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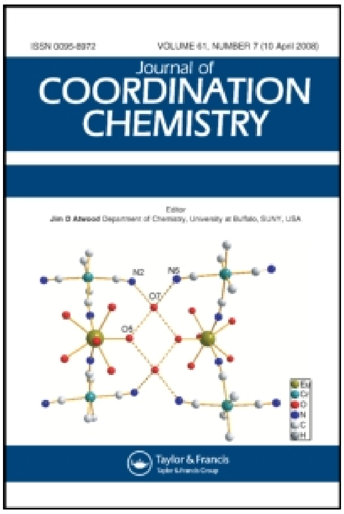

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Synthesis, crystal structure and magnetic properties of an imidazolate bridged dinuclear nickel(ii) complex; μ-(im)-[(232-tet)ni]$_2$(clo$_4$)$_3$

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF AN IMIDAZOLATE BRIDGED DINUCLEAR NICKEL(II) COMPLEX; μ-(Im)-[(232-TET)Ni]$_2$(ClO$_4$)$_3$

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An imidazolate bridged dinuclear nickel(II) complex, μ-(Im)-[(232-tet)Ni]$_2$(ClO$_4$)$_3$, where 232-tet = *N,N'-bis*(2-aminoethyl)-1,3-propanediamine, Im = imidazolate anion, has been synthesized and its crystal structure determined. Crystals are monoclinic, space group $C2$, with a = 11.982(4), b = 12.320(2), c = 11.711(4) Å, β = 110.97(2)° and Z = 2. Least-squares refinement of the structure leads to R and R_w factors of 0.036 and 0.044, respectively. The structure consists of discrete dinuclear cations, μ-(Im)-[(232-tet)Ni]$_2^{3+}$, with the intramolecular nickel(II)-nickel(II) separation being 6.190(3) Å, and three perchlorate counter anions. Each nickel(II) atom is five-coordinated in a square pyramid with the four N atoms of the 232-tet ligand in the basal positions and one N atom of the Im anion in the apical position. The Ni-N(Im) and average Ni-N (232-tet) bondlengths are 2.049(4) and 2.086(4) Å, respectively. Magnetic susceptibility measurements in the temperature range 1.5 to 300K show that the two nickel(II) atoms of the dinuclear unit are antiferromagnetically coupled with $J = -12.5$ cm^{-1}, $g = 2.19$, T_N being *ca* 25K.

Keywords: nickel; imidazolate; crystal structure; antiferromagnetic coupling

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INTRODUCTION

The study of magnetic interactions in dinuclear and polynuclear metal complexes is still a main subject in inorganic chemistry. Much of this work has concerned transition metal complexes bridged by oxalate, cyanate, thiocyanate, selenocyanate, *etc*. These efforts have resulted in a better fundamental understanding of spin exchange through multiatomic bridges and in the synthesis of molecular materials exhibiting new but predictable magnetic properties.[1, 2]

The bridging ligands can be divided into two groups, one where one atom forms the bridge and one where several atoms form the bridge, *i.e.*, in the first case the two metals have the same ligator atom, and in the second case the two metals have different ligator atoms. Typical examples of the first group are μ-oxo, μ-hydroxo, μ-alkoxo, and μ-halogenato, while the second group is represented by μ-acetato, μ-oxalato, μ-cyanato, μ-squarato, μ-selenoctanato, μ-thiocyanato and μ-imidazolate.

The imidazolate anion, the deprotonated form of imidazole, can serve as a bridging ligand between transition metal ions. Such complexes provide an opportunity to proble further the electronic and magnetic exchange interactions mediated by polyatomic bridging ligands, especially nitrogen heterocycles.[3] Although oligomeric and polymeric imidazolate bridged metal complexes are quite common in the solid state,[4-5] dinuclear metal complexes are rate except for copper complexes. Herein we report the synthesis, crystal structure and magnetic properties of a new dinuclear nickel(II) complex bridged by imidazolate.

EXPERIMENTAL

Physical Measurements

Elemental analyses for carbon, hydrogen, nitrogen were performed with a Perkin-Elmer elemental analyser (model 240C). The IR spectrum was recorded with a Nicolet 170SX FT-IR spectrophotometer using on KBr discs. Magnetic measurement on a powder sample was carried out in the 1.5 to 300K temperature range by means of a Faraday magnetometer. The magnetic field was 14967G. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine). Diamagnetic corrections were estimated from Pascal's constants.[6] Electronic spectra were obtained using a Shimadzu UV 3100 spectrophotometer.

Preparation

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

N,N′-bis(2-aminoethyl)-1,3-propanediamine, 232-tet, was prepared according to the procedure of Hamilton and Alexander.[7] To an aqueous solution of nickel perchlorate hexahydrate (732 mg, 2 mmol) was added an aqueous solution of 232-tet (320 mg, 2 mmol) with stirring. A aqueous solution of sodium imidazolate (90 mg, 1 mmol) was then added dropwise to the solution. After standing the solution at room temperature for several days, well-shaped, blue single crystals were obtained by slow evaporation; yield: 682 mg, 85%. Found: C, 26.07; H, 5.55; N, 17.29. Calculated for $Ni_2C_{17}H_{43}Cl_3N_{10}O_{12}$ (%): C, 25.42; H, 5.40; N, 17.44.

X-ray Crystallography

Diffraction data were collected at 296K with an Enraf-Nonius CAD4 four-circle diffractometer [8] using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). Crystal data and details of data collection are given in Table I. Unit cell parameters and the orientation matrix were determined from angular settings of 25 carefully centred reflections. The intensities of three standard reflections measured every 400 reflections showed no significant variation. Intensity data were collected by the $\omega/2\theta$ scans technique with a scan range of $0.50 + 0.35 \tan\theta$ and a scan speed less than 5.49° min^{-1}. Intensities were corrected for absorption by empirical ψ scans. Some 1605 reflections having $I > 3\sigma(I)$ were considered as independent and used in the structure analysis. The structure was solved by direct methods and refined by full-matrix least-squares techniques.[9] In all structure-factor calculations the atomic scattering factors were taken from ref. 10. The effect of anomalous dispersion was included for all non-hydrogen atoms. Non-H atom coordinates were obtained by successive Fourier syntheses. After all coordinates and anisotropic thermal parameters of non-H atoms were refined, the hydrogen atom coordinates were obtained from difference Fourier maps. Finally, coordinates and anisotropic thermal parameters of non-H atoms, and isotropic thermal parameters of H atoms were refined. The final conventional R and R_w factors were 0.036 and 0.044, respectively. The highest and lowest peaks in the final Fourier difference map had an electron density of 0.59 and -0.64 eÅ^{-3}. All calculations were performed by an MICRO VAX 3100 computer with TEXSAN [11] and ORTEPII [12] programs. The cation structure is illustrated in Figure 1. Fractional atomic coordinates for all non-hydrogen atoms are listed in Table II and selected bondlengths and angles are given in Table III.

TABLE I Crystal data and details of data collection for μ-(Im)-[(232-tet)Ni]$_2$(ClO$_4$)$_3$.

Formula	$Ni_2C_{17}H_{43}Cl_3N_{10}O_{12}$
formula weight	803.35
Crystal system	Monolinic
Space group	$C2$
a (Å)	11.982(4)
b (Å)	12.320(2)
c (Å)	11.711(4)
β (°)	110.97(2)
V (Å^3)	1614(2)
Z	2
$F(000)$	836
D_{calc} (g cm^{-3})	1.65
Crystal size (mm)	0.15 × 0.15 × 0.12
μ (Mo-Kα) (cm^{-1})	14.89
Data collection instrument	Enraf-Nonius CAD4
Radiation type, Wavelength λ (Å)	Mo$K\alpha$, 0.71073
Temperature (K)	296
Data collection's method	$\omega/2\theta$ scans
Range of h, k, l	0 ~ 14, 0 ~ 15, −14 ~ 14
No. of reflections measured	1745
No. of independent reflections	1685
No. of observed reflections	1605
Criterion for observed reflections	$I > 3\sigma(I)$
No. of parameters refined	199
R, R_w	0.036, 0.044
weighting scheme	$w = 1/\sigma^2(F)$
S	1.37
Maximum Δ/σ	0.07
$\Delta\rho_{max}$(eÅ^{-3})	0.59
$\Delta\rho_{min}$(eÅ^{-3})	−0.64

RESULTS AND DISCUSSION

Description of Structure

The structure of title compound consists of three perchlorate anions and a dinuclear μ-(Im)-[(232-tet)Ni]$_2^{3+}$ cation with a two-fold axis through C(1) and the mid-point of the C(2)-C(2)^a (a: $-x$, y, $-z$) bond of the imidazolate ring. The dinuclear cation consists of two (232-tet)Ni(II) units bridged by an imidazolate anion forming a homobinuclear complex. The intramolecular Ni···Ni separation is 6.190(3) Å, whereas the shortest intermolecular Ni···Ni^b (b: 1-x, y, $1-z$) distance is 7.237(3) Å. The nickel(II) coordination geometry is square pyramidal with the four N atoms of the 232-tet ligand in the basal positions and one N atom of the Im anion in the apical position. The imidazolate anion joins two adjacent coordination polyhedra with its N atoms occupying apical positions in both

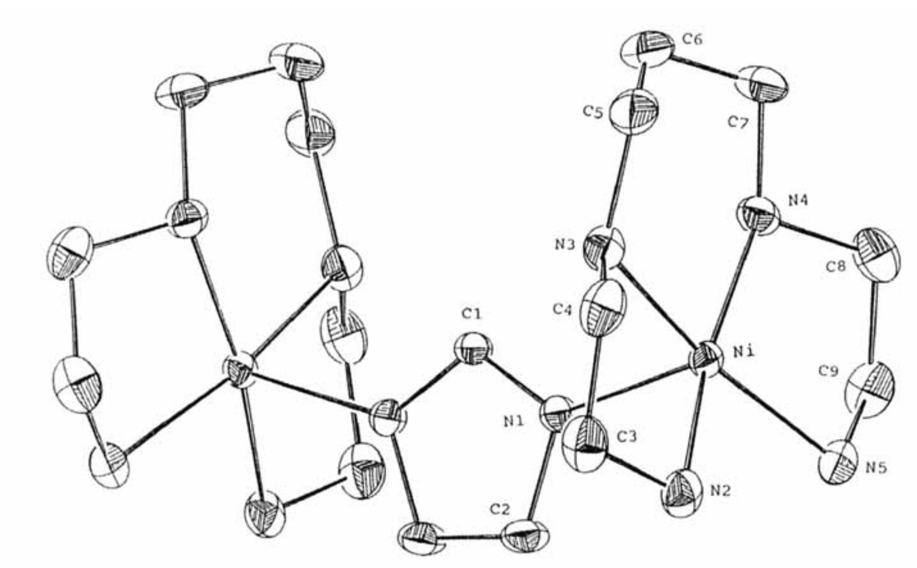

FIGURE 1 The cation structure showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

TABLE II Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2); $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*a_i a_j$.

Atom	x/a	y/b	z/c	B_{eq}
Ni	0.22920(4)	0.0083	0.23191(4)	2.06(2)
N1	0.0839(3)	−0.0364(3)	0.0831(4)	2.4(1)
N2	0.2080(4)	−0.1118(4)	0.3501(4)	3.2(2)
N3	0.1321(4)	0.1018(4)	0.3103(4)	3.1(2)
N4	0.2789(4)	0.1372(4)	0.1449(4)	2.8(2)
N5	0.3553(4)	−0.0777(4)	0.1835(4)	2.9(2)
C1	0	0.0226(7)	0	2.4(2)
C2	0.0506(5)	−0.1409(4)	0.0506(5)	3.7(2)
C3	0.1151(6)	−0.0721(6)	0.3962(6)	3.9(3)
C4	0.1329(6)	0.0460(6)	0.4214(6)	4.0(2)
C5	0.1624(5)	0.2192(5)	0.3323(7)	4.3(2)
C6	0.1733(6)	0.2761(5)	0.2211(7)	4.8(3)
C7	0.2832(6)	0.2485(5)	0.1941(7)	4.2(2)
C8	0.3915(5)	0.1049(6)	0.1308(6)	3.9(2)
C9	0.3842(5)	−0.0117(6)	0.0919(5)	3.9(3)

TABLE III Selected bond distances and angles for μ-(Im)-[(232-tet)Ni]$_2$(ClO$_4$)$_3$ (Å, °).

Ni-N1	2.049(4)	N1-C2	1.362(6)	N5-C9	1.483(7)
Ni-N2	2.103(5)	N2-C3	1.484(8)	C2a-C2	1.36(1)
Ni-N3	2.072(4)	N3-C4	1.468(8)	C3-C4	1.48(1)
Ni-N4	2.085(4)	N3-C5	1.490(8)	C5-C6	1.53(1)
Ni-N5	2.084(4)	N4-C8	1.472(7)	C6-C7	1.50(1)
N1-C1	1.337(6)	N4-C7	1.481(7)	C8-C9	1.50(1)
N1-Ni-N3	94.9(2)	C1-N1-C2	104.0(4)	C9-N5-Ni	107.3(3)
N1-Ni-N5	96.3(2)	C1-N1-Ni	131.4(4)	N1a-C1-N1	114.1(7)
N1-Ni-N4	95.4(2)	C2-N1-Ni	124.6(3)	C2a-C2-N1	109.0(3)
N1-Ni-N2	96.0(2)	C3-N2-Ni	106.9(4)	N2-C3-C4	108.9(5)
N3-Ni-N5	168.8(2)	C4-N3-C5	112.2(5)	N3-C4-C3	109.1(6)
N3-Ni-N4	95.6(2)	C4-N3-Ni	107.8(3)	N3-C5-C6	112.8(5)
N3-Ni-N2	83.1(2)	C5-N3-Ni	118.4(4)	C7-C6-C5	115.2(5)
N5-Ni-N4	83.9(2)	C8-N4-C7	112.9(5)	N4-C7-C6	112.4(5)
N5-Ni-N2	95.2(2)	C8-N4-Ni	106.4(3)	N4-C8-C9	109.7(5)
N4-Ni-N2	168.6(2)	C7-N4-Ni	119.4(4)	N5-C9-C8	108.0(4)

polyhedra. The geometries at the two nickel(II) atoms are identical. The two nickel(II) atoms and imidazolate ring atoms [Ni, Ni^a, C(1), N(1), N(1)^a, C(2), C(2)^a, a: $-x$, y, $-z$] are coplanar, with the maximum deviation from the least-squares plane being 0.017(4) Å. The four N atoms of the 232-tet ligand [N(2), N(3), N(4), N(5)] are coplanar, approximately perpendicular to the imidazolate ring plane, with the Ni atom lying 0.2052(5) Å out of this plane. The dihedral angle between the two planes is 90.85°. The four Ni-N bond lengths in the basal positions are within the narrow range 2.072(4) ~ 2.103(5) Å [average, 2.086(5) Å] and are comparable with values found in other nickel(II) complexes with polyamine ligands.[13-17] The Ni-N(Im) bondlength is 2.049(4) Å. N-Ni-N angles of the five-membered chelate rings, 83.1(2) and 83.9(2)°, are smaller than those of the six-membered ring 95.6(2)°. Bondlengths and angles in the imidazolate anion are similar to those found in imidazolate bridged copper complexes.[18]

The perchlorate anions in the structure are ordered, with Cl-O bondlengths in the range 1.385(6) ~ 1.447(5) Å [average, 1.423(6) Å] and O-Cl-O bond angles 105.8(3) ~ 113.5(8)° [average, 109.5(8)°].

Magnetic Properties

The temperature dependence of the molar magnetic susceptibility, χ_m, of μ-(Im)-[(232-tet)Ni]$_2$(ClO$_4$)$_3$, is shown in Figure 2. The value at room temperature is in the range for two S = 1 states, and increases as the temperature is lowered until a maximum at *ca* 25K is reached after which there is a rapid decrease. Such behaviour is characteristic of an intramolecular antiferromagnetic interaction between the two single-ion triplet states with a small portion of non-coupled nickel(II) impurity. Representing the intramolecular magnetic interaction with the isotropic spin Hamiltonian $\hat{H} = -J\hat{S}_A \bullet \hat{S}_B$, where J is the exchange integral and $S_A = S_B = 1$ (local spin), χ_m may be expressed as shown in (*1*).

$$\chi_m = \frac{2N\beta^2g^2}{kT}\left(\frac{exp(J/kT) + 5exp(3J/kT)}{1 + 3exp(J/kT) + 5exp(3J/kT)}\right)(1-\rho) + \frac{2N\beta^2g^2}{3kT}\rho + N_\alpha \qquad (1)$$

In this expression N, β, k and g have their usual meaning. The second term accounts for the noncoupled impurity, and the last term, N_α, is the temperature independent paramagnetism. Although Ginberg *et al.* [19] have also considered the effect of single ion zero-field interactions on the magnetic susceptibility of Ni(II) dinuclear complexes, Hendrickson *et al.* [20] showed that a large variance in the zero-field splitting, D, does not change the position of the maximum. Since this position determines the value of J, D has little effect on the evaluation of J.

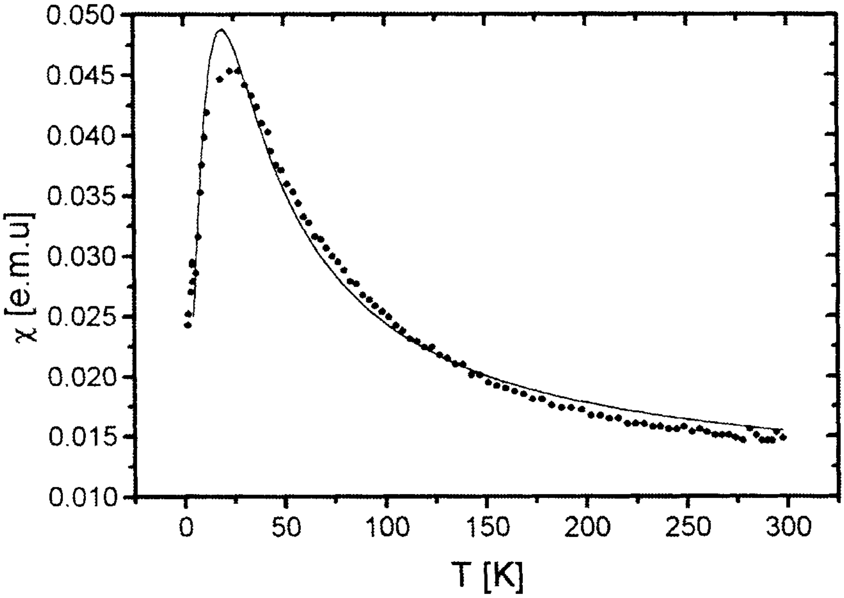

FIGURE 2 Molar paramagnetic susceptibility *vs* temperature curve for the complex. Experimental data are represented by squares, whereas the solid line is the theoretical line obtained by least-squares fitting of all experimental data.

Owing to the large stabilization of the singlet ground state, the effect of zero-field splitting on the magnetic behaviour is expected to be negligible. Least-squares fitting of all experimental data leads to $J = -12.5\ \mathrm{cm}^{-1}$, $g = 2.19$, $\rho = 0.056$ and $N_\alpha = 0.0106$, with agreement factor $R = \Sigma[\chi_{expt}(i)-\chi_{calcd}(i)]^2/\Sigma[\chi_{expt}(i)]^2$ of 3.83×10^{-6}. The X-band polycrystalline powder ESR spectrum does not exhibit any signal due to the large zero-field splitting of the nickel(II) ions.

The magnetic exchange coupling constants in bridged imidazolate complexes have been widely studies and commonly vary from 0 to $-87\ \mathrm{cm}^{-1}$. Many correlations between the magnitude of the change coupling, J, and structural parameters have been proposed.[21] The question of greatest interest is whether the intramolecular antiferromagnetic interactions in these complexes are propagated by a predominantly σ or π exchange pathway. The magnitude of antiferromagnetic exchange is a reflection of the interaction of the orbitals of the bridging ligand with the metal ions in which the unpaired electrons reside. The square pyramidal geometry of d^8 Ni(II) atoms in the dinuclear complex discussed here suggests that it has $(d_{x^2-y^2})^1(d_{z^2})^1$ ground state. Interaction of the two $d_{x^2-y^2}$ magnetic orbitals and two d_{z^2} magnetic orbitals in a dinuclear complex occurs if there are bridge ligand orbitals of the correct symmetry and energy. The d_{z^2} magnetic orbitals of Ni(II) atoms point from the metal toward the N atoms of the bridged imidazolate anion, and overlap σ orbitals of the N atoms of Im anion. The principal magnetic exchange pathway is considered to be σ in the nature. Because of the symmetry properties of the σ-interaction, the d_{z^2} orbitals on the Ni(II) atoms and the σ-orbitals on the bridged imidazolate N atoms are involved in the exchange pathway for unpaired spin density. Thus the antiferromagnetic interaction can be interpreted as a symmetry allowed σ-superexchange pathway. On the basis of theoretical calculations,[22, 23] it has been demonstrated that a maximum value of J is obtained when the M−N bond is parallel to the imidazolate carbon-carbon bond, therefore favouring a σ exchange pathway. An increase in the M−N−C angles (α) and in the angle β between the vectors M−N should then produce a stronger coupling. In the case of the present compound, values of α angle [131.4(4)°] and β [146.7(7)°] are larger than those of Schiff-base complexes.[23, 24] The $d_{x^2-y^2}$ orbitals of the Ni(II) atoms point from the metal toward the four N atoms and overlap the terminal ligand; their symmetry does not match with p-π orbitals of Im anion if the dihedral angles between the imidazolate ring and nickel(II) coordination planes are 0 or 90°, when no magnetic exchange interaction occurs. The π interaction would be appreciable only if the dihedral angles were considerably different from 0 or 90°. The actual values are 90.85(5) and 90.86(5)° making it likely that the σ exchange pathway dominates in this compound.

Supplementary Data

Lists of H atom positions, anisotropic thermal parameters and observed and calculated structure factors are available from the authors on request.

Acknowledgements

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