1** (○), **2** (◊), **3** (∇), and **4** (□). The solid lines are the best fit curves through eq 3 (see text).

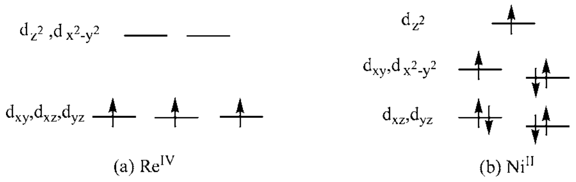
Having these considerations in mind, the magnetic data of the heterodinuclear compounds **1–4** were treated through the Hamiltonian of eq 3

$$\hat{H} = -J\hat{S}_{Re}\cdot\hat{S}_M + D_{Re}[\hat{S}_{zRe}^{\ 2} - 5/4] + D_M[\hat{S}_{zM}^{\ 2} - n(n+2)/12] + \beta H(g_{Re}\hat{S}_{Re} + g_M\hat{S}_M) \qquad (3)$$

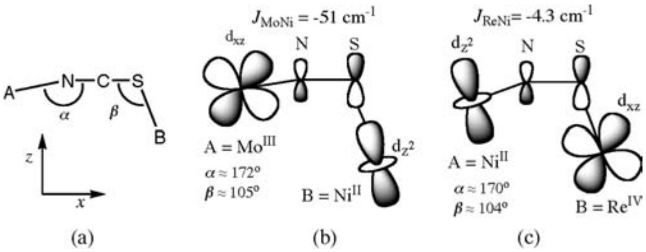
where J is the exchange coupling parameter between the Re(IV) and M(II) local spins, $2D_{Re}$ is the energy gap between the $M_S = \pm 3/2$ and $M_S = \pm 1/2$ Kramers doublets, D_M is the zero- field splitting of M(II) ions, and n is the number of unpaired electrons on M(II) [n = 2, 3, 4, and 5 for Ni(II), Co(II), Fe(II), and Mn(II), respectively]. The last term in eq 3 accounts for the Zeeman effects of the two metal ions. It deserves to be noted that because of the five-coordinated environment of the M(II) ions, a ground term orbitally nondegenerate for all M(II) ions is in order. Moreover, in order to avoid overparametrization, we have assumed $g_{\parallel} = g_{\perp} = g$ for the metal ions. Least-squares fit of the magnetic data of **1–4** using matrix-diagonalization techniques through the VMPAG program[49] provided the parameters listed in Table 3. A satisfactory match between the magnetic data and the calculated curves is obtained for all the compounds in the whole temperature ranges investigated.

We would finish this contribution with a brief discussion of the best-fit parameters for **1–4** which are listed in Table 3. The values of the average Landé factors of the involved metal ions (g_{Re} and g_M) are reasonable and those of the D_{Re} are close to that of the **A2** precursor and also lie within the range of those previously reported for other magneto-structurally characterized compounds. As far as the values of the D_M are concerned, they are in the range of the reported values for five-coordinated M(II) metal ions.[50] Finally, the values of the magnetic coupling in **1**−**4** show the occurrence of weak antiferromagnetic interactions between the Re(IV) and M(II) ions through the single end-to-end thiocyanate bridge, the intramolecular Re···M separation covering the range 5.903(1)−6.117(3) Å. Due to the possible intermolecular interactions in **1**−**4** (weak S···S contacts), the computed values of J would correspond to the upper limit. It deserves to be noted that it was impossible to reproduce the magnetic data of **1**−**4** by using a θ parameter accounting for the magnetic coupling.

Scheme I. Magnetic Orbitals of Re(IV) (Octahedral) and Ni(II) (Distorted Trigonal Bipyramidal) in Compound 1



Scheme II. Orbital Picture Illustrating the Exchange Pathways for Re(IV)(*μ*-SCN)Ni(II) and Ni(II)(*μ*-SCN)Mo(III) Fragments



At first sight, these results seem surprising given that in a recent magneto-structural report concerning the related heterobimetallic Ni^{II} ($3d^8$)-(μ-SCN)-M^{III} [M = Cr ($3d^3$) and Mo ($4d^3$)] systems, large antiferromagnetic interactions were observed through the end-to-end thiocyanate bridge, J_{NiCr} = −25 cm^{-1} and J_{NiMo} = −51 cm^{-1}.[6g] In particular, this last large antiferromagnetic coupling contrasts with the weak magnetic interaction in the parent Ni^{II} ($3d^8$)-(μ-NCS)-Re^{IV} ($5d^3$) (compound **1**). A visualization of the overlap between the magnetic orbitals involved in the Ni^{II}-(μ-NCS)-Re^{IV} (**1**) and Ni^{II}-(μ-SCN)-Mo^{III} fragments (see Schemes I and II) would account for this apparent anomaly. The magnetic orbitals of the Re(IV) ($5d^3$) and Ni(II) ($3d^8$) ions in octahedral and distorted trigonal bipyramidal surroundings respectively, are shown in Scheme I, whereas the relevant magnetic orbitals involved in the exchange pathway through the end-to-end thiocyanate bridge are depicted in Scheme II. The curious linkage isomerism of the bridging thiocyanato in the Re(IV)−Ni(II) system (compound **1**) leads to the opposite situation respect to the Mo(III)−Ni(II) system. As a result of this reversal of the bridge, one can see the good overlap expected (and then the stronger antiferromagnetic interaction) between the magnetic orbitals in the Mo(III)−Ni(II) system (Scheme IIb), whereas a very poor overlap (a situation of quasi orthogonality) is predicted for the Re(IV)−Ni(II) pair (Scheme IIc). The quasi linearity at the A−N−C fragment (α values of 172 and 170°) versus the large bending at the B−S−C one (β values of 105 and 104°) are the structural factors responsible for the different magnetic couplings observed. This situation can be extrapolated to the other Re(IV)-M(II) compounds of the present work with M = Co(II) (**2**), Fe(II) (**3**), and Mn(II) (**4**) with $3d^7$, $3d^6$, and $3d^5$ electronic configurations, respectively. At that respect, the exchange coupling parameter J_{ReM} is expressed by means of the individual interaction J_{ij} after eq 4[51]

$$J_{ReM} = (1/n_i n_j) \sum_{i,j} J_{ij} \tag{4}$$

where n_i and n_j are the number of unpaired electrons on the Re(IV) (n_i = 3) and M(II) ions [n_j = 2 (Ni), 3 (Co), 4 (Fe), and 5 (Mn)]. The weakening of the antiferromagnetic coupling observed when going from Ni(II) to Mn(II) (see Table 3) is associated to the fact that the increase of the magnetic orbitals [two in Ni(II) versus five in Mn(II)] makes possible the occurrence of orthogonality between some of the involved magnetic orbitals and, then, positive contributions to the magnetic coupling that would counterbalance the negative terms.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files of compounds **1**−**4** in CIF format and $\chi_M T$ versus T (Figure S1) and M versus T (Figure S2) plots for compound **A1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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