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Magnetic Exchange Interactions in Transition Metal Dimers. 8. Di-μ-chloro-Bridged Nickel(II) Complexes

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Variable-temperature (4.2–267 K) magnetic susceptibility data are presented for the three structurally characterized Ni(II) dimeric compounds: $[Ni(qnqn)Cl_2]_2$, $[Ni(dmp)Cl_2]_2$, and $[HN(C_2H_4)_3NCH_3]_2[Ni_2Cl_8]$, where qnqn is *trans*-2-(2′-quinolyl)methylene-3-quinuclidinone and dmp is 2,9-dimethyl-1,10-phenanthroline. In each compound, there is a weak antiferromagnetic exchange interaction present with $J = -4.4, -5.1$, and $-(2.0 \pm 1.0)$ cm^{-1}, respectively ($-2J\mathbf{S}_1 \cdot \mathbf{S}_2$ Hamiltonian). In the case of the last compound, the interaction is very weak and this, apparently in combination with a small amount of some monomeric paramagnetic impurity, leads to a greater uncertainty in the determination of J. The structures of all three nickel dimers are those of two square pyramids sharing a common basal edge with di-μ-chloro bridging. The relationship between structure and exchange parameter is discussed for the three nickel dimers and for related copper di-μ-chloro-bridged dimers. In addition, the susceptibility data for structurally uncharacterized $[Ni_2(dien)_2(H_2O)_2Cl_2]Cl_2$ (dien is diethylenetriamine) point to a ferromagnetic interaction with $J \simeq +5$ cm^{-1} in support of the proposed structure of two octahedral nickel moieties bridged by two chloride ions.

Introduction

The study of electron exchange interactions in transition metal clusters is, in effect, a study of bonding forces in such molecular species. Recent work on transition metal clusters has been reviewed.[2-5] Of late, interest in magnetic susceptibilities has turned to calculations involving electron exchange interactions and diamagnetism.[6] Electron exchange interactions are important in many systems. For example, the level of electron mobility in a given system can depend on the magnitude of electron exchange interaction present. This can be seen in the variation of electrical conductivity in certain extended systems and is perhaps reflected in the rate of electron transfer both in precursors formed in redox reactions and in mixed-valence species.

Hatfield and co-workers[5,7] have studied the electron exchange interactions present in a series of Cu(II) di-μ-hydroxo-bridged dimers and they have found that the exchange parameter, i.e., J in the spin Hamiltonian $-2J\mathbf{S}_1 \cdot \mathbf{S}_2$, can be linearly correlated with the Cu–O–Cu bridging angle in the range of 95.6 to 104.1°, where J varies from +86 to -254 cm^{-1}, respectively. The slope of the correlation was found to be -39.8 cm^{-1} deg^{-1} for the six Cu(II) compounds studied. Magnetic and structural data have also been reported[7] for four di-μ-chloro-bridged Cu(II) dimers. No simple correlation was found, but it was observed that the J value appeared to depend on the Cu–Cl–Cu angle as well as the Cu–Cl bridging bond lengths.

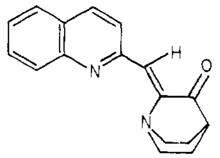
In this paper, we report the magnetic susceptibility data to 4.2 K for three Ni(II) di-μ-chloro-bridged dimers whose structures have been confirmed by x-ray crystallography. Of interest are the variable-temperature magnetic data[8] for the ferromagnetically interacting compound $[Ni_2(en)_4Cl_2]Cl_2$, where $J = +9$ cm^{-1}, and the configuration interaction calculation[9] of the exchange interaction between two nickel ions bridged at 90° with a chloride ion. Very recently, Knetsch and Groeneveld[10] reported $J \simeq +9$ cm^{-1} for the di-chloride-bridged dimeric compound $[Ni(EG)_2Cl_2]_2$, where EG is ethylene glycol.

Experimental Section

Compound Preparation. Samples of the yellow isomer of $[Ni(qnqn)Cl_2]_2$, where qnqn is *trans*-2-(2′-quinolyl)methylene-3-quinuclidinone, were prepared as previously reported.[11] The preparation and x-ray structure of yellow-brown $[Ni(dmp)_2Cl_2]\cdot 2CHCl_3$, where dmp is 2,9-dimethyl-1,10-phenanthroline, have also been reported.[12] Samples of the moderately hygroscopic, deep purple $[HN(C_2H_4)_3NCH_3]_2[Ni_2Cl_8]$ (the cation is *N*-methyl-*N*′-diazabicyclo[2.2.2]octonium, commonly called *N*-methyldabconium ion) were prepared under nitrogen in a drybox as prescribed.[13] It was necessary to reflux the heterogeneous mixture of *N*-methyldabconium dichloride, $NiCl_2$, and ethanol for several hours in order to consume all of the insoluble *N*-methyldabconium dichloride. A sample of $[Ni_2(dien)_2(H_2O)_2Cl_2]Cl_2$ was prepared as reported.[14] Analytical data for the four compounds are collected in Table I.

Table I. Analytical Data

Compd		% C	% H	% N	% Ni
$[Ni(qnqn)Cl_2]_2$	Found	51.82	4.05	7.18	14.61
	Calcd	51.83	4.09	7.11	14.90
$[Ni(dmp)Cl_2]_2$	Found	49.22	3.61	8.18	17.22
	Calcd	49.77	3.58	8.29	17.38
$[HN(C_2H_4)_3NCH_3]_2[Ni_2Cl_8]$	Found	25.82	4.98	8.49	18.09
	Calcd	25.58	4.91	8.52	17.86
$[Ni_2(dien)_2(H_2O)_2Cl_2]Cl_2$	Found	19.16	6.03	16.75	23.41
	Calcd	19.26	6.04	17.08	23.51



qnqn

Magnetic Susceptibility. A PAR Model 150A magnetometer operated at 12.3 kG and with a $CuSO_4 \cdot 5H_2O$ standard was used in the 4.2–267 K magnetic susceptibility measurements. Background corrections were made at all temperatures and a calibrated GaAs diode was used for sample temperature determination. The molecular susceptibilities were corrected for compound diamagnetism which was estimated from tabulated Pascal's constants. For each compound, the resulting corrected molar paramagnetic susceptibilities were fit to the equations[8] for isotropic exchange including single-ion zero-field splitting between two Ni(II) centers using the simplex function minimization procedure as per the computer program STEPT.[15] The equations that we use are perturbation equations, of course, and it could be said that small exchange J values (and zero-field D values) are not accurately determined when Zeeman energies are approaching a comparable magnitude. Matrix diagonalization would be the best approach, but we have *not* done this because on the one hand the J values (and D values) obtained in our fittings are just marginally comparable to Zeeman energies and on the other hand the parameters are somewhat correlated.

Results

Magnetic susceptibility data in the range of 4.2–267 K were collected for three samples of yellow $[Ni(qnqn)Cl_2]_2$. For each of the three data sets, there is a maximum in the susceptibility at 11.4 K and the effective magnetic moment per Ni atom (μ_{eff}/Ni) ranges from 3.16 μ_B at 267 K to 0.91 μ_B at 4.2 K.[16] The data set with the largest number of points is given in Table

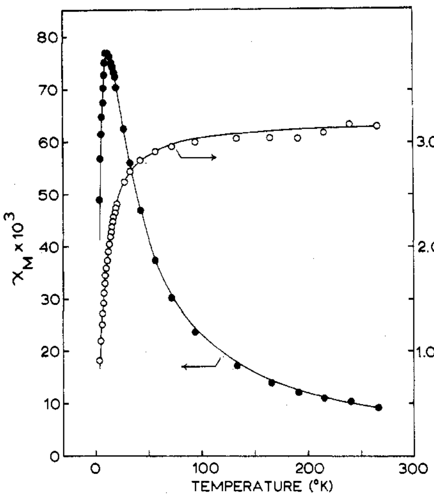


Figure 1. Corrected molar paramagnetic susceptibility per dimer (χ_M in cgsu/mol) and effective magnetic moment per Ni(II) (μ_{eff} in μ_B) as a function of temperature for the compound [Ni(qnqn)-Cl_2]$_2$. The solid lines are least-squares fit theoretical values for $J = -4.4$ cm^{-1}, $g = 2.25$, $D = -7.0$ cm^{-1}, and $Z'J' = -0.035$ cm^{-1} and are drawn at low temperatures such that they terminate at 4.2 K.

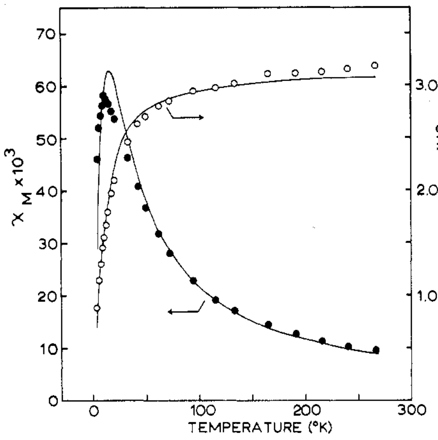


Figure 2. Corrected molar paramagnetic susceptibility per dimer (χ_M in cgsu/mol) and effective magnetic moment per Ni(II) (μ_{eff} in μ_B) as a function of temperature for the compound [Ni(dmp)Cl_2]$_2$. The solid lines are least-squares fit theoretical values for $J = -5.1$ cm^{-1}, $g = 2.20$, $D = -8.8$ cm^{-1}, and $Z'J' = -0.035$ cm^{-1} and are drawn at low temperatures such that they terminate at 4.2 K.

II[17] and is plotted as points in Figure 1. Clearly, there is an antiferromagnetic exchange interaction present in yellow [Ni(qnqn)Cl_2]$_2$. A fitting of these results with a Ni(II) dimer isotropic exchange model[8] gave $J = -4.4$ cm^{-1}, $g = 2.25$, single-ion zero-field parameter $D = -7.0$ cm^{-1}, and an *inter*-dimer effective exchange interaction of $Z'J' = -0.035$ cm^{-1}. In Figure 1, the fit to this model is represented by solid lines for both the susceptibility and the μ_{eff} vs. temperature curves. As can be seen, the fit for the [Ni(qnqn)Cl_2]$_2$ data is quite good in that the position of susceptibility maximum is reasonably well reproduced and there appears to be no appreciable deviation in fitting at low temperature; such a deviation can be indicative of the presence of small amounts of paramagnetic monomer impurities.[2]

The compound [Ni(dmp)Cl_2]$_2$ shows a maximum in the susceptibility at 10.5 K. In the range of 267–4.2 K, the μ_{eff}/Ni varies from 3.19 to 0.90 μ_B and again there is an antiferromagnetic interaction. Figure 2 shows, however, that the theoretical fit to the [Ni(dmp)Cl_2]$_2$ data is not as good as for [Ni(qnqn)Cl_2]$_2$. There is perhaps a small (<2%) amount of some monomeric impurity. The parameters for the best fit of the [Ni(dmp)Cl_2]$_2$ data are $J = -5.1$ cm^{-1}, $g = 2.20$, $D = -8.8$ cm^{-1}, and $Z'J' = -0.035$ cm^{-1}. The exchange parameter is about the same as that for the qnqn dimer.

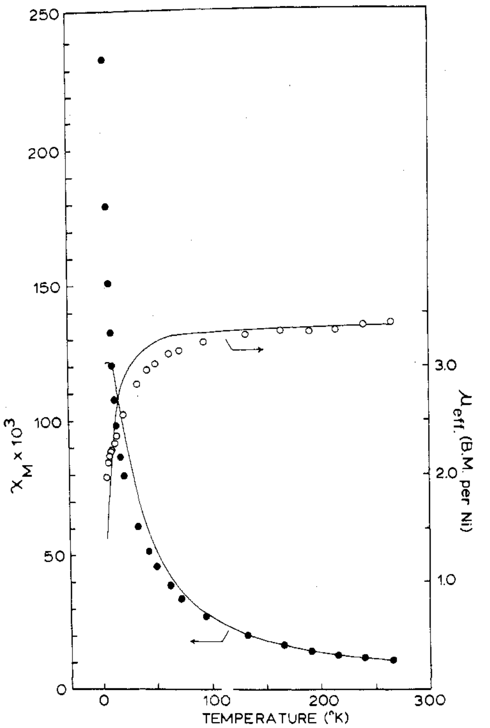


Figure 3. Corrected molar paramagnetic susceptibility per dimer (χ_M in cgsu/mol) and effective magnetic moment per Ni(II) (μ_{eff} in μ_B) as a function of temperature for the compound [$HN(C_2H_4)_3$-NCH_3]$_2$[Ni_2Cl_8]. The solid lines are least-squares fit theoretical values for $J = -1.3$ cm^{-1}, $g = 2.38$, $D = -26.1$ cm^{-1}, and $Z'J' = -0.010$ cm^{-1} and terminate at 4.2 K.

Susceptibility data for [$HN(C_2H_4)_3NCH_3$]$_2$[Ni_2Cl_8] are given in Table IV[17] and Figure 3. In this case, there is also an antiferromagnetic exchange interaction, but, unfortunately, there is no maximum in the susceptibility curve. The effective magnetic moment per nickel goes from 3.42 μ_B at 267 K to 1.98 μ_B at 4.2 K. Least-squares fitting of the data yields the following parameters: $J = -1.3$ cm^{-1}, $g = 2.38$, $D = -26.1$ cm^{-1}, and $Z'J' = -0.010$ cm^{-1}. The solid lines in Figure 3 represent this fit, a fit that shows appreciable deviation from the experimental data at the low temperatures. It appears that a weak antiferromagnetic interaction in combination with some monomeric paramagnetic impurity would account for the data. The analytical data are very good for this sample of [$HN(C_2H_4)_3NCH_3$]$_2$[Ni_2Cl_8]; see Table I. Several unsuccessful attempts were made to prepare another sample of this compound with an even better analytical analysis for a second susceptibility run. In light of the reported[13] chemical characteristics of the compound and the elemental analysis, a 7% impurity of [$N(C_2H_4)_3NCH_3$][$NiCl_3$] was assumed to be present. This had the effect of reducing the value of μ_{eff} at 267 K to 3.38 and 1.76 μ_B at 4.2 K. Least-squares fitting of the data corrected for such an impurity does give a somewhat improved fit (see Table IV)[17] and the J value changes to -2.5 cm^{-1}. At this time, perhaps the best that we can say for [$HN(C_2H_4)_3NCH_3$]$_2$[Ni_2Cl_8] is that there is an antiferromagnetic exchange interaction and $J = -(2.0 \pm 1.0)$ cm^{-1}.

The variable-temperature magnetic susceptibility data for [$Ni_2(dien)_2(H_2O)_2Cl_2$]Cl_2 are given in Table V[17] and are illustrated in Figure 4. This compound was reported by Curtis and Powell[14] to consist of (distorted) octahedral nickel moieties bridged by two chloride ions. Some support for the presence of a dimer in this compound is visible in the μ_{eff}/Ni vs. temperature curve. There is a slight increase in μ_{eff}/Ni at low

Table VI. Magnetic and Structural Data for Chloro-Bridged Ni(II) and Cu(II) Dimers[a]

Complex	Structure,[h] bridging mode	J, cm^{-1}	M–M distance, Å	M–Cl–M angle, deg	M–Cl(bridge) distance, Å	M–basal plane distance, Å
$[Ni(qnqn)Cl_2]_2$	sp, equatorial edge	−4.4	3.652 (1)	98.23 (5)	2.408 (2) 2.422 (2)	0.40
$[Ni(dmp)Cl_2]_2$	sp, equatorial edge	−5.1	3.602 (2)	98.0 (1)	2.378 (3) 2.394 (3)	0.39
$[Ni_2Cl_8{}^{4-}]$[b]	sp, equatorial edge	−(2.0 ± 1.0)	3.669 (2)	99.29 (6)	2.366 (2) 2.449 (2)	0.502 (2)
$[Ni_2(en)_2Cl_2{}^{2+}]$[c]	Octahedral	+9	3.67	94.1	2.485 2.522	
$[Ni_2(dien)_2(H_2O)_2Cl]Cl_2$	Octahedral?	+4.8				
$[Ni(ethylene\ glycol)_2Cl_2]_2$[d]	Octahedral	~+9	3.458 (1)	86.97 (5)	2.383 (1)	
$[(guaninium)CuCl_3]_2 \cdot 2H_2O$	tbp, equatorial-to-apex edge	−41.3	3.575	98	2.447 2.288	
$[Cu_2Cl_8{}^{4-}]$[e]	tbp, equatorial-to-apex edge	−7.3	3.722 (5)	95.2 (1)	2.325 (5) 2.703 (5)	
$[(2\text{-}mepy)_2CuCl_2]_2$[f]	sp, base-to-apex edge	−3.7	4.41	101.4	2.26 3.37	0.006
$[(DMG)CuCl_2]_2$[g]	sp, base-to-apex edge	+3.2	3.445 (3)	88.0	2.24 2.70	0.15

[a] References to structural and magnetic work on the Cu(II) dimers can be found in ref 7; nickel structural work is referred to in the text. [b] The cation is *N*-methyldabconium ion.[13] [c] Magnetic data are for the Cl^- salt,[8] while structural work is for ClO_4^- salt, see L. Kh. Minacheva, A. S. Antsyshkina, and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **12**, 845 (1971). The Ni–Cl–Ni angle was calculated using the reported atomic coordinates and computer program JAM. [d] Magnetic data from ref 10; structural data from B.-M. Antti, *Acta Chem. Scand., Ser. A*, **29**, 76 (1975). [e] As found in $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$. [f] The ligand 2-mepy is 2-methylpyridine.[7] [g] The ligand DMG is dimethylglyoxime.[7] [h] Structural codes are: sp, square pyramidal; tbp, trigonal bipyramidal.

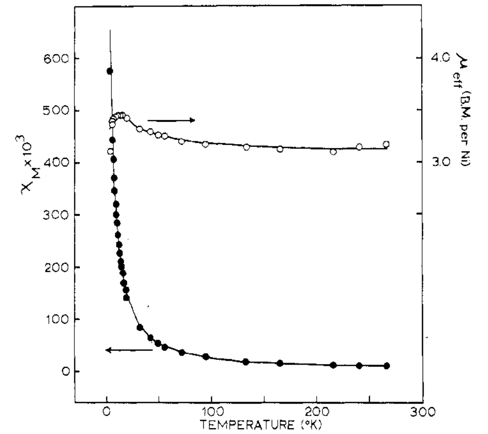


Figure 4. Corrected molar paramagnetic susceptibility per dimer (χ_M in cgsu/mol) and effective magnetic moment per Ni(II) (μ_{eff} in μ_B) as a function of temperature for the compound $[Ni_2(dien)_2(H_2O)_2Cl_2]Cl_2$. The solid lines are least-squares fit theoretical values for $J = +4.9\ cm^{-1}$, $g = 2.15$, $D = 18\ cm^{-1}$, and $Z'J' = 0.010\ cm^{-1}$ and terminate at 4.2 K.

temperatures with a maximum of 3.48 μ_B at ~14 K, indicative of a weak ferromagnetic interaction. Computer fitting gives $J = 4.9\ cm^{-1}$, $g = 2.15$, $D = 18\ cm^{-1}$, and $Z'J' = 0.010\ cm^{-1}$. It is difficult to obtain an accurate value of J for such a ferromagnetic interaction;[8] however, it is clear that if this pseudooctahedral complex is indeed dimeric, then the exchange interaction is slightly ferromagnetic. This is in agreement with the ferromagnetic interaction found[8] for $[Ni_2(en)_4Cl_2]Cl_2$.

Discussion

Table VI summarizes the exchange parameters ($-2J\mathbf{S}_1 \cdot \mathbf{S}_2$ Hamiltonian) and structural features for the three structurally characterized Ni(II) chloro-bridged compounds measured in this work and the previously reported[8] values for $[Ni_2(en)_4Cl_2]Cl_2$, $[Ni(EG)_2Cl_2]_2$, and four chloro-bridged Cu(II) systems.[7] In comparison to exchange parameters for the dihydroxo-bridged Cu(II) dimers, the exchange parameters in Table VI encompass a much smaller range of values. This is probably expected because the exchange varies as the fourth power of the orbital overlap[2] and because the metal–Cl bridging bond distances are appreciably greater than the bridging Cu–O distances of 1.90–1.95 Å in the copper hydroxo dimers. The metal–metal distances are also much greater in the chloro-bridged dimers. Any direct metal–metal interaction, albeit probably quite weak in these Cu(II) and Ni(II) dimers, would contribute an antiferromagnetic exchange pathway.

There are two square-pyramidal Cu(II) dimers in Table VI. The three structurally characterized chloro-bridged Ni(II) dimers studied in this work also have approximate square-pyramidal metal coordination geometries. In both of the square-pyramidal Cu(II) dimers, the dimerization results from the association of two planar units; the chlorine bonded in the basal plane of one copper ion interacts in the axial direction with the second copper atom. In one of these complexes, the interplanar Cu–Cl distance is 3.37 Å and in spite of this large separation there is an antiferromagnetic interaction of $J = -3.7\ cm^{-1}$. In these complexes, the two copper atoms are very close to the equatorial plane of coordination.

In contrast to the mode of dimerization in the Cu(II) complexes, each of the three Ni(II) dimers can be best described as consisting of two square pyramids related by an inversion center and sharing a common basal edge consisting of two chloride ions. In all three Ni(II) dimers, the nickel ions are located above the basal plane. The distances from the basal planes are 0.39 Å for $[Ni(qnqn)Cl_2]_2$,[18] 0.39 Å for $[Ni(dmp)Cl_2]_2$,[12] and 0.502 Å for $[Ni_2Cl_8{}^{4-}]$.[19] Thus, there are at least three major structural differences between the three Ni(II) dimers and the two square-pyramidal copper dimers: the mode of bridging, the metal–Cl(bridge) distances and angles, and the distance of the metal atom from the basal plane. In addition, the Ni(II) ion has two unpaired electrons and consequently a greater number of possible exchange pathways and, in spite of this, we find that the Ni(II) dimers have smaller values of J.

As was mentioned in the Introduction, in the di-μ-hydroxo-bridged copper series, there is a correlation of J vs. the bridging Cu–O–Cu angle and, for a change of 1°, a change of ~40 cm^{-1} is expected in the J value;[7] the interaction becomes less antiferromagnetic as the bridging angle approaches 90°. As can be seen in Table VI, the Ni–Cl–Ni bridging angle in $[Ni_2Cl_8{}^{4-}]$ is approximately 1° larger than the values found for the other two Ni(II) dimers. However,

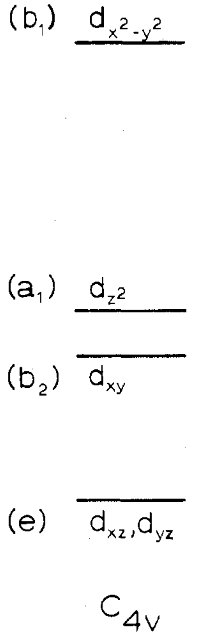


Figure 5. Approximate ordering of one-electron orbitals for a square-pyramidal, C_{4v}-symmetry metal complex.

the magnetic data for the *N*-methyldabconium salt of $Ni_2Cl_8{}^{4-}$ points to a weaker antiferromagnetic interaction than is present in the two other square-pyramidal nickel dimers. The nickel atoms in $Ni_2Cl_8{}^{4-}$ are further (i.e., ~0.1 Å) out of the basal plane than for the nickel atoms in the other two dimers and perhaps this difference largely accounts for the attenuation in antiferromagnetic interaction. It should be noted that the copper di-μ-hydroxo Cu_2O_2 units are all nearly planar.

The J value for $[Ni(EG)_2Cl_2]_2$ is not known[10] very accurately, but it should prove very interesting to evaluate this J value in view of the small Ni–Cl–Ni angle of 86.97 (5)°.

With the information at hand, it is not possible to precisely explain the magnitude of any particular exchange parameter or even to semiquantitatively explain the J values for a series of *structurally different* nickel dimers. A brief look at the "inner workings" of the electron exchange interaction will recall the difficulty of interpretation and manifold of factors associated with such an interaction. The spin Hamiltonian, $\mathbf{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2$, is an *effective* way of gauging the *net* interaction that develops as two Ni(II) ions with their associated ligands (bridges) are brought into a bonding interaction distance.

In the specific case of a *monomeric* C_{4v}-symmetry square-pyramidal Ni(II) complex, the relevant *one-electron* orbitals are approximately ordered as indicated in Figure 5. The two unpaired electrons per nickel atom are located, one each in the d_{z^2} and $d_{x^2-y^2}$ one-electron orbitals (z axis is along the fourfold rotational axis). The isolated square-pyramidal nickel complex thus has a ${}^3B_1$ ground state. Two of these ${}^3\mathbf{B}_1$ ground state systems interact to form a dimer which has three energetically close energy levels: one has no unpaired electrons per dimeric complex and is a spin singlet ($S' = 0$); another has two unpaired electrons and is a spin triplet ($S' = 1$); and the third is a spin quintet ($S' = 2$). All three states are assumed to be orbitally nondegenerate. The spin Hamiltonian treats this effectively in the sense that, under certain assumptions,[2] it tells us that there are three levels, a singlet, a triplet, and a quintet. Furthermore, if the energy of the singlet is taken as zero, the triplet lies at $-2J$ energy and the quintet at $-6J$.

In our nickel dimers, we are dealing with small ($\approx$10 cm^{-1}) energy differences between the three low-lying electronic *states* of the dimer. These small energy differences are the *net* result of a large number of various electrostatic interactions. Molecular orbitals form across the bridging chlorine centers as the dimer forms; the molecular orbitals form from the $d_{x^2-y^2}$ and d_{z^2} metal and (3p, 3s) chlorine atomic orbitals. Thus, the degree of nickel–chlorine covalency will be important. The electrons are put into the molecular orbitals and the energies of the three different electronic states are evaluated. The three electronic states can have different total kinetic energies and potential energies, the latter due, in part, to differences in electron repulsion terms of the Coulomb and exchange type. Excited electronic states of the correct symmetry and spin-multiplicity will be admixed into the three low-lying dimer electronic states. Calculations of exchange parameters to date have of necessity only been approximate. For example, Barraclough and Brookes,[9] using a configuration interaction method, have calculated the exchange parameter for the interaction between two Ni(II) ions through a 90° bridging chloride anion. The calculated value of $J = +1.2$ cm^{-1} is to be compared with the $J = +9$ cm^{-1} value given in Table VI for $[Ni_2(en)_2Cl_2]^{2+}$, which has a bridging angle of 94.1°.

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Registry No. $[Ni(qnqn)Cl_2]_2$, 42847-02-9; $[Ni(dmp)Cl_2]_2$, 29115-92-2; $[HN(C_2H_4)_3NCH_3]_2[Ni_2Cl_8]$, 30051-45-7; $[Ni_2(dien)_2(H_2O)_2Cl_2]Cl_2$, 22470-21-9.

Supplementary Material Available: Tables II–V, magnetic susceptibility data (6 pages). Ordering information is given on any current masthead page.

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