Linear Dependence of Spin Exchange Coupling Constant on Bridge Angle in Phenoxy-bridged Dinickel(II) Complexes

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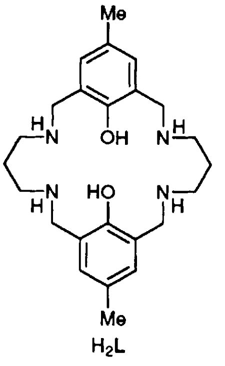
A magneto-structural relationship showing linear dependence of antiferromagnetic exchange coupling constant ($-J$) on Ni–O–Ni bridge angle as well as the intramolecular Ni···Ni distance has been obtained with a series of phenoxy-bridged macrocyclic dinickel(II) complexes with centrosymmetric structures.

Following the work of Bleaney and Bowers[1] on the magnetic and ESR properties of dimeric copper(II) acetate, exchange coupled polynuclear complexes have been studied extensively with special emphasis on magneto-structural relationships.[2] However, since such correlations involve interactions between the unpaired electrons in the magnetic orbitals of the metal atoms and the orbitals of the bridging ligand atoms and their orientations, a large number of structural parameters seem to affect the superexchange mechanism even in dinuclear systems.[3] The demonstration of a linear dependence of exchange coupling constant (J) on Cu–O–Cu bridge angle in planar dihydroxy-bridged dicopper(II) complexes has turned out to be one of the most useful and best known magneto-structural correlations.[4]

Recently,[5] we have reported variable-temperature (5–300 K) magnetic susceptibilities of six phenoxy-bridged dinickel(II) complexes derived from the macrocyclic ligand, H_2L. The complexes, $[Ni_2L(H_2O)_4][ClO_4]_2\cdot 4NH_2CONH_2$ **1**,[6] $[Ni_2L(NCS)_2(H_2O)_2]\cdot 2(Me)_2NCHO$ **2**,[5] $[Ni_2L(MeOH)_2(ClO_4)_2]\cdot 2NH(C_2H_5)_3ClO_4$ **3**,[7] $[Ni_2L(imidazole)_2][ClO_4]_2$ **4**,[8] $[Ni_2L(pyridine)_2][ClO_4]_2$ **5**,[8] and $[Ni_2L(O_2CCH_2NH_3)(H_2O)_2][ClO_4]_2\cdot 2H_2O$ **6**,[9] which differ among themselves due to the variation of the axial ligands, exhibit antiferromagnetic interactions, whose magnitude ($-J$) ranges between 1 and 67 cm^{-1}. The substantial variation of the value of $-J$ has been rationalized[5] in terms of stereochemical changes. In the six-coordinated complexes, **1–3**, increased tetragonal distortions around nickel(II) are accompanied by increased antiferromagnetic interactions. Change in stereochemistry from octahedral to square pyramidal geometry in complexes **4** and **5** leads to further increase in the values of $-J$. Complex **6**, which is most weakly antiferromagnetic ($-J = 1\ cm^{-1}$), differs from the others in that it contains an additional superexchange pathway involving the carboxylate bridge of the zwitterionic glycine, which is perpendicular to the Ni_2O_2 pathway. With the availability of the crystal structure of **4**,† we now demonstrate that for complexes **1–5**, all of which have centrosymmetric structures, the value of the exchange coupling constants is directly proportional to the Ni–O–Ni bridge angles (Θ) or Ni···Ni distances (d).



H_2L

The ORTEP view for the complex cation $[Ni_2L(imidazole)_2]^{2+}$ (Fig. 1) shows that two square pyramidal nickel(II) centres are bridged by two phenoxide oxygens and the distorted Ni_2O_2 plane is completed by two secondary amine

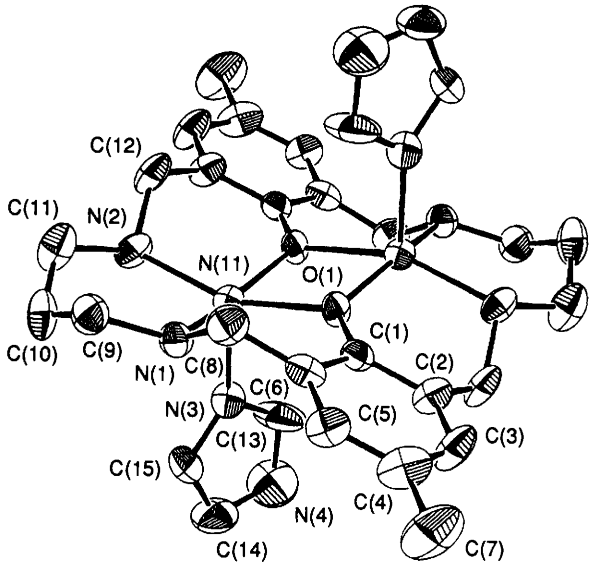


Fig. 1 Perspective view of the $[Ni_2L(imidazole)_2]^{2+}$ cation along with selected bond distances (Å) and angles (°): Ni(1)–O(1) 2.022(6), Ni(1)–O(1') 2.015(6), Ni(1)–N(1) 2.071(7), Ni(1)–N(2) 2.083(7), Ni(1)–N(3) 2.007(7), Ni(1)–Ni(1') 3.182(3). Ni(1)–O(1)–Ni(1') 104.1(3), O(1)–Ni(1)–O(1') 75.9(3), O(1)–Ni(1)–N(1) 91.5(3), O(1)–Ni(1)–N(2) 157.8(3), O(1)–Ni(1)–N(3) 98.1(3), O(1)–Ni(1')–N(1') 161.9(3), O(1)–Ni(1')–N(1') 161.9(3), O(1)–Ni(1')–N(2') 90.5(3), O(1)–Ni(1')–N(3') 97.0(3), N(1)–Ni(1)–N(2) 97.1(3), N(1)–Ni(1)–N(3) 97.7(3), N(2)–Ni(1)–N(3) 101.0(3)

Table 1 Magneto-structural parameters for complexes **1–5**

Complex	$Ni–N_{eq}$/Å	$Ni–O_{eq}$/Å	$Ni–X_{ax}$/Å	$Ni–Y_{ax}$/Å	Ni···Ni/Å	Ni–O–Ni/°	J^a/cm^{-1}
$[Ni_2L(H_2O)_4][ClO_4]_2\cdot 4NH_2CONH_2$ **1**[b]	2.078	2.031	2.116	2.167	3.10	99.5	−17.0(2)
$[Ni_2L(NCS)_2(H_2O)_2]\cdot 2(CH_3)_2NCHO$ **2**[c]	2.070	2.040	2.080	2.213	3.11	99.2	−21.3(1)
$[Ni_2L(CH_3OH)_2(ClO_4)_2]\cdot 2NH(C_2H_5)_3ClO_4$ **3**[d]	2.060	2.028	2.105	2.411	3.135	101.3	−29.5(1)
$[Ni_2L(imidazole)_2][ClO_4]_2$ **4**[e]	2.077	2.019	2.007	—	3.182	104.1	−49.8(1)
$[Ni_2L(pyridine)_2][ClO_4]_2$ **5**[f]	2.091	2.011	2.038	—	3.206	105.7	−67.1(1)

[a] E.s.d.'s are given in parenthesis. [b] Ref. 6. [c] Ref. 5. [d] Ref. 7. [e] This work. [f] Ref. 8

nitrogens. The imidazole ligands are bound in a *trans* fashion above and below the dinuclear centres. The centre of inversion is at the middle of Ni_2O_2 plane. The apical displacement of the nickel(II) centre towards the imidazole is 0.307 Å, which is somewhat less compared to that observed in complex **5** (0.332 Å). Related to the apical displacement of the metal centre is the distance of the Ni–N(axial) bond, which is longer for **5** [2.038(5) Å] compared to that of **4** [2.007(7) Å]. Clearly, variation of the Ni–O–Ni bridge angle should ultimately depend on the Ni–N(axial) bond strength. The equilibrium constants determined for the reaction [eqn. (1)],

$$[Ni_2L(MeOH)_4]^{2+} + 2B \rightleftharpoons [Ni_2L(B)_2]^{2+} + 4MeOH \quad (1)$$

with several heterocyclic bases (B) have shown[8] that the formation constant for complex **4** (K_1 = 115 dm^3 mol^{-1}) is an order of magnitude greater than that of **5** (K_1 = 11 dm^3 mol^{-1}).

The essential structural parameters and *J* values for complexes **1–5** are given in Table 1. The values of exchange coupling constant, *J*, were determined[5] by taking into consideration the contributions due to zero-field splitting of nickel(II) and interdimer exchange coupling constant, although essentially the same *J* values were obtained when the isotropic Heisenberg-Dirac–Van Vleck model was used. It may be noted that for all the complexes the in-plane metal-ligand donor distances do not show any significant variation. On the other hand, as the extent of antiferromagnetic interaction increases along the series, progressive increase in the intramolecular Ni···Ni distance (*d*) as well as Ni–O–Ni bridge angle (θ) occurs. A good straight line fit (correlation coefficient = 0.986) is obtained for a plot of $-J$ *vs* θ (Fig. 2). A similar straight line (correlation coefficient 0.992) was obtained in $-J$ *vs. d* plot. The extrapolated line in Fig. 1 at J = 0 gives the cross-over angle of 97°. It is interesting to note that for dihydroxy-bridged dicopper(II) complexes the cross-over point is at *ca* 97.5° (ref. 4), indicating an almost identical bridge-angle dependence of coupling constants for both dicopper(II) and dinickel(II) systems. This is not unexpected because even though $d_{x^2-y^2}$ and d_{z^2} are the magnetic orbitals for nickel(II), the involvement of symmetric d_{z^2} orbitals in exchange coupling will be minimal in centrosymmetric complexes. Consequently, just as for copper(II), the equatorial exchange interactions decide the magnetic behaviour of the present series of complexes. Earlier,[10] we have reported a value of *J*, -410 cm^{-1}, for the dicopper(II) complex [$Cu_2L(ClO_4)_2$] with the Cu–O–Cu bridge angle of 102.8°. For a nickel(II) complex with the same bridge angle the interpolated *J* value is -45 cm^{-1}. Keeping in mind that for comparison of copper(II) and nickel(II) systems $4JS^2$ values should be considered because the two metal ions concerned have different numbers of unpaired electrons, the much weaker antiferromagnetic interaction in the dinickel species is quite evident. One important structural parameter that might be responsible for the better overlap of $d_{x^2-y^2}$–(s,p)–$d_{x^2-y^2}$ orbitals and hence stronger antiferromagnetic coupling in the dicopper(II) complex is the much shorter Cu–O(phenoxide) distance (1.918 Å) as compared to the Ni–O(phenoxide) distance (2.025 ± 0.015 Å).

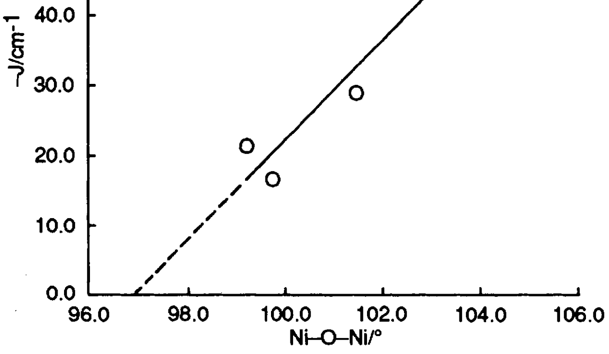


Fig. 2 Plot of antiferromagnetic coupling constant ($-J$) *vs.* Ni–O–Ni bridge angle (θ) for complexes **1–5**

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Footnote

† *Crystal data* for **4**: $C_{30}H_{42}N_8O_{10}Ni_2Cl_2$, M = 863.02, monoclinic, space group $P2_1/n$ (No. 14), a = 9.001(2), b = 11.797(3), c = 17.538(2) Å, β = 99.33(1)°, U = 1837.7(6) Å^3, Z = 2, D_c = 1.559 g cm^{-3}, MoKα = 0.71069 Å, μ = 12.38 cm^{-1}. Intensity data were measured at 299 K using a Rigaku AFC6S diffractometer with graphite monochromated Mo-Kα radiation in the ω–2θ scan mode. With $2\theta_{max}$ = 50.1°, a total of 3647 reflections were measured, of which 3422 (R_{int} = 0.192) were unique. The intensities of three control reflections measured after every 150 showed no decay of the crystal. Lorentz-polarization and absorption corrections were made. The structure was solved by direct methods.[11] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were fixed in their calculated positions. The final cycle of full-matrix least-squares refinement was based on 1491 observed reflections [$(I) > 2.0\,\sigma(I)$] and converged to R = 0.056 and Rw = 0.042. Final difference map showed peaks varying between +0.46 and −0.46 eÅ^{-3}. Atom scattering factors were taken from ref. 12. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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