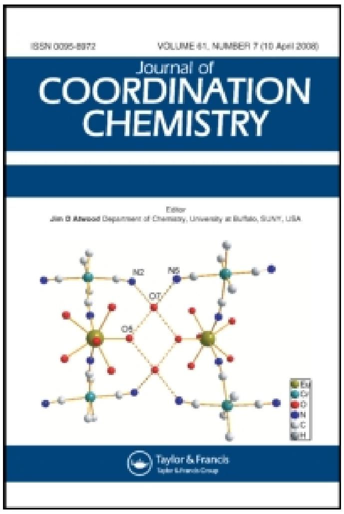

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The Magnetic Properties of the Tetranuclear Nickel(II) Complex with [(3,5-Dichloro-2-Pyridyl)Azo]-8-Hydroxyquinoline-5-Sulfonate

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THE MAGNETIC PROPERTIES OF THE TETRANUCLEAR NICKEL(II) COMPLEX WITH [(3,5-DICHLORO-2-PYRIDYL)AZO]-8-HYDROXYQUINOLINE-5-SULFONATE

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Magnetic exchange between the four nickel(II) sites in the title tetranuclear complex has been studied. Experimental magnetic susceptibilities of the complex are well interpreted in terms of the theoretical equation. The four nickel(II) sites are antiferromagnetically coupled with $J = -11\,\mathrm{cm}^{-1}$ and $g = 2.25$ through oxygen atoms with the large Ni-O-Ni angles (*ca* 140°).

KEY WORDS: Magnetic properties, tetranuclear nickel(II) complex, multidentate ligand

INTRODUCTION

Previously,[1] we have prepared a tetranuclear nickel(II) complex with the multidentate ligand 7-[(3,5-dichloro-2-pyridyl)azo]-8-hydroxyquinoline-5-sulfonate (Hpahqs) and characterized its structure by X-ray crystallography. In this complex, except for one N atom in each azo group, all other donor atoms in the ligand are fully used in coordination to nickel(II), and the four nickel(II) sites are bridged by O atoms in the hydroxyquinoline moieties, thus forming a novel square array structure.

In the present work, magnetic exchange (antiferromagnetic interactions) between the four nickel(II) sites in the tetranuclear complex $[Ni_4(pahqs)_4(H_2O)_4]\cdot 20H_2O$ has been studied.

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EXPERIMENTAL

The preparation and determination of the magnetic susceptibilities of the complex $[Ni_4(pahqs)_4(H_2O)_4]\cdot 20H_2O$ was described in our previous papers.[1] The effective magnetic moments per nickel(II) ion were calculated with the equation $\mu_{eff}=2.83[(\chi_A-N_\alpha)T]^{1/2}$, where χ_A is the molar magnetic susceptibility corrected for the diamagnetism of the constituting atoms using Pascal's constants,[2] and N_α is the temperature-independent paramagnetism per mole of nickel(II). The observed magnetic susceptibility data fitted to (*1*) and the best fit parameters of J and g, obtained by a nonlinear least-squares procedure. The quality of fit was estimated by means of a discrepancy index, $\sigma_{dis}=[\Sigma(\chi_{obsd}-\chi_{calcd})^2/\Sigma\chi_{obsd}^2]^{1/2}$.

RESULTS AND DISCUSSION

The molecular structure and structural characteristics of the tetranuclear complex have been discussed previously.[1] Variation of magnetic susceptibility (χ_A) and effective magnetic moment (μ_{eff}) with temperature observed for the present complex is illustrated in Figure 1. The magnetic properties of tetranuclear clusters have been reviewed elsewhere.[3] For such compounds the exchange Hamiltonian

$$H=-2\Sigma J_{ij}S_iS_j$$

has eigenvalues which can be obtained by making use of the vector coupling model.[4]

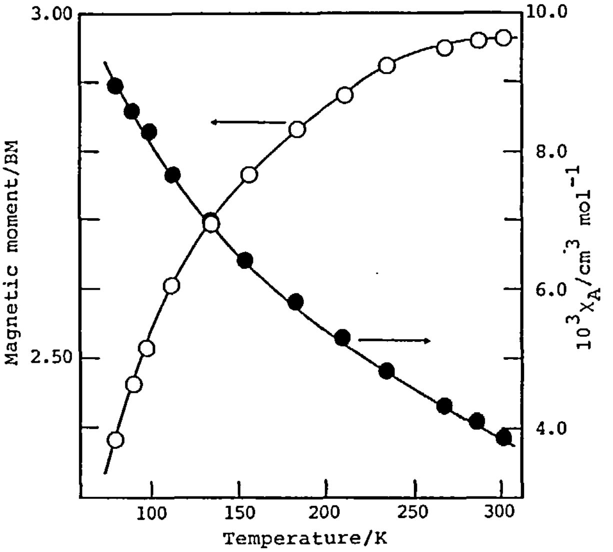

FIGURE 1 Temperature dependence of magnetic moments (μ_{eff}/Ni) and magnetic susceptibilities (χ_A). The full line represents a fit to (*1*) to give $J=-11\ cm^{-1}$ and $g=2.25$.

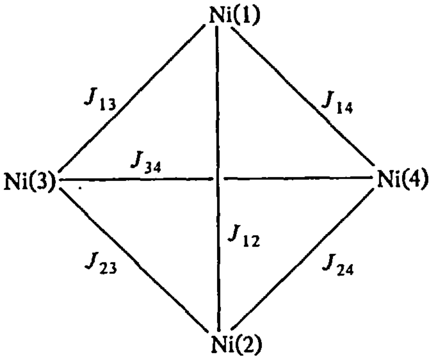

FIGURE 2 Magnetic exchange model for the four nickel(II) sites; $J_{13}=J_{23}=J_{24}=J_{14}=J$.

For an isolated quadrilateral tetramer, this Hamiltonian is

$$H=-2J[S_1S_3+S_2S_3+S_1S_4+S_2S_4]-2J_{12}S_1S_2-2J_{34}S_3S_4.$$

J_{ij} is the exchange integral between adjacent nickel atoms (1,3; 2,3; 1,4 and 2,4) and J_{12} and J_{34} are the exchange integrals between the two terminal nickel atoms (1,2 and 3,4) in the tetramer (Figure 2). We assume $J=J_{13}=J_{23}=J_{24}=J_{14}$, since the geometry around each of the four nickel(II) was a distorted octahedron with similar bond angles,[1] and the Ni–O–Ni angles around the four nickel(II) sites were almost the same (*ca* 140°).[1] The expected values of the spin angular momentum operators S_i are the same and we write it as S. By taking

$$S'=S_1+S_2+S_3+S_4$$
$$S_{12}=S_1+S_2$$
$$S_{34}=S_3+S_4,$$

the Hamiltonian can be rewritten as

$$H=-J[S'^2-S_{12}^2-S_{34}^2]-J_{12}[S_{12}^2-S_1^2-S_2^2]-J_{34}[S_{34}^2-S_3^2-S_4^2].$$

The energy levels under this Hamiltonian are simply

$$E(S')=-J[S'(S'+1)-S_{12}(S_{12}+1)-S_{34}(S_{34}+1)]$$
$$-J_{12}S_{12}(S_{12}+1)-J_{34}S_{34}(S_{34}+1).$$

The states, $(S',S_{12},S_{34};E)$, formed by the spin-spin coupling for the Ni(II)$_4$-system are as follows: $(4,2,2;-8J)$, $(3,2,2;0)$, $(3,2,1;-4J+4J_{34})$, $(3,1,2;-4J+4J_{12})$, $(2,2,2;6J)$, $(2,2,1;2J+4J_{34})$, $(2,2,0;6J_{34})$, $(2,1,2;2J+4J_{12})$, $(2,1,1;-2J+4J_{12}$

$+4J_{34}$), ($2,0,2;6J_{12}$), ($1,2,2;10J$), ($1,2,1;6J+4J_{34}$), ($1,1,2;6J+4J_{12}$), ($1,1,1;$ $2J+4J_{12}+4J_{34}$), ($1,1,0;$ $4J_{12}+6J_{34}$), ($1,0,1;6J_{12}+4J_{34}$), ($0,2,2;12J$), ($0,1,1;$ $4J+4J_{12}+4J_{34}$), ($0,0,0;6J_{12}+6J_{34}$). By applying the van Vleck equation, the magnetic susceptibility expression for this system is given by

$$\chi_A=(1/4)\chi_M=(\mathrm{N}g^2\beta^2/2\kappa T)(A/B)+N_\alpha \qquad (1)$$

where $A = 14 + 30\exp(-8x) + 14\exp(-4x+4y) + 14\exp(-4x+4z) + 5\exp(-2x+4y+4z) + 5\exp(6y) + 5\exp(6z) + \exp(4y+6z) + \exp(6y+4z) + 5\exp(2x+4y) + 5\exp(2x+4z) + \exp(2x+4y+4z) + 5\exp(6x) + \exp(6x+4y) + \exp(6x+4z) + \exp(10x)$, $B = 7 + 9\exp(-8x) + 7\exp(-4x+4y) + 7\exp(-4x+4z) + 5\exp(-2x+4y+4z) + 5\exp(6y) + 5\exp(6z) + 3\exp(4y+6z) + 3\exp(6y+4z) + \exp(6y+6z) + 5\exp(2x+4y) + 5\exp(2x+4z) + 3\exp(2x+4y+4z) + \exp(4x+4y+4z) + 5\exp(6x) + 3\exp(6x+4y) + 3\exp(6x+4z) + 3\exp(10x) + \exp(12x)$, $x=-J/\kappa T$, $y=-J_{12}/\kappa T$, and $z=-J_{34}/\kappa T$, respectively. The magnetic susceptibilities of [Ni(pahqs)]$_4$ were well interpreted in terms of the (*1*). The least-squares best fit of (*1*) to the experimental susceptibilities is found for $g=2.24$, $J=-11\,\mathrm{cm}^{-1}$, and with the assumption $J_{12}=J_{34}=0$, since direct exchange interaction between the two terminal nickel atoms will not take place because of their large separation (*ca* 5.8 Å); there is no superexchange interaction between these nickel atoms because they have no bridging atoms.[1] N_α is fixed at $230\times10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$.[5] The use of N_α as an adjustable parameter in the fitting procedure does not materially affect the values obtained for g and J($g=2.25$, $J=-11\,\mathrm{cm}^{-1}$, and $N_\alpha=198\times10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$). The best fits between the experimental and the theoretical susceptibilities are shown in Figure 1. Magnetic behaviour with a negative J value indicates the presence of antiferromagnetic spin coupling among the four nickel(II) sites *via* bridging oxygen atoms in the tetrameric unit of the complex.

It is reasonable to suggest that the Ni–O–Ni angles, which are larger than 90°, lead to the antiferromagnetic interaction.[6] In other words, in this complex, the geometry around each of the four nickel(II) ions (t_{2g}^6, e_g^2) is a distored octahedron; all the nickel(II) are bridged by the O atom (sp^2 hybridization) of the hydroxyquinolinate with *ca* 140° angles for Ni–O–Ni.[1] Accordingly, superexchange between the two adjacent $e_g((d_{x_2-y_2})^1,(d_{z_2})^1)$ orbitals of the nickel atoms would occur through sp^2 orbitals of the bridging oxygen atom following the σ pathway.[7]

$$\begin{array}{cccc} \upharpoonleft & \downharpoonleft\upharpoonright & \downharpoonleft\upharpoonright & \upharpoonleft\downharpoonright \\ d_{x_2-y_2}(\mathrm{Ni})\| & \mathrm{sp}^2(\mathrm{O})\| & \mathrm{sp}^2(\mathrm{O})\| & d_{x_2-y_2}(\mathrm{Ni}) \end{array}$$

The resulting interaction between the two adjacent nickel atoms must be antiferromagnetic as is observed experimentally.

ACKNOWLEDGEMENTS

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REFERENCES

1. H. Huang, F. Kai, Y. Asai, M. Hirohata and M. Nakamura, *Chem. Lett.*, 65 (1991); H. Huang, F. Kai, Y. Asai, M. Hirohata and M. Nakamura, *Bull. Chem. Soc. Jpn.*, **64**, 2464 (1991).
2. P. W. Selwood, "Magnetic Chemistry," (Interscience Publishers, New York, 1956), p. 78 and 91.
3. See, for example, R. L. Carlin, "Magnetochemistry," (Springer-Verlag, New York, 1986), Ch. 5, p. 70.
4. K. Kambe, *J. Phys. Soc. Jpn.*, **5**, 48 (1950).
5. A. P. Ginsberg, R. L. Martin and R. C. Sherwood, *Inorg. Chem.*, **7**, 932 (1968).
6. W. L. Gladfelter, M. W. Lynch, W. P. Schaefer, D. N. Hendrickson and H. B. Gray, *Inorg. Chem.*, **20**, 2390 (1980), and refs. therein.
7. Y. Muto, "Kireito Kagaku," Ed. K. Ueno, (Nankodou, Inc., Tokyo, 1976), Vol. 2, pp. 437–469, and refs. therein.