Ferromagnetic Coupling in Di-μ-chloro-tetrakis(ethane-1,2-diamine)dinickel(II) Dichloride, Diperchlorate, and Bis(tetraphenylborate)

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The temperature dependence of the magnetic susceptibilities of the three title compounds has been studied in the range 3.6—300 K. The quantitative interpretation of the magnetic data is complicated by the low-temperature monoclinic–triclinic transition as seen for $[Ni_2(en)_4Cl_2]Cl_2$ by heat-capacity and *X*-ray investigations. It is most likely that the same transition also occurs in the two other compounds. The exchange-interaction parameters *J* of the Hamiltonian $-J_1\hat{S}_1 . J\hat{S}_2$ are found to be equal to 13.3, 17.8, and 19.0 cm^{-1} respectively for the dichloride, diperchlorate, and bis(tetraphenylborate). These values are correlated with the sizes of the Ni–Cl–Ni bridging angles in the dimeric units and discussed in the framework of a previously described orbital model.

AMONG all the binuclear complexes with paramagnetic metallic centres there are few which exhibit intramolecular ferromagnetic coupling. Such a situation was foreseen by Anderson [1] who showed that the 'kinetic' contribution due to the overlap of the magnetic orbitals was generally more important than the potential contribution which couples the spins parallel in the low-energy state. Goodenough,[2] Kanamori,[3] then Anderson [1] pointed out that a particularly favourable geometry for a ferromagnetic coupling was the interaction between two d^8 ions in an octahedral environment with a M–X–M bridging angle close to 90°. This prediction was checked by Ginsberg *et al.*[4] who showed that in the compound $[Ni_2(en)_4Cl_2]Cl_2$, with en = ethane-1,2-diamine, containing the binuclear cation $[Ni_2(en)_4Cl_2]^{2+}$ as isolated unit, the coupling between the nickel(II) ions was actually ferromagnetic. A similar situation was reported for other $[Ni_2(en)_4X_2]Cl_2$ complexes with X = Br, CN, or SCN,[4] $[Ni_2(tren)_2(SCN)_2][BPh_4]_2$ (tren = 2,2′,2″-triaminotriethylamine),[5] $[Ni_2(eg)_4Cl_2]Cl_2$ (eg = ethylene glycol),[6] and for $[Ni_2(dien)_2(OH_2)_2Cl_2]Cl_2$ (dien = diethylenetriamine).[7] A ferromagnetic coupling was also found in nickel(II) linear chains made out of octahedra sharing opposite edges.[8,9] Although the magnetic data for $[Ni_2(en)_4Cl_2]Cl_2$ published by Ginsberg *et al.*[4] unambiguously prove that the nickel(II) ions are coupled ferromagnetically, the quantitative interpretation of these data remains rather difficult for several reasons. (*i*) Generally, the determination of spin-Hamiltonian parameters by fitting the experimental magnetic data is less accurate for pairs of ferromagnetically coupled ions than for pairs of antiferromagnetically coupled ions. For this latter situation, plots of susceptibility against temperature deviate drastically from the Curie law and exhibit a maximum at a temperature which depends essentially on the exchange-interaction parameter *J*. (*ii*) For a paramagnetic nickel(II) complex, the spin degeneracy of the ground spin triplet is removed by the zero-field splitting. This phenomenon may be of the same order of magnitude as, or even more important than, the exchange interaction. In $[Ni_2(en)_4Cl_2]^{2+}$ the site symmetry of each nickel(II) ion is close to C_{2v}, so that two zero-field splitting parameters *D* and *E* describing the axial and rhombic anisotropies respectively must be introduced in the spin Hamiltonian. (*iii*) Although the shortest intermolecular Ni–Ni distance is 7.725 Å in $[Ni_2(en)_4Cl_2]Cl_2$,[10] and still larger in the two other compounds studied in this paper, the intermolecular coupling may not be neglected. If it is antiferromagnetic, its effect at very low temperature is similar to that of the zero-field splitting. By investigating the magnetic behaviour of the complexes $[Ni_2(en)_4Cl_2]Y_2$ (Y = Cl, ClO_4, or BPh_4) with counter anions of increasing size we hope to be able to define the effect of the intermolecular coupling. (*iv*) The last but not the least difficulty in the interpretation of the magnetic properties of nickel dimers arises from the fact that $[Ni_2(en)_4Cl_2]Cl_2$ undergoes a monoclinic–triclinic phase transition over the range 27—10 K.[11] Although not studied in detail, a similar phenomenon seems to occur in $[Ni_2(en)_4Cl_2][ClO_4]_2$ and $[Ni_2(en)_4Cl_2][BPh_4]_2$.

In this work, taking into account the difficulties emphasized above, we have attempted to determine and compare the exchange-interaction parameters in three nickel(II) dimers which differ only by the nature and thus the size of their counter anions. The influence of structural modifications in similar compounds on the value of the exchange-interaction parameter has been extensively studied in the last few years. The most striking result was obtained by Hatfield and co-workers [12] who found a linear correlation between the *J* parameter and the bridging angle in eight, essentially planar, hydroxo-bridged copper(II) dimers. The crystal structures of two of the three compounds studied in this work have been determined by *X*-ray diffraction.[10] The Ni–Cl–Ni bridging angles are 96.6 and 95.4° respectively when the counter anions Y are Cl$^-$ and $[ClO_4]^-$. It is very probable that this angle is still smaller for Y = $[BPh_4]^-$. Moreover, different asymmetries exist in the Ni–Cl bond lengths in the dichloride and the diperchlorate. In the discussion we shall interpret our results by making use of an orbital model of the exchange interaction previously described and already used several times.[13,14]

EXPERIMENTAL

Synthesis.—The complex $[Ni_2(en)_4Cl_2]Cl_2$ was prepared according to the previously described method [15] and recrystallized by slow diffusion of ethanol in a methanolic solution of the compound. The perchlorate analogue was obtained by slow diffusion of ethanol in a methanolic solution containing stoicheiometric amounts of $[Ni_2(en)_4Cl_2]Cl_2$ and $Na[ClO_4]$. The crystals of $[Ni_2(en)_4Cl_2][ClO_4]_2$ were picked out under a binocular lens, redissolved in methanol, and recrystallized by slow diffusion of ethanol into this solution. The tetraphenylborate salt was obtained by the same procedure from $[Ni_2(en)_4Cl_2]Cl_2$ and $Na[BPh_4]$. For the three compounds, the chemical analysis of all the elements agree well with the calculated percentages.

Magnetic Measurements.—The magnetic measurements were carried out in the temperature range 3.6—300 K on powder samples with a Faraday-type magnetometer, equipped with a continuous-flow cryostat designed by Oxford Instruments. The temperature is given by a gold–iron/chromel thermocouple. A magnetic induction of *ca.* 4 kG was used.* The independence of the susceptibility from the magnetic induction was checked at several temperatures; this shows the absence of ferromagnetic impurities in the samples. Mercury(II) tetrathiocyanatocobaltate(II) was used as a susceptibility standard. The absolute accuracy of the temperature is 0.1 K above 14 K and ±0.2 K below 14 K and the relative accuracy of the apparent increase in weight of the samples when the magnetic field is applied is *ca.* 1%. The corrections for diamagnetism were estimated from the atomic values of Pascal, except for the anion $[BPh_4]^-$ the diamagnetism of which was obtained by measuring the magnetic susceptibility of $Na[BPh_4]$ and substracting the contribution of Na^+ as given by Pascal's tables.[16] These corrections are -312×10^{-6} cm^3 mol^{-1} for the dichloride, -329×10^{-6} cm^3 mol^{-1} for the diperchlorate, and -839×10^{-6} cm^3 mol^{-1} for the bis(tetraphenylborate). Finally, for the three compounds, the temperature-independent paramagnetism was estimated at 150×10^{-6} cm^3 mol^{-1}.

RESULTS

Phase Transition in $[Ni_2(en)_4Cl_2]Cl_2$.—Evidence for the presence of a low-temperature phase transition in $[Ni_2(en)_4Cl_2]Cl_2$ was described elsewhere.[11] However, owing to the importance of this result for the present work, we briefly recall its different steps. The temperature dependence of the heat capacity for $[Ni_2(en)_4Cl_2]Cl_2$, plotted in Figure 1, exhibits a broad peak in the range 10—27 K with a maximum of 35.3 J K^{-1} mol^{-1} at 22.8 K. Subtracting the estimated lattice heat capacity, we obtain the curve (*c*) in Figure 1 which reaches a maximum of 26 J K^{-1} mol^{-1} around 22 K. Using the spin Hamiltonian (1) with parameters *J*, *D*, and *E* as already defined, we showed that no set of parameters *J*, *D*, and *E* led to a satisfactory interpretation of the experimental heat-capacity curve. The highest value of the magnetic heat capacity resulting from the Hamiltonian (1) is 12.3 J K^{-1} mol^{-1}. The broad peak in the heat-capacity curve also does not arise from the onset of an antiferromagnetic order at <27 K; indeed, the magnetic susceptibility does not exhibit any maximum around this temperature. It follows, therefore, that the heat-capacity curve for $[Ni_2(en)_4Cl_2]Cl_2$ between 10 and 27 K is most likely related to a phase transition. The *X*-ray powder-diffraction diagram studied at several temperatures between 300 and 4.2 K fully confirms that the compound undergoes a monoclinic–triclinic transition. The compound crystallizes in the monoclinic space group $P2_1/n$ at room temperature. The shape of the diffraction peak $021 - 02\bar{1}$, the splitting of which characterizes the monoclinic–triclinic transition, is shown in Figure 2. Its profile stays symmetric and its width at half-height does not change between 300 and 27 K. From 27 K, the temperature at which one begins to observe a heat-capacity peak, the line broadens and splits into two components. Between 25 and 4.2 K, this splitting remains practically constant.

$$\mathscr{H} = -J\hat{S}_1.\hat{S}_2 + D(S_{1z}^2 + S_{2z}^2) + \frac{E}{2}(S_{1+}^2 + S_{1-}^2 + S_{2+}^2 + S_{2-}^2) \quad (1)$$

Magnetic Curves.—The magnetic behaviour of the three compounds $[Ni_2(en)_4Cl_2]Y_2$ with Y = Cl, ClO_4, or BPh_4, is shown in Figure 3 in the form of the temperature dependence of the product of the molar magnetic susceptibility χ_M with the temperature *T* in the range 3.6—300 K. For the three compounds, this product increases upon cooling from room temperature, reaches a maximum at 19.5 K, then quickly decreases below this temperature. At room temperature, the values of the three magnetic susceptibilities are quite similar; on the other hand, the value of the maximum of $\chi_M T$ is larger for $[Ni_2(en)_4Cl_2][BPh_4]_2$ (3.56 cm^3 K mol^{-1}) than for $[Ni_2(en)_4Cl_2][ClO_4]_2$ (3.29 cm^3 K mol^{-1}) and for $[Ni_2(en)_4Cl_2]Cl_2$ (2.93 cm^3 K mol^{-1}). A slight discontinuity observed for several samples in the slope of the curve of $\chi_M T$ against *T* appears at 27 K for $[Ni_2(en)_4Cl_2]Cl_2$. This discontinuity also seems to appear very weakly for $[Ni_2(en)_4Cl_2][ClO_4]_2$; it is not perceptible for $[Ni_2(en)_4Cl_2][BPh_4]_2$. Very striking is the fact that for the three compounds the maximum of $\chi_M T$ occurs at exactly the same temperature of 19.5 K. From Ginsberg *et al.*,[4] this maximum results from the combined effect of the intermolecular antiferromagnetic coupling and of the zero-field splitting. It is not possible to assume that the two phenomena remain quantitatively unchanged whatever the nature of the counter anion may be. In particular, the intermolecular coupling should decrease when the size of the counter anion increases.

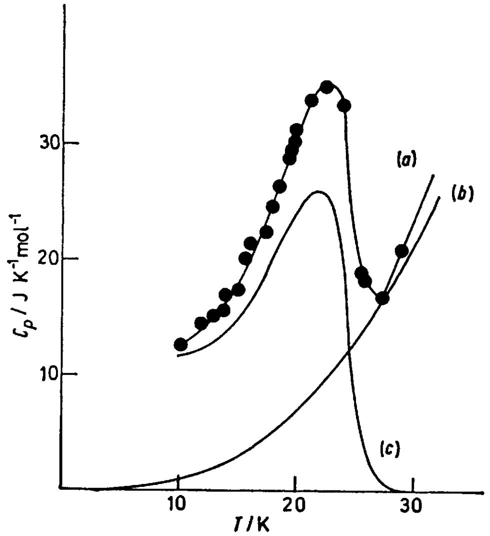

FIGURE 1 Heat-capacity curves $C_p = f(T)$ for $[Ni_2(en)_4Cl_2]Cl_2$: (*a*) experimental; (*b*) estimated lattice heat capacity $C_L = f(T)$; (*c*) $C_p - C_L = f(T)$

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* Throughout this paper: 1 G = 10^{-4} T; 1 eV ≈ 1.60×10^{-19} J.

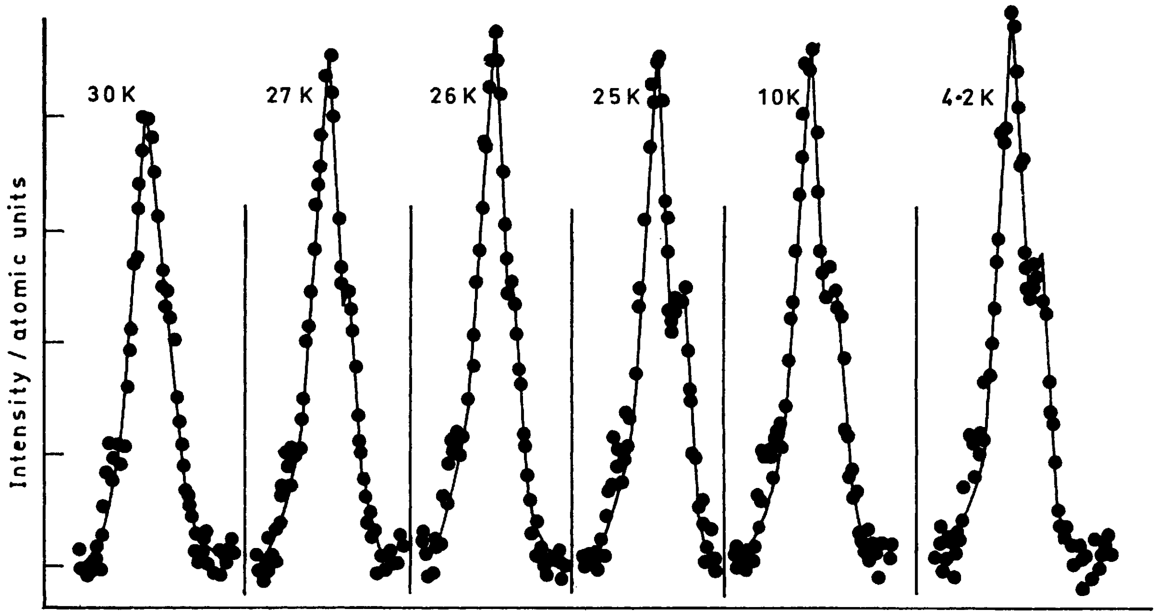


FIGURE 2 Shape of the *X*-ray diffraction peak 021 — $02\bar{1}$ at several temperatures between 30 and 4.2 K

In the same way, the zero-field splitting should be significantly modified by a change of geometry around each nickel(II) ion. Although this may not be rigorously excluded, it seems highly unlikely that in the series $[Ni_2(en)_4Cl_2]Y_2$ the variations of the intermolecular coupling and of the zero-field splitting are such that, by some compensation effect, the maximum of χ_MT remains unchanged. Therefore, we believe that this maximum in χ_MT at 19.5 K results to a large extent from the phase transition that was found in $[Ni_2(en)_4Cl_2]Cl_2$ and which would also occur in the two other compounds. We do not yet know the nature of the molecular motions accompanying the monoclinic–triclinic transition; it could involve the NH_2 and (or) CH_2 groups.[17]

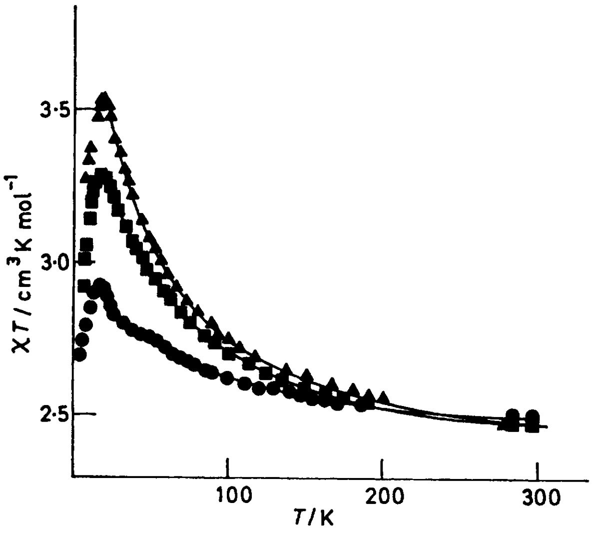


FIGURE 3 Temperature dependence of the product of the molar magnetic susceptibility with the temperature for (●) $[Ni_2(en)_4Cl_2]Cl_2$, (■) $[Ni_2(en)_4Cl_2][ClO_4]_2$, and (▲) $[Ni_2(en)_4Cl_2][BPh_4]_2$. The best-fit theoretical curves are given as continuous lines. For clarity, the points between 200 and 280 K are not indicated

The existence of the phase transition that we assume to occur in the three compounds should have significant consequences as far as the quantitative interpretation of the magnetic data is concerned. Thus, there is no reason for the *J*, *D*, and *E* parameters of the spin Hamiltonian to remain unchanged on going from the monoclinic to the triclinic phase. We have therefore adopted the following strategy: we looked for the best agreement between experiment and theory only in the temperature range 27—300 K. In particular, we did not attempt to get theoretical curves of χ_MT against T with a maximum located exactly at 19.5 K. To avoid an overparametrization of the problem and although this has no theoretical justification, we assumed that *E* was negligible compared to *D*. The intermolecular coupling was introduced by multiplying the susceptibility obtained from Hamiltonian (1) by $T/(T + \theta)$. The calculation of the magnetic susceptibilities was carried out using standard programming techniques. The sets of *g*, *J*, *D*, and θ parameters leading to the best fit were determined by a least-squares subroutine and are given in Table 1, uncertainty limits being assigned by comparing the effect of small changes in the parameters with the estimated experimental uncertainty. For $[Ni_2(en)_4Cl_2]Cl_2$ and $[Ni_2(en)_4Cl_2][BPh_4]_2$, alternative sets of parameters were obtained [$g = 2.211(3)$, $J = 13.4(3)$ cm^{-1}, $D = -0.5(5)$, $\theta = 3.0(5)$ K; and $g = 2.161(3)$, $J = 19.2(3)$ cm^{-1}, $D = 3.0(7)$ cm^{-1}, $\theta = -0.7(5)$ K] which were considered to be less reliable than those of Table 1 because *D* did not vary in a continuous way through the series Cl$^-$, $[ClO_4]^-$, and $[BPh_4]^-$.

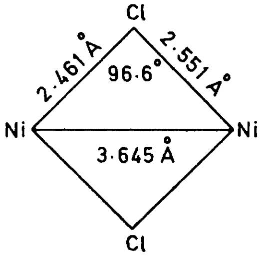
TABLE 1

Spin-Hamiltonian parameters with estimated uncertainties in the last figure in parentheses

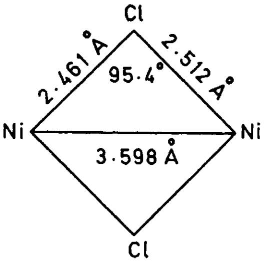
Compound	g	J/cm^{-1}	D/cm^{-1}	θ/K
$[Ni_2(en)_4Cl_2]Cl_2$	2.211(3)	13.3(2)	−3.6(7)	3.0(5)
$[Ni_2(en)_4Cl_2][ClO_4]_2$	2.175(3)	17.8(2)	−4.2(7)	0.5(5)
$[Ni_2(en)_4Cl_2][BPh_4]_2$	2.162(3)	19.0(2)	−7.7(7)	−0.8(5)

DISCUSSION

In the interpretation of the results of Table 1, we must take advantage of the fact that we are studying three compounds of a series, the only difference being the size of the counter anions. As far as D is concerned, its sign is such that the single-ion ground state is a doublet. It must be kept in mind that, owing to the symmetry of the metallic sites, the ground doublet is in fact split by rhombic distortion. It can be seen from Table 1 that the axial distortion increases with the size of the counter anion. It is probable that the bulkier the counter anion is the stronger is the distortion around each nickel(II) ion. As expected, the intermolecular coupling of antiferromagnetic nature characterized by the Weiss temperature θ decreases when the size of the counter anion increases. The negative value of θ for $[Ni_2(en)_4Cl_2]Cl_2$ in which the dimeric units are rather far from each other is surprising. This should not be interpreted in terms of ferromagnetic coupling but rather as an artefact of the calculation coming either from a slight shift in the reading of the temperatures or from a more complicated phenomenon such as an increase of J upon cooling down to 27 K. Let us focus now on the exchange-interaction parameter J. This slowly increases with the size of the counter anion. The Ni_2Cl_2 networks for the dichloride and the diperchlorate are shown below. They are centrosymmetric. When one goes from the former to the latter, the bridging angle Ni–Cl–Ni decreases. As expected the Ni–Ni distance also decreases. Moreover, a pronounced asymmetry exists within the two sets of Ni–Cl bonds, this being greater in the dichloride than in the diperchlorate. The crystal structure of $[Ni_2(en)_4Cl_2][BPh_4]_2$ is not known, nevertheless it is legitimate to suppose that with the very bulky counter anion $[BPh_4]^-$ the bridging angle is still smaller than in the diperchlorate.



Dichloride



Diperchlorate

Thus, in the chloro-bridged nickel(II) dimers, the variation of J with the bridging angle occurs in the same direction as in the hydroxo-bridged copper(II) dimers.[12] However, it is much less significant in the former compounds than in the latter. For the hydroxo-bridged copper(II) dimers, a decrease of 1° in the bridging angle produces an enhancement of 74 cm^{-1} in J. In contrast, for the chloro-bridged nickel(II) dimers, a decrease of 1.2° in the angle Ni–Cl–Ni between the dichloride and the diperchlorate only produces an enhancement of 4 cm^{-1} in J. Can we suggest an explanation for this result? We would like to show that within the framework of the orbital model proposed by one of us to describe the exchange interaction, it is possible, if not to give a definitive answer, at least to propose some elements of an answer. In this model [13,14] J is defined as the sum of an antiferromagnetic contribution J_{AF} and a ferromagnetic contribution J_{F} [equations (2)—(4)] where

$$J = J_{\mathrm{AF}} + J_{\mathrm{F}} \tag{2}$$

$$J_{\mathrm{AF}} = -\frac{2}{n^2}\sum_{\mu} S_{\mu\mu}\Delta_{\mu} \tag{3}$$

$$J_{\mathrm{F}} = \frac{2}{n^2}\sum_{\mu,\nu} J_{\mu\nu} \tag{4}$$

$S_{\mu\mu}$ is the overlap integral between two magnetic orbitals of Γ_μ site symmetry centred on each metal ion, Δ_μ is the energy gap between the two molecular orbitals built from these magnetic orbitals, $J_{\mu\nu}$ is a two-electron exchange integral, and n is the number of unpaired electrons around each metallic centre.

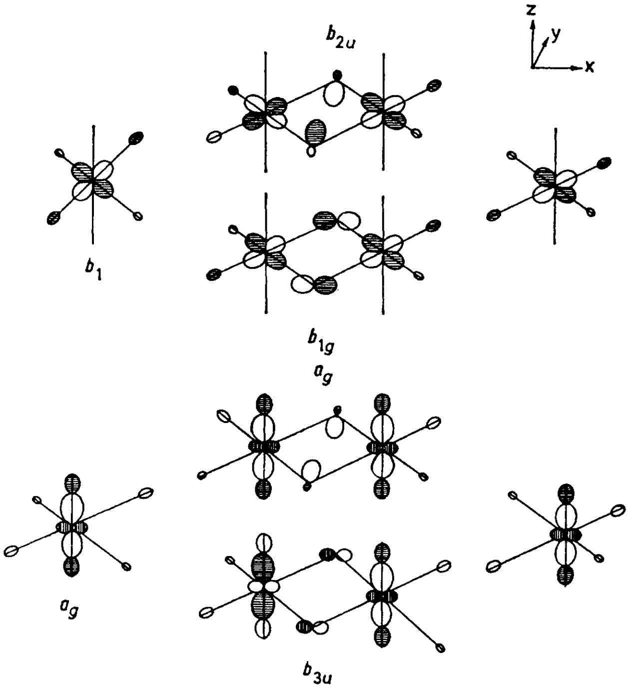
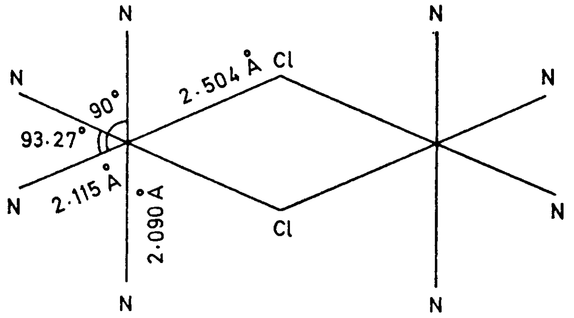


FIGURE 4 Magnetic orbitals and molecular orbitals built from these magnetic orbitals for $[Ni_2(en)_4Cl_2]^{2+}$

So far, it does not yet appear possible to estimate, even in a semiquantitative way, the variation of the ferromagnetic contribution with structural changes. On the other hand, such an estimation for the antiferromagnetic contribution has already been proposed and leads to satisfying results.[18-20] First, we seek how J_{AF} varies with the angle Ni–Cl–Ni. In expression (3), the dominant factor is Δ_μ since it has been shown that, as a first approximation, the overlap integral $S_{\mu\mu}$ is itself proportional to Δ_μ.[21] We assume C_{2v} symmetry for the metallic sites and D_{2h} symmetry for the whole binuclear cation $[Ni_2(en)_4Cl_2]^{2+}$. The two magnetic orbitals around each nickel(II) ion constructed from the d_{z^2} and d_{xy} metallic orbitals (referring to the axis shown in Figure 4) respectively transform as a_1 and b_1. The interaction of the a_1 magnetic orbitals leads to two molecular orbitals transforming as a_g and b_{3u} and the interaction of the b_1 magnetic orbitals leads to the b_{1g} and b_{2u} molecular orbitals. The magnetic orbitals and the molecular orbitals built from them are schematized in Figure 4. We carried out a calculation of the variation in energies of the a_g–b_{3u} and b_{1g}–b_{2u} molecular orbitals with the bridging angle Ni–Cl–Ni for the hypothetical complex $[Ni_2(NH_3)_4Cl_2]^{2+}$ taking the values of the distances and angles as shown below.[10] For this calculation, we used the version FORTICON 8 of the extended Hückel method.[22] The parametrization is given in the Appendix. Figure 5 gives the variations of the energies of the molecular orbitals with the angle Ni–Cl–Ni. The following conclusions can be drawn. (*i*) In the whole angular range considered, *i.e.* between 85 and 105°, the a_g and b_{3u} molecular orbitals are very close in energy. In other words Δ_{a_1} is small. This arises from the small value of the overlaps between the in-plane $3p_x$ and $3p_y$ chlorine orbitals and the d_{z^2} metallic orbital pointing perpendicularly to the Ni_2Cl_2 plane. (*ii*) The slopes of the curves $\varepsilon(b_{1g})$ and $\varepsilon(b_{2u})$ against the angle Ni–Cl–Ni are very similar. In particular, in contrast to what is observed with the hydroxo-bridged copper(II) dimers, there is no crossover.[18-23] Consequently Δ_{b_1} varies only slightly with the angle Ni–Cl–Ni. This latter point may be interpreted as follows. The variation of the metal–chlorine $\langle d_{xy}|3p_x\rangle$ and $\langle d_{xy}|\ 3p_y\rangle$ overlaps with Ni–Cl–Ni angle shows a crossover for Ni–Cl–Ni 90°. For Ni–Cl–Ni >90°, $|\langle d_{xy}|\ 3p_x\rangle|$ is greater than $|\langle d_{xy}|\ 3p_y\rangle|$ and for Ni–Cl–Ni <90° the opposite situation holds. This should lead to a crossover for the variation of $\varepsilon(b_{1g})$ and $\varepsilon(b_{2u})$ with Ni–Cl–Ni angle where $\varepsilon(b_{1g}) > \varepsilon(b_{2u})$ for Ni–Cl–Ni >90° and $\varepsilon(b_{1g}) < \varepsilon(b_{2u})$ for Ni–Cl–Ni <90°. However, another factor must be taken into consideration, namely the chlorine–chlorine overlap. Owing to the diffuseness of the chlorine 3*p* orbitals the σ-type $\langle 3p_y|3p_y\rangle$ overlap is not negligible. It leads to a destabilization of the b_{2u} molecular orbital with regard to the b_{1g}. This destabilization is enhanced when the Cl–Cl distance decreases, *i.e.* when angle Ni–Cl–Ni increases. Both factors, metal–chlorine and chlorine–chlorine overlaps, act in opposite directions, so that the plots of $\varepsilon(b_{1g})$ and $\varepsilon(b_{2u})$ against Ni–Cl–Ni angle have similar slopes. We checked that for the same value of the bridging angles the chlorine–chlorine $\langle 3p_y|3p_y\rangle$ overlap in the nickel(II) dimers is roughly twice as strong as the oxygen–oxygen $\langle 2p_y|2p_y\rangle$ overlap in the copper(II) dimers (0.020 5 and 0.011 0 respectively for bridging angles of 90°). To study the influence of the asymmetry within the Ni_2Cl_2 network we carried out a calculation of the variation in energies ε of the molecular orbitals built from the two pairs of magnetic orbitals with the difference *D* between the Ni–Cl bond lengths, the bridging angle Ni–Cl–Ni remaining constant and equal to 95°. For $D \neq 0$, the whole molecular symmetry is



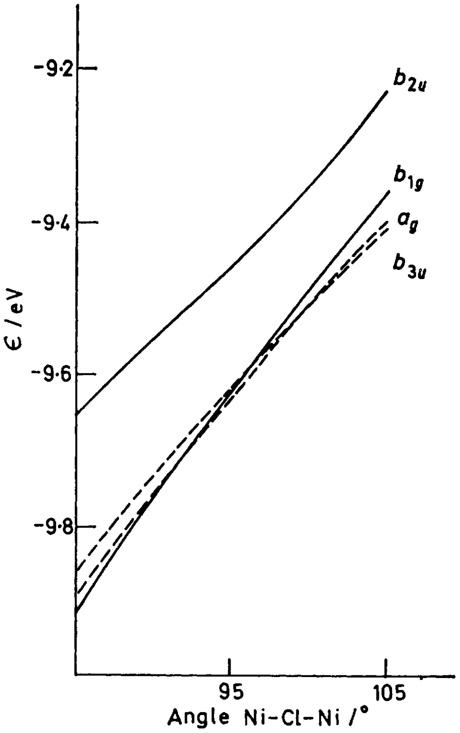


FIGURE 5 Variation of the energies of the a_g — b_{3u} and b_{1g} — b_{2u} molecular orbitals with the bridging angle Ni–Cl–Ni

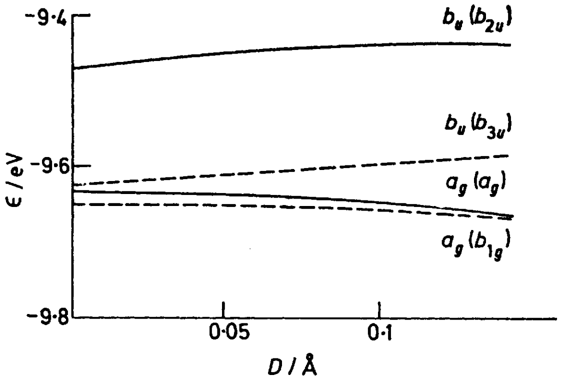


FIGURE 6 Variation of the energies of the a_g (a_g), b_u (b_{3u}), a_g (b_{1g}), and b_u (b_{2u}) molecular orbitals with the difference *D* between the Ni–Cl bond lengths in the Ni_2Cl_2 network

only C_{2h} and the molecular orbitals transform as $2A_g + 2B_u$. The plots of ε against D are given in Figure 6. They show that a variation of D from 0.09 (in the dichloride) to 0.06 Å (in the diperchlorate) has a very weak influence on the energies of the molecular orbitals.

From this study, two results may be deduced. If the very weak contribution from the a_1 magnetic orbitals is neglected, J_{AF} in the chloro-bridged nickel(II) dimers reduces to $-\frac{1}{2}S_{b_1}\Delta_{b_1}$. This contribution is $-2S_{b_1}\Delta_{b_1}$ for the copper(II) dimers. Thus, one perceives that the antiferromagnetic contribution is smaller for the nickel(II) than for the copper(II) dimers. In other respects, this antiferromagnetic contribution for the nickel(II) dimers is weakly sensitive to small variations of the bridging angle Ni–Cl–Ni and of the asymmetry within the Ni–Cl bonds.

Conclusion.—Two studies have already been devoted to the investigation of the magnetic behaviour of $[Ni_2(en)_4Cl_2]Cl_2$. In the first, Ginsberg *et al.*[4] established the ferromagnetic nature of the intramolecular coupling. They found a J value of *ca.* 20 cm^{-1} which is significantly larger than the one determined in this work. In the second,[24] the single-crystal magnetic susceptibilities were determined between 1.5 and 25 K. The authors who were aware of the monoclinic–triclinic phase transition adopted the point of view that, since the phase transition occurred at very low temperature, there was no drastic reorientation of the relatively large dimeric unit. They determined a J value of *ca.* 7 cm^{-1}. Our approach is at the same time opposite and complementary to the one adopted in this latter study. We think that the D and J parameters may be quite sensitive to very small molecular motions accompanying the phase transition and we have limited the quantitative interpretation of the magnetic data to the range of existence of the monoclinic phase.

Finally, as far as the theoretical aspect of this work is concerned, we are conscious that the results obtained do not provide all the elements for an understanding of the mechanism of the exchange interaction in nickel(II) dimers. The ferromagnetic contribution is actually preponderant and we focused our theoretical approach on J_{AF}. This work emphasizes the dramatic need for further and decisive progress in understanding the main factors governing the magnitude of the ferromagnetic coupling.

APPENDIX

The calculation performed in this work is of the extended-Hückel type, with charge iteration on all the atoms, Madelung corrections, and weighted H_{ij} formula. The atomic orbitals are simple Slater-type orbitals for hydrogen, nitrogen, chlorine, and nickel except for metallic 3*d* orbitals for which we chose two-component orbitals. Orbital exponents for the non-metallic atoms are chosen using Slater's rules; 4*s* and 4*p* exponents for copper come from Burns,[25] assuming a charge of +1 on the transition ions in the complex. Exponents and relative weights for metallic 3*d* orbitals are taken from Richardson *et al.*[26] The A_μ, B_μ, C_μ, and $g_{\mu\mu}$ parameters are given in Table 2. The K parameter of the Wolfsberg–Helmholz approximation is taken as 1.75. The energies are corrected for the shift due to the +2 charge of the binuclear cation.

TABLE 2

Parameters (in eV) used in the iterative extended-Hückel calculations

		A_μ	B_μ	C_μ	$g_{\mu\mu}$
Ni	4*s*	0.911	8.561	7.540	6.200
	4*p*	0.986	6.552	3.890	4.300
	4*d*	0	9.448	8.704	13.600
Cl	3*s*	0	10.660	25.930	10.700
	3*p*	0	10.660	13.820	10.700
N	2*s*	0	13.700	26.400	13.700
	2*p*	0	13.700	13.400	13.700

A list of the magnetic data can be obtained on request from the authors.

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