

Ab Initio Calculations of the Magnetic Exchange Coupling in Sulfur-Bridged Binuclear Ni(II) Complexes

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ABSTRACT: The geometry dependence of the exchange integrals and the total energies of sulfur-bridged complexes of the types $L_5NiSNiL_5$, $L_4NiS_2NiL_4$, and $L_3NiS_3NiL_3$ is studied by quantum chemical ab initio methods. The linear monobridged complex is antiferromagnetic, the bi- and triply-bridged complexes are ferromagnetic for NiSNi angles between 85° and 100° and antiferromagnetic for smaller and larger angles. The superexchange mechanism is analyzed, and a comparison with oxygen-bridged complexes and experimental data is performed. © 1997 John Wiley & Sons, Inc. *Int J Quant Chem* 65: 633–641, 1997

Introduction

Though sulfur-bridged binuclear Ni(II) units are the active sites in some enzymes, e.g., urease [1–3], not much is known about the magnetic coupling of the spins at the two Ni^{2+} cations in S-bridged binuclear Ni(II) complexes of the general form $LNiS_nNiL$, $n = 1, 2, 3$, with one, two, or three sulfur bridges (L stands for any terminal ligands). In urease, it seems that the Ni(II) ions are all high spin and exhibit a weak antiferromagnetic coupling ($J = -6 \text{ cm}^{-1}$) [1–3]. Trinuclear

complexes of the form $LNiS_3NiS_3CoL$ and $LNiS_3NiS_3NiL$ with octahedrally coordinated Ni(II) ions have been recently synthesized by Beissel et al. [4]. The analysis of magnetic susceptibility measurements yielded values of about -30 cm^{-1} for the exchange coupling between two adjacent Ni(II) ions bridged by three S atoms (which, however, are not isolated S atoms or S^{2-} anions, but belong to the ligand system). Such values indicate that the antiferromagnetic coupling is stronger than in similar oxygen-bridged complexes, but it is not certain whether differences in the geometries, partial d -occupations of the sulfur atoms in the bridging unit or other reasons are the source for the stronger antiferromagnetism in S-bridged systems. One trinuclear sulfur-bridged nickel thiolate cluster with an almost planar Ni_3S_3 ring has been reported recently in the literature as

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well [5]. This complex, however, contains Ni^{2+} cations in square-planar coordination and is diamagnetic. To the best of our knowledge, no further bi- or trinuclear S-bridged Ni(II) complexes are known for which both X-ray structures and magnetic susceptibility data have been determined.

In a previous work [6] we have presented *ab initio* calculations for the exchange coupling in oxygen-bridged NiONi and NiO₂Ni systems, together with an analysis of the geometry dependence of the exchange integral J . The present work extends this study to S-bridged Ni(II) complexes of the form LNiS_nNiL , $n = 1, 2, 3$. Since the Ni–S distances vary considerably in different compounds, we analyzed the geometry dependence of the total energies and of the exchange integrals in the mono- and bridged complexes and compared the results to those of oxygen-bridged complexes.

The study is organized as follows: The second section gives a brief description of the method of calculation. The third section contains the results for the linear monobridged complexes, the fourth and fifth sections those for the bi-bridged and triply-bridged complexes, respectively. The last section gives a short summary.

Method of Calculation

The present calculations have been performed in essentially the same way as in our previous study [6] on oxygen-bridged Ni(II) complexes. They consist of mainly three steps:

1. A self-consistent field (SCF) or, more precisely, a restricted open-shell Hartree–Fock (ROHF) calculation for the high-multiplicity state: For all complexes in this study this is a quintet state since the two Ni(II) ions, each of them with a d^8 configuration and a spatially nondegenerate ${}^3A_{2g}$ ($S = 1$) ground state in octahedral coordination, can be coupled to a quintet ($S = 2$), a triplet ($S = 1$), and a singlet ($S = 0$) state.
2. A full valence configuration interaction (VCI) calculation [7] using the ROHF orbitals of the first step, or alternatively a complete active space SCF (CASSCF) calculation [8] for all three states (quintet, triplet, singlet) simultaneously or for each of the states separately in order to reoptimize the orbitals for the triplet

and singlet states. There is virtually no difference between these three treatments since the three electronic states are very close in energy. The active space for the VCI and CASSCF calculations consisted of the four e_g -type $3d$ atomic orbitals (AOs) at the two Ni atoms (for more details see Ref. [6]).

3. Dynamic correlation effects are included on top of the VCI or CASSCF calculation by the multiconfiguration coupled electron pair approach (MC-CEPA) method [9]. We have always correlated the ten $3d$ AOs at the metal atoms and the $3s, 3p$ valence orbitals at the bridging S atoms. In general, the averaged coupled pair functional (ACPF) variant of our MC-CEPA program [9] has been used, since this variant yields the most reliable values for the exchange splittings [6].

It has been found before [6, 10–12] that the inclusion of dynamic correlation effects is necessary if one wants to calculate reliable values for exchange integrals. The main reason is that the antiferromagnetic contribution, J_{AF} , to the total exchange integral J is determined by the extent to which “ionic” (charge transfer) configurations are mixed to the dominant “neutral” (covalent) ones in the VCI. As long as the ionic configurations are built up from orbitals which have been optimized for covalent states and no relaxation effects are accounted for, their energies are too high and consequently their contribution to J_{AF} is too small. In a separate study [10] we present “effective” CI calculations in which the VCI matrix is modified in such a way as to simulate these relaxation effects in an effective and cheap manner. In the present work we have simply scaled the antiferromagnetic contribution with a weighting factor, which has been determined by a comparison between VCI and ACPF results. More details are given in the section on the bridged $\text{L}_4\text{NiS}_2\text{NiL}_4$ complex.

In order to save computer time, we have replaced the bulky terminal ligands, which are necessary in the experimental work to stabilize the rather unstable bi- and trinuclear complexes, by the He-like model ligands introduced in the earlier studies of this series [6, 11, 12]. In the present calculations the same parameters have been used as optimized before for the NiONi and NiO₂Ni complexes [6], i.e., an effective charge of 1.80 for the He-like model ligands L and a Ni–L distance

of 1.725 Å. In all complexes the number of terminal ligands was chosen in such a way that each metal ion had a full though distorted octahedral coordination.

The two Gaussian basis sets that have been used in the present calculations are summarized in Table I. The basis set for the model ligand is identical to the one optimized before for NiONi [6]. For Ni and S, the basis I has double zeta (DZ) quality, basis II has triple zeta plus polarization (TZP) quality.

Since the difference in the antiferromagnetic coupling through O and S bridges may be attributed to a partial *d*-occupation in the S^{2-} bridging ions, we have systematically varied the *d* exponent at the S-atom between 0.0 (no *d* functions) and 1.5 and monitored its influence on both the total energies and the value of *J*, i.e., the splitting between the lowest singlet, triplet, and quintet states. These tests have been performed for a linear NiSNi complex at a fixed Ni–S distance of 2.20 Å (i.e., slightly shorter than the equilibrium distance, compare next section) and for a bent NiS₂Ni complex in the vicinity of its SCF equilibrium structure with $R(\text{Ni–S}) = 2.35$ Å and $\angle \text{NiSNi} = 90^\circ$ (see fourth section). Basis set I was used for these tests. The results of these calculations can be summarized shortly as follows: The optimum value for the *d* exponent—as judged from the gain in the total energies—is about 0.2 at the CASSCF and 0.3 at the ACPF level. The gain in total energy is rather small at the CASSCF level (≈ 0.020 a.u. for the linear NiSNi complex and ≈ 0.050 a.u. for NiS₂Ni), but large at the ACPF level (≈ 0.120 a.u. for NiSNi; NiS₂Ni was not treated at this level). The *J* values, on the other hand, are hardly affected by the change of the *d* exponent: At the

CASSCF level there is no noticeable influence of the *d* functions on *J*. This holds both for the NiSNi and the NiS₂Ni complexes, but for the bridged complex with an NiSNi angle of 90° the antiferromagnetic part of the magnetic coupling is so small that statements concerning the *d* contribution are not conclusive. At the ACPF level, the contribution of the *d* AOs to *J* is in the order of 10% for the linear NiSNi unit.

The results of these basis tests indicate that the *d* orbitals at the bridging sulfur atoms do not directly influence the active orbitals, but are only needed for describing dynamic correlation and relaxation effects. All calculations reported in the next sections are performed with basis II and a *d* exponent of 0.3 (compare Table I).

Linear L₅NiSNiL₅ Complex

Table II contains our results for the total energy of the $^1A_{1g}$ ground state and for the exchange integral *J* in the linear monobridged L₅NiSNiL₅ complex, as functions of the Ni–S distance. Only the results of the ACPF variant of our MC-CEPA program [9] are included. As mentioned above, all metal 3*d* and the sulfur 3*s*3*p* orbitals have been correlated.

From the data of Table II one can conclude that the equilibrium distance amounts to 2.32 Å at the VCI (or SCF) level and is slightly shortened to 2.28 Å at the ACPF level. A direct comparison with experiment is not possible since no X-ray structure of a complex with a linear NiSNi bridge is known and since our calculations have been performed with the model ligands, which make the complex charge neutral. Bulky terminal ligands, effective

TABLE I
Gaussian basis sets for S-bridged binuclear Ni(II) complexes.

Atom	Type	Contraction	Ref.
		Basis I	
Ligand	TZ	$7s \rightarrow 3s(5,2^*1)$ (30.2, 9.8, 3.5, 1.4, 0.55, 0.17, 0.05)	6
Ni	DZ	$12s6p4d \rightarrow 7, 5^*1; 4, 2^*1; 2, 2^*1$	13
S	DZ	$9s5p \rightarrow 4, 5^*1; 2, 3^*1 + 1s(0.1), 1p(0.1)$	14
		Basis II	
Ligand	TZ	As basis I	
Ni	TZP	$14s9p5d \rightarrow 10, 4^*1; 6, 3^*1; 3, 2^*1 + s(0.35), f(2.0)$	15
S	TZP	$11s7p \rightarrow 5, 6^*1; 4, 3^*1 + 2s(1.0, 0.075), 2p(1.0, 0.075), 1d(0.3)$	14

TABLE II
VCI and ACPF results for the total energy and the exchange integral J in the linear $L_5NiSNiL_5$ complex.^{ab}

$R(Ni-S)$ Å	$E(^1A_{1g})$ a.u. VCI	$J_{0 \rightarrow 1}$ cm^{-1} VCI	$J_{1 \rightarrow 2}$ cm^{-1} VCI	$E(^1A_{1g})$ a.u. ACPF	$J_{0 \rightarrow 1}$ cm^{-1} ACPF	$J_{1 \rightarrow 2}$ cm^{-1} ACPF
2.20	-3433.083 115	-44.1	-45.2	-3433.657 409	-112.7	-116.2
2.25	.087 559	-39.1	-39.9	.659 846	-101.7	-104.5
2.30	.089 419	-34.5	-35.1	.659 905	-91.9	-94.0
2.35	.089 163	-30.5	-31.1	.658 081	-83.3	-84.9
2.40	0.87 171	-27.2	-27.5	.654 691	-76.2	-77.2

^a L = He-like model ligand [6].^b $J_{0 \rightarrow 1} = 1/2[E(S=1) - E(S=0)]$; $J_{1 \rightarrow 2} = 1/4[E(S=2) - E(S=1)]$.

charges on the complexes, counter ions, etc. might have some influence on the exact value of the equilibrium distance, in particular since the potential curve is rather flat and its minimum is much less pronounced than, e.g., in $L_5NiONiL_5$ [6]. On the other hand, Ni-S distances of about 2.30 Å seem reasonable for octahedrally coordinated Ni atoms [1, 16, 17].

The exchange integral J is negative for all distances and decays nearly exponentially with increasing distance R , both at the VCI and the ACPF levels. As for the linear NiONi unit the J values at the ACPF level, i.e., after inclusion of dynamical correlation effects, are nearly a factor of 3 larger than at the VCI level. Again, we attribute this failure of the "active orbital" approach [18] to the fact that in the VCI or CASSCF treatments the energies of the charge transfer states are calculated with the unrelaxed orbitals optimized for the covalent ground state [10]. Finally, the splitting between the singlet ground state and the first excited triplet and quintet states shows a regular Landé pattern with a ratio 2:4, both in the VCI and ACPF treatments.

If we compare the absolute value of the exchange integral in the linear NiSNi unit (Table II) with our previous results for the NiONi bridge [6] at the respective equilibrium distances, we find that the antiferromagnetic coupling through the S bridge is slightly, but not substantially, larger than through the O bridge: For $L_5NiONiL_5$ at $R(Ni-O) = 2.08$ Å we found $J = -24$ cm^{-1} (VCI) and $J = -80$ cm^{-1} (best ACPF value) [6] while the corresponding values for the $L_5NiSNiL_5$ complex at $R(Ni-S) = 2.30$ Å are -35 and -94 cm^{-1} . This is again an indication that a partial occupation of the $3d$ AOs in the bridging sulfur atom is no impor-

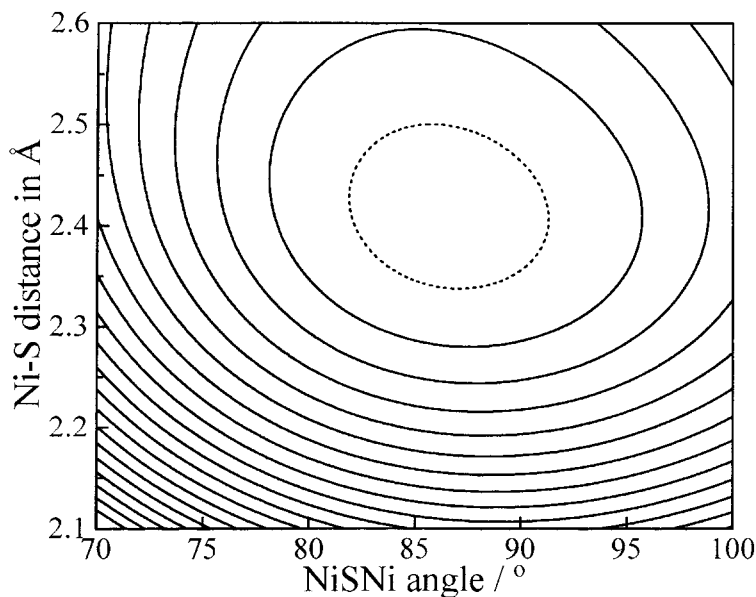
tant effect for the antiferromagnetic coupling through S bridges. It is more important that J depends quite sensitively on the Ni-S distance.

Bi-bridged $L_4NiS_2NiL_4$ Complex

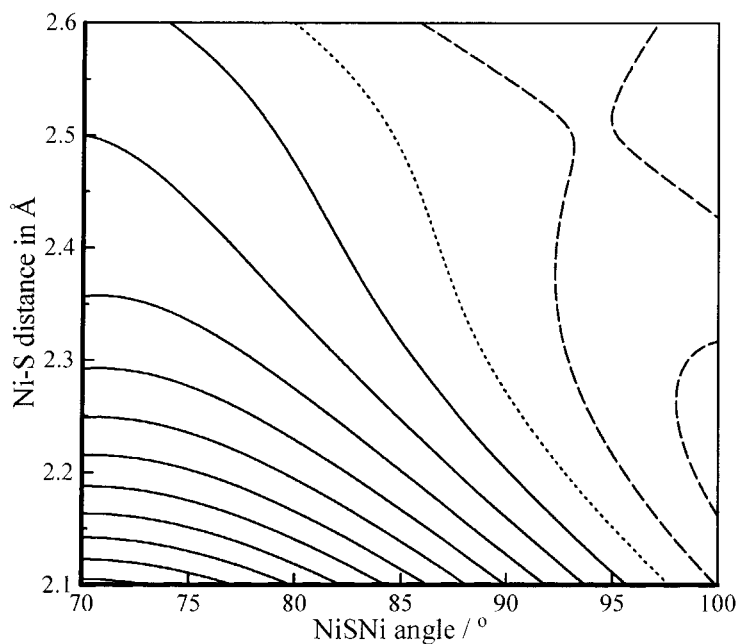
Figure 1 contains contour plots for (a) the total energy of the lowest quintet state and (b) the exchange integral of the bi-bridged $L_4NiS_2NiL_4$ complex as functions of the Ni-S distance and the NiSNi angle, calculated at the VCI level with basis II without the f functions at the Ni atoms.

Figure 1(a) shows that the potential energy surface possesses a rather shallow minimum. At the VCI level the equilibrium geometry corresponds to a Ni-S distance of 2.41 Å and a NiSNi angle of 86.3°. The elongation of the Ni-S bond length as compared to the value for the NiSNi unit with a single linear sulfur bridge (2.32 Å, previous section) and the fact that the NiSNi bond angle is markedly below 90° indicate that the bulky S^{2-} anions try to avoid each other. The direct comparison with experimental data is again difficult, since most Ni(II) complexes with S-donor ligands have a square planar coordination [5, 17] and, again, our model ligands are not directly related to real ligands. However, bond angles between 85° and 94° have been reported for bi-bridged NiS_2Ni units [17]. On the other hand, the binuclear Ni(II) complex with two SPh bridges and octahedrally coordinated Ni(II) ions, as synthesized by Baidya et al. [16], exhibits much longer Ni-S distances (2.41 and 2.52 Å) and a larger NiSNi angle of 105.3°.

Figure 1(b) shows that the exchange integral changes sign just in the region of the minimum of the potential surface. The traditional explanation



(a)



(b)

FIGURE 1. (a) Contour plot for the total energy of the lowest quintet state of the $L_4NiS_2NiL_4$ complex. ROHF, basis II without f functions at Ni. The lowest contour (dotted line) has an energy of -3826.225 a.u., the spacing of the contours is 0.010 a.u. = 26.24 kJ/mol. (b) Contour plot of the exchange integral in the $L_4NiS_2NiL_4$ complex. The spacing of the contours is 5 cm^{-1} ; full contours represent negative, dashed ones positive values of J , the nodeline is dotted.

[6, 18, 19] is that the magnetic orbitals are orthogonal at an NiS-Ni angle of about 90° or slightly larger. The antiferromagnetic superexchange contribution in this region of the potential energy surface is therefore smaller than the direct cou-

pling, hence the coupling is ferromagnetic in the region of about 85° to 100° [6] and antiferromagnetic for smaller and larger angles. This explanation is corroborated by the present calculations. Figure 1(b) shows that J is very sensitively depen-

dent on the geometry of the bridging unit, therefore an interpretation of experimental data for J is meaningless unless an X-ray structure is available.

As is well known [18], the exchange integral J consists of two contributions, the direct ferromagnetic exchange coupling, J_F , between the magnetic orbitals and the antiferromagnetic superexchange coupling, J_{AF} , which is caused by an admixture of ionic configurations to the predominantly covalent wave functions of the low-lying spin states [11]:

$$J = J_F + J_{AF}.$$

The ferromagnetic contribution J_F can be determined separately in a first step from a modified VCI calculation in which the active orbitals are localized, e.g., by a Boys localization procedure [20], and only the "neutral" (covalent) determinants, i.e., those determinants in which exactly two electrons occupy the localized e_g -type orbitals at each Ni center, are included. The "ionic" (charge transfer) determinants which are responsible for the superexchange coupling are thus excluded from the VCI and only the direct exchange coupling J_F between the localized magnetic orbitals is obtained. Of course, the value of J_F depends to a certain extent on the localization scheme.

In a second step, the full VCI calculation containing both neutral and ionic determinants is performed. It yields the total exchange splitting J , i.e., the sum of J_F and J_{AF} . However, as long as ROHF or CASSCF orbitals are used which have been optimized for the predominantly covalent low-ly-

ing spin states, J_F is described correctly but J_{AF} is largely underestimated. The reason is that the energies of the ionic states calculated with nonrelaxed covalent orbitals are much too high. CI calculations with single and double excitations into the full virtual space are necessary to properly account for the relaxation effects in the charge transfer states [10]. Our previous experience with ACPF and MC-CEPA calculations for various binuclear systems [6, 10–12] has shown that the antiferromagnetic contribution J_{AF} is enhanced by a factor of 2–3 after inclusion of dynamic correlation and relaxation effects. Stated differently, the relaxation effects lower the excitation energies of the charge transfer states by as much as a factor of 2 or even more.

In order to avoid the very time consuming ACPF calculations at every point of the two-dimensional potential energy surface for the $L_4NiS_2NiL_4$ complex, we have simply scaled the VCI result for the antiferromagnetic part J_{AF} by a scaling factor ξ , fixing J_F at its VCI value. ξ was determined semiempirically by comparing the VCI results and ACPF results at some preselected points. Table III shows that the ACPF results can be reasonably well simulated by a scaled VCI exchange interaction

$$J_{SC} = J_F + \xi J_{AF}$$

with a scaling factor $\xi = 2.0$.

Figure 2 shows a full two-dimensional contour plot of the scaled exchange integral J_{SC} using

TABLE III
Decomposition of the exchange integral J in the $L_4NiS_2NiL_4$ complex in a direct (J_F) and a superexchange (J_{AF}) contribution^a

Distance ^b	NiSNI angle	J (VCI) ^c	J_F	J_{AF}	J_{SC} ^d = $J_F + 2^*J_{AF}$	J (ACPF) ^e
2.0	90°	-47.52	24.80	-72.32	-119.83	
2.1	90°	-17.34	16.19	-33.52	-50.86	
2.2	90°	-4.17	11.08	-15.25	-19.42	-19.7
2.3	90°	0.99	7.74	-6.75	-5.76	
2.2	100°	9.44	14.43	-4.99	4.44	8.9
2.2	80°	-23.04	9.66	-32.70	-55.75	-50.3

^a Basis II, without f functions, J in cm^{-1} .

^b Ni-S distance in Å.

^c J calculated at VCI level.

^d The antiferromagnetic contribution to J was scaled by a factor of 2.0 to obtain good agreement with the ACPF results.

^e ACPF results.

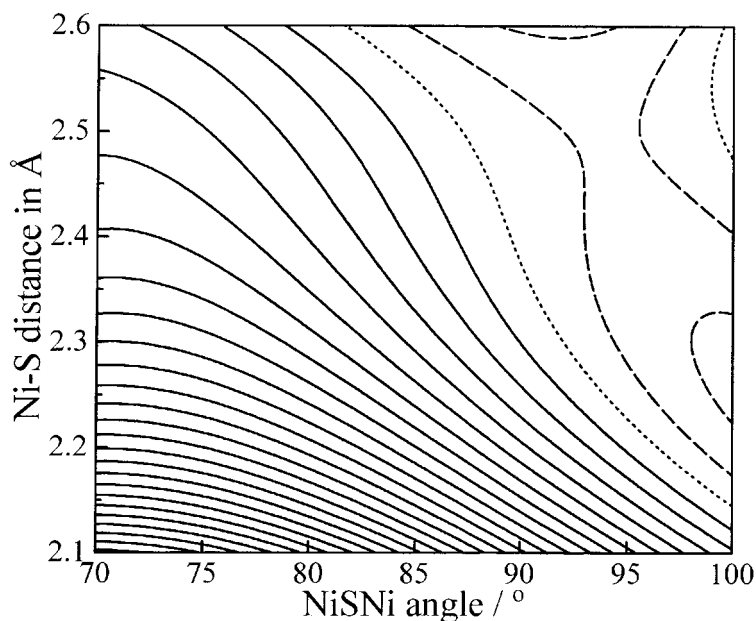


FIGURE 2. Same as Figure 1(b), the antiferromagnetic part of J was scaled by a factor of 2.0.

consistently $\xi = 2.0$. The comparison between the unmodified VCI results in Figure 1(b), and the scaled VCI results in Figure 2 shows that the ferromagnetic part of J remains unchanged while the antiferromagnetic part of J is strongly enhanced after the inclusion of dynamic correlation effects, either by real ACPF calculations or by the scaling of J_{AF} . Therefore, the region of positive values and the position of the node line are very similar in Figures 1(b) and 2, while the increase toward larger antiferromagnetic values of J for smaller Ni-S distances and bond angles is much steeper at the scaled VCI level.

The dependence of the exchange integral J on the Ni-S distance and on the NiSNi angle, found in the present study for $L_4Ni_2NiL_4$, is very similar to the behavior in the corresponding O-bridged $L_4NiO_2NiL_4$ complex [6].

$L_3NiS_3NiL_3$

We did not calculate full two-dimensional surfaces of the total energy and the exchange integral for the triply S-bridged complex $L_3NiS_3NiL_3$. The reason is that due to the use of the nearly charge neutral model ligands our $L_3NiS_3NiL_3$ complex

has a total charge of -3.2 and no stable equilibrium geometry could be found. If the Ni-S distance is fixed to the experimental value of 2.36 \AA observed by Beissel et al. [4] in the trinuclear NiS_3NiS_3Ni unit, the optimum NiSNi angle turns out to be smaller ($\approx 71^\circ$) than the experimental equilibrium value (79° [4]). The electrostatic repulsion between the three negative S^{2-} anions is too large in our model and has to be reduced by using either singly charged SR^- anions or by adding reasonable counterions.

The behavior of J as a function of the Ni-S bond length and the NiSNi angle in the triply S-bridged $L_3NiS_3NiL_3$ complex is very similar to what was found before in the bibringed complex. This is nicely documented in Figure 3. From the similarity of the curves for the $L_4Ni_2NiL_4$ complex with an NiSNi angle of 80° and for $L_3NiS_3NiL_3$ at 79° , we conclude that the scaled VCI results for J as presented in Figure 2 for the bibringed complex can as well be used to predict the magneto-structural relations in triply S-bridged Ni(II) complexes.

At the experimental geometry ($R(Ni-S) = 2.36 \text{ \AA}$ with an NiSNi angle of 79° [4]) we obtained $J = -9.5 \text{ cm}^{-1}$ with $J_F = 7.0 \text{ cm}^{-1}$ and $J_{AF} = -16.5 \text{ cm}^{-1}$. If we again scale J_{AF} by a factor of 2,

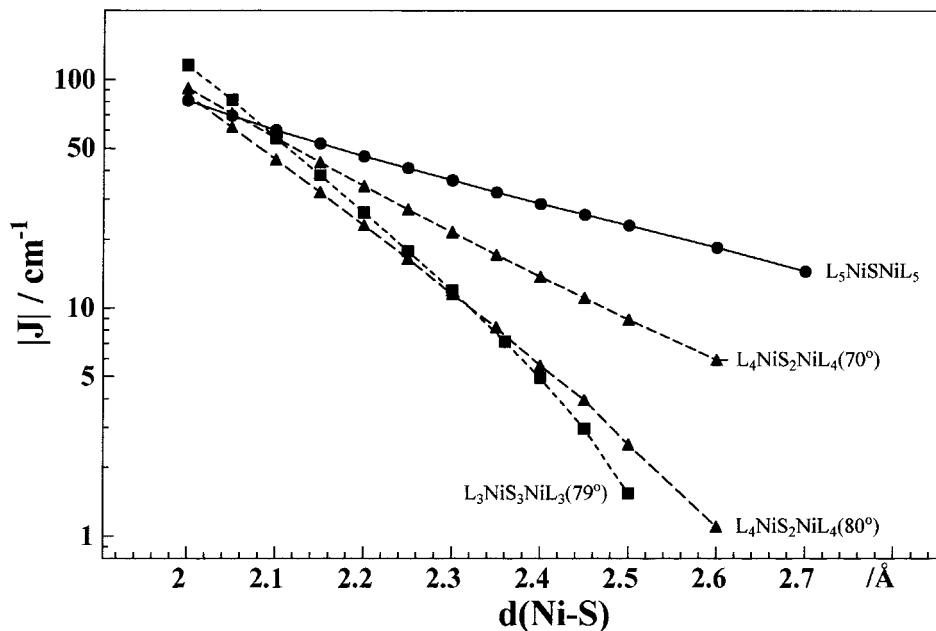


FIGURE 3. Exchange integral J as a function of the Ni-S distance in mono-, bi-, and triply S-bridged binuclear Ni(II) complexes. VCI level, basis II.

we obtained $J = J_F + 2J_{AF} = -26 \text{ cm}^{-1}$, which is in agreement with the experimental value $J = -27.0 \text{ cm}^{-1}$, reported by Beissel et al. for the trinuclear $\text{NiS}_3\text{NiS}_3\text{Ni}$ complex [4].

Summary and Conclusions

In the present study we calculated the exchange integral J in mono-, bi-, and triply S-bridged binuclear Ni(II) complexes, we examined the geometry dependence of J and the total energy of the complexes, and compared the results to oxygen-bridged complexes. Inclusion of the $3d$ orbitals at the bridging sulfur ions lowers the total energy of the complexes, but has nearly no influence on J . The superexchange mechanism is the same as in oxygen-bridged complexes. Even the angular behavior of J is quite similar. The complexes are ferromagnetic for NiSNi angles between 85° and 100° and antiferromagnetic for smaller and larger angles.

In contrast to the oxygen-bridged Ni(II) complexes in which the Ni-O distances are quite similar in different compounds, the experimentally known values for Ni-S distances in different complexes with octahedrally coordinated Ni vary between 2.3 and 2.5 Å. This is caused by very shallow potential surfaces. Because of the strong

geometry dependence of J and the change of its sign in the region of the minimum of the potential surfaces, the values for J will be different in different complexes.

In order to avoid the time-consuming ACPF calculations, we used a scaled VCI in which J_{AF} was weighted with a factor of 2. With this method we found very good agreement between our calculated value for J in a triply S-bridged complex and the experimental data of Beissel et al. [4].

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