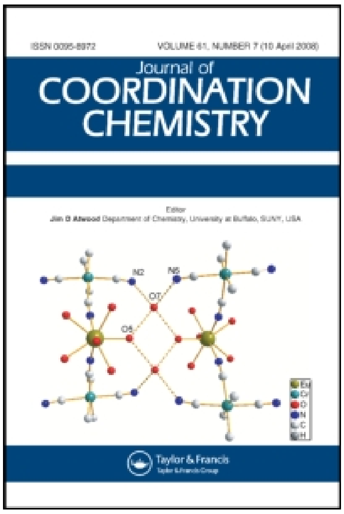

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF A TEREPHTHALATO-BRIDGED BINUCLEAR NICKEL(II) COMPLEX

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A new terephthalato-bridged binuclear nickel(II) complex with a tetraazamacrocyclic compound as the terminal ligand, $[Ni_2(cth)_2(\mu\text{-TPHA})](ClO_4)_2$ (**1**) [cth = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane] has been synthesized and characterized. According to X-ray crystallographic studies on the solvated species $\mathbf{1}\cdot 2CH_3OH$, each Ni(II) ion lies ina distorted octahedral environment, and the terephthalato ligand bridges two Ni(II) ions in a bis bidentate fashion. Cryomagnetic measurements revealed Curie-Weiss behaviour with $\theta = -1.4\,K$. Such behaviour may be due to a very weak intramolecular superexchange interaction through the extended bridge, a weak intermolecular exchange interaction or the local zero-field splitting of Ni(II) ions.

Keywords: Nickel(II); Terephthalato ion; Crystal structure; Magnetic properties

INTRODUCTION

Magnetochemistry of polynuclear complexes has been of considerable interest in recent years for elucidating magnetic exchange phenomena, for designing new molecular magnetic materials and for investigating the role of polymetallic active sites in biological processes [1–4]. One of the

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fundamental questions in this area relates to the distance dependence of superexchange interactions. To address this question, inorganic chemists have synthesized a number of dicopper(II) complexes where the metal ions are bridged by extended dicarboxylato ligands such as μ-terephthalato (TPHA) [5–12]. The intramolecuar $\mathrm{Cu}\cdots\mathrm{Cu}$ distances in these complexes are about 11 Å or more, but the supposed singlet-triplet energy gap ($2J$) obtained by fitting experimental data to $\hat{\boldsymbol{H}} = -2J\hat{\boldsymbol{S}}_1\hat{\boldsymbol{S}}_2$ varies from nearly zero to $-140\,\mathrm{cm}^{-1}$. Although it is difficult to distinguish the intramolecular interaction from the intermolecular one, some disappointingly weak interactions have been suggested to be intermolecular. It has been demonstrated that intramolecular coupling of considerable magnitude is possible even over distances > 15 Å, provided a favourable orbital pathway is available [5].

While many terephthalato-bridged dicopper(II) complexes have been investigated concerning long-range superexchange coupling, very little work has been devoted to the dinickel(II) species. The first complex of this kind was $[\mathrm{Ni_2(bpy)_4(\mu\text{-}TPHA)}](\mathrm{ClO_4})_2$ [13]. Its structure has been determined, but magnetic studies were not available. The magnetic investigation of a 2-bromoterephthalato(BTPHA)-bridged dinickel(II) complex, $[\mathrm{Ni_2(phen)_4(\mu\text{-}BTPHA)}](\mathrm{ClO_4})_2$, whose structure has not yet been reported, gave $J = -1.1\,\mathrm{cm}^{-1}$ [14]. Here we report the synthesis, crystal structure, spectra and magnetic properties of a new terephthalato-bridged dinickel(II) complex with a tetraazamacrocyclic compound as the terminal ligand. Its formula is $[\mathrm{Ni_2(cth)_2(\mu\text{-}TPHA)}](\mathrm{ClO_4})_2$ (**1**), where cth denotes *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

EXPERIMENTAL

Materials and Synthesis

All starting chemicals were of A. R. grade and used as received; $[\mathrm{Ni(cth)}](\mathrm{ClO_4})_2$ was prepared as described in the literature [15].

To a solution of $[\mathrm{Ni(cth)}](\mathrm{ClO_4})_2$ (1.0 mmol, 0.54 g) in methanol (20 cm^3) was added with constant stirring a solution of piperidinium terephthalate (0.5 mmol, 0.12 g) in methanol (10 cm^3). The mixture was refluxed for 3 h and then left to cool. The resulting blue polycrystals were filtered off, washed with methanol and dried in air. Yield, 88%. *Anal.* Found (%): C, 45.59; H, 7.55; N, 10.51. Calc. for $\mathrm{C_{40}H_{76}Cl_2N_8Ni_2O_{12}}$ (**1**): C, 45.78; H, 7.30; N, 10.68. Main IR bands (cm^{-1}): 3250 m, 2950 m, 1545 s, 1455 m, 1410 s, 1267 w, 1165 s, 1085 *vs* (br), 955 m, 836 s, 750 s. The product was dissolved in methanol/acetonitrile (1:1), and slow evaporation of the solution at room temperature afforded well-shaped crystals. X-ray analysis revealed a composition of **1**·2CH_3OH, but the crystals lost solvent molecules and powdered in air in a few hours.

Physical Measurements

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyser. IR spectra were recorded on a Shimadzu IR-408 spectrometer using KBr pellets, and electronic spectra on a Shimadzu UV-365 UV-VIS-NIR recording spectrophotometer. Variable-temperature magnetic susceptibilities over 4 – 300 K were measured on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

X-ray Crystallography

A selected crystal of dimensions 0.40 × 0.25 × 0.20 mm was sealed in a Lindemann capillary. Diffraction data were collected on a Bruker Smart 1000 area detector with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). A total of 5032 unique reflections ($R_{\text{int}} = 0.0463$) were measured at 298(2) K within $3.10 \leq 2\theta \leq 50.6$. The structure was solved by direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [16]. Hydrogen atoms were generated geometrically and refined isotropically. A total of 323 parameters were refined. The final refinement converged at $R_1 = 0.0522$, $wR_2 = 0.1422$ for 3337 observed reflections with $I \geq 2\sigma(I)$, and $R_1 = 0.0863$, $wR_2 = 0.1620$ for all data. The largest final difference peak and hole were 0.917 and -0.513 e Å^3, respectively. Final atomic coordinates for all non-hydrogen atoms and equivalent thermal parameters are listed in Table I.

Crystal Data

$C_{42}H_{84}Cl_2N_8Ni_2O_{14}$, $M = 1113.49$, monoclinic, $P2_1/n$, $a = 8.0378(10)$ Å, $b = 16.959(2)$ Å, $c = 20.943(3)$ Å, $\beta = 94.253(2)$ Å, $V = 2846.9(6)$ Å^3, $Z = 2$, $F(000) = 1188$, $D_c = 1.299$ g cm^{-3}, $\mu = 0.818$ mm^{-1}.

TABLE I Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å × 10^3) for **1**·$2CH_3OH$

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Ni(1)	3351(1)	7481(1)	1041(1)	30(1)
N(4)	5857(4)	7432(2)	1364(2)	34(1)
N(1)	4215(5)	7719(3)	126(2)	41(1)
N(2)	2709(5)	8662(2)	1155(2)	38(1)
N(3)	2570(5)	7348(2)	1988(2)	43(1)
O(1)	969(3)	6973(2)	682(2)	41(1)
O(2)	3268(3)	6272(2)	761(2)	45(1)
O(4)	7517(8)	8850(3)	2221(3)	131(2)
O(5)	5454(7)	9789(4)	2032(4)	167(3)
O(3)	6942(10)	9337(4)	1234(3)	162(3)
O(6)	8171(6)	10135(3)	2018(3)	112(2)
O(7)	9688(17)	8833(8)	4003(6)	252(7)
C(6)	3144(7)	9086(3)	45(3)	57(1)
C(9)	2327(7)	8160(3)	2217(2)	56(1)
C(14)	6037(6)	7841(3)	252(2)	52(1)
C(13)	6715(6)	7290(3)	773(2)	49(1)
C(3)	1493(6)	4896(3)	361(3)	50(1)
C(11)	5394(5)	6989(3)	2465(2)	50(1)
C(4)	– 682(5)	5749(3)	– 71(2)	48(1)
C(12)	6285(5)	6828(3)	1866(2)	44(1)
C(1)	1730(5)	6335(3)	598(2)	39(1)
C(2)	815(5)	5642(2)	288(2)	39(1)
C(10)	3516(6)	6808(3)	2459(2)	52(1)
C(5)	3368(7)	8317(3)	– 310(2)	53(1)
C(20)	8175(6)	6791(4)	2042(3)	66(2)
C(8)	1591(6)	8658(3)	1683(2)	56(1)
C(7)	1981(6)	9110(3)	591(2)	49(1)
C(16)	1663(7)	7972(4)	– 559(3)	67(2)
C(19)	3137(6)	5957(3)	2260(3)	70(2)
C(17)	1603(8)	9964(3)	771(3)	79(2)
C(18)	2962(7)	6934(5)	3141(3)	86(2)
C(15)	4376(9)	8481(4)	– 890(3)	87(2)
C(21)	8360(20)	9463(11)	3809(7)	258(12)
Cl(2)	7020(2)	9540(1)	1884(1)	70(1)

RESULTS AND DISCUSSION

Spectroscopic Characterization

The IR spectrum of complex **1** exhibits a sharp medium band at 3250 cm^{-1} and a broad, strong band at 1085 cm^{-1}, characteristic of NH groups and perchlorate ions, respectively. The strong bands at 1545 and 1410 cm^{-1} are assignable to $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$, respectively. The small gap (135 cm^{-1}, well less than 200 cm^{-1}) between the two bands indicates a bidentate mode of coordination of the carboxylate group [17].

The electronic spectrum of the complex in acetonitrile exhibits three weak bands ($\varepsilon < 60\,M^{-1}cm^{-1}$) at 350, 575 and 940 nm, attributable to the ${}^3A_{2g}\rightarrow{}^3T_{1g}$ (P), ${}^3A_{2g}\rightarrow{}^3T_{1g}$ (F) and ${}^3A_{2g}\rightarrow{}^3T_{2g}$ transitions, respectively, for the Ni(II) ion in an octahedral environment. From the above data, the ligand-field parameters Dq and B have been calculated to be 1064 and $936\,\mathrm{cm}^{-1}$, respectively [18]. Assuming $B_0 = 1031\,\mathrm{cm}^{-1}$ for the free Ni(II) ion, the nephelauxetic coefficient β for the complex is 0.91. This value is not far from unity, suggesting a small portion of covalency in the M-L bonds.

Description of the Structure

The structure of complex **1** consists of the binuclear $[\mathrm{Ni_2(cth)_2(\mu\text{-}TPHA)}]^{2+}$ cation, non-coordinated perchlorate ions and methanol molecules. A perspective view of the binuclear unit with the atom numbering scheme is depicted in Figure 1. Selected bond lengths and angles are listed in Table II.

As suggested by the IR spectrum, the terephthalato ligand bridges two nickel ions in a bis bidentate fashion. The binuclear cation is centrosymmetric, with a crystallographic centre located at the centre of the benzene ring. The nickel atom resides in a distorted octahedral environment. The equatorial plane is defined by two oxygen atoms from the bridging ligand and two nitrogen atoms from the terminal tetraazamacrocyclic ligand, the axial positions being occupied by the other two nitrogen atoms from the terminal ligand. The Ni-O distances average 2.16 Å, and the axial Ni-N distances (av. 2.13 Å) are appreciably longer than the equatorial ones (av. 2.08 Å). The largest distortion of the geometry from octahedral arises from the significant deviation of the bite angle of the carboxylato group from 90° (O2-Ni1-O1, 61.1°). In addition, the O1-Ni1-N4 angle is 154.3°, much

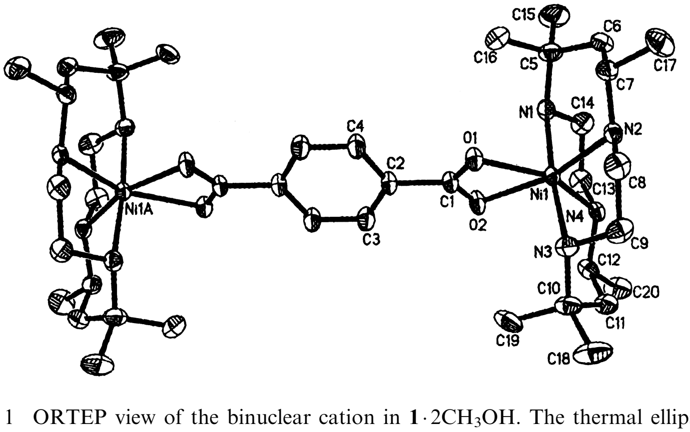

FIGURE 1 ORTEP view of the binuclear cation in $\mathbf{1}\cdot 2\mathrm{CH_3OH}$. The thermal ellipsoids are drawn at the 30% possibility level.

TABLE II Selected bond lengths (Å) and angles (deg) for **1**·$2CH_3OH$

Ni(1)-N(4)	2.078(3)	Ni(1)-O(2)	2.132(3)
Ni(1)-N(2)	2.088(4)	Ni(1)-N(3)	2.137(4)
Ni(1)-N(1)	2.123(4)	Ni(1)-O(1)	2.181(3)
O(1)-C(1)	1.262(5)	O(2)-C(1)	1.262(5)
N(4)-Ni(1)-N(1)	85.87(15)	N(1)-Ni(1)-O(2)	86.60(15)
N(2)-Ni(1)-N(1)	91.23(16)	N(4)-Ni(1)-O(1)	154.31(13)
N(4)-Ni(1)-N(3)	92.13(15)	N(2)-Ni(1)-O(1)	101.56(13)
N(2)-Ni(1)-N(3)	84.38(15)	N(1)-Ni(1)-O(1)	95.88(14)
N(1)-Ni(1)-N(3)	174.60(16)	N(4)-Ni(1)-O(2)	93.51(13)
N(4)-Ni(1)-N(2)	104.03(15)	O(2)-Ni(1)-N(3)	98.54(15)
N(3)-Ni(1)-O(1)	88.10(14)	N(2)-Ni(1)-O(2)	162.13(13)
O(2)-Ni(1)-O(1)	61.13(11)	O(1)-C(1)-O(2)	120.7(4)
C(1)-O(1)-Ni(1)	88.0(2)	C(1)-O(2)-Ni(1)	90.1(3)

smaller than 180°. The nickel atom is displaced out of the mean equatorial plane by only 0.0075(18) Å, and the deviations of the equatorial donor atoms from the plane is 0.047 – 0.077 Å. Concerning the terephthalato ligand, its eight carbon atoms are strictly coplanar within experimental error. The oxygen atoms O1 and O2 of the carboxylato group and the nickel atom are respectively 0.341, – 0.386 and – 0.197 Å out of this plane. The dihedral angle between the benzene ring and the carboxylato groups is 19.4° and that between the benzene ring and the mean equatorial planes around the nickel atoms is 16.5°. Inside the binuclear cation, the two nickel atoms, connected by the terephthalato group, are separated by 10.74 Å, a value significantly larger than that for $[(bpy)_4Ni_2(\mu\text{-TPHA})]^{2+}$ (9.45 Å) [13]. Some *inter*molecular Ni···Ni distances are much shorter. The shortest (8.04 Å) occurs between two nickel atoms related by the $(x-1, y, z)$ operation and the second shortest (9.93 Å) is found for Ni1···Ni1$(1-x, 1-y, -z)$. The non-coordinated perchlorate ions and methanol molecules reside between trinuclear cations. There are no indications of significant hydrogen bonding between these components.

Magnetic Properties

Variable-temperature magnetic susceptibilities for **1** were measured in the 5 – 300 K temperature range and are shown as χ_M^{-1} and μ_{eff} *versus* T plots in Figure 2. The experimental μ_{eff} value per Ni(II) ion at room temperature is *ca* 3.04 B.M., within the range expected for a high-spin Ni(II) ion. Upon cooling, the magnetic moment decreases slightly to a value of 2.98 B.M. at 24 K and then decreases more and more rapidly. The χ_M^{-1} *versus* T plot is essentially linear, and least-squares fitting of the data to the Curie-Weiss law gave $C = 1.15\,cm^3\,mol^{-1}\,K$ and $\theta = -1.4\,K$.

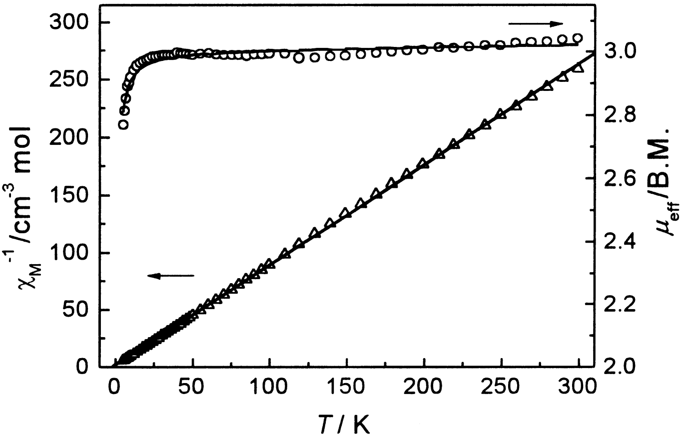

FIGURE 2 Plots of χ_M^{-1} *vs.* T and μ_{eff} *vs.* T for complex **1**. The solid lines represent the best fits to the Curie-Weiss law and Eq. (1) (see text for the fitted parameters).

This Curie-Weiss behaviour may arise from antiferromagnetic interactions between Ni(II) ions. Assuming an isotropic exchange between two Ni(II) ions ($\hat{\boldsymbol{H}} = -2J\hat{\boldsymbol{S}}_1\hat{\boldsymbol{S}}_2$), the magnetic susceptibility per Ni(II) ion can be expressed as [19] is (1),

$$\chi_M = \frac{Ng^2\beta^2}{kT}\frac{\exp(2J/kT) + 5\exp(6J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT)} + N\alpha \qquad (1)$$

where $N\alpha$ denotes the temperature-dependent paramagnetism. The best fit of experimental data to Eq. (1) yielded $J = -0.33\,\text{cm}^{-1}$, $g = 2.12$, $N\alpha = 52 \times 10^{-6}\,\text{cm}^3\,\text{mol}^{-1}$ with the agreement factor $R = \sum(\chi_{obsd} - \chi_{calcd})^2/\sum\chi_{obsd}^2 = 8.9 \times 10^{-5}$. The J value is so small that one can not attribute it unambiguously to the intramolecular interaction. Although there are no significant intermolecular bonding interactions in **1**, some intermolecular Ni···Ni distances are significantly shorter than the intramolecular one, and a weak intermolecular magnetic interaction cannot be excluded. A previous report on a mononuclear Cu(II) complex containing the benzoato ligand, in which there are also no significant extramolecular bonding interactions, has demonstrated a weak antiferromagnetic between Cu(II) ions, with the shortest Cu···Cu distance being 7.231 Å [5].

Still another possible origin of the magnetic behavior of **1** at low temperature is the zero-field splitting of the Ni(II) ion in a distorted octahedral environment. Taking this effect into account, and assuming no magnetic exchange between Ni(II) ions, the magnetic susceptibility per

Ni(II) ion can be expressed as [19] in (2),

$$\langle \chi_M \rangle = \frac{2Ng^2\beta^2}{3kT}\frac{(2kT/D)[1-\exp(-D/kT)]+\exp(-D/kT)}{1+2\exp(-D/kT)} + N\alpha \qquad (2)$$

where the ZFS effect is assumed to be axial for the sake of simplicity and $\langle \chi_\mathrm{M} \rangle = (\chi_\| + 2\chi_\perp)/3$. The fit of experimental data to Eq. (2) was even more satisfactory than that to Eq. (1). The fitted parameters are $D = -7.6\,\mathrm{cm}^{-1}$, $g = 2.11$, $N\alpha = 76 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ with $R = 3.9 \times 10^{-5}$, or $D = 6.0\,\mathrm{cm}^{-1}$, $g = 2.11$, $N\alpha = 74 \times 10^{-6}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ with $R = 3.8 \times 10^{-5}$. It has been stated that, for Ni(II) ions, the sign of the D parameter cannot be determined from magnetic measurements [19].

At this stage, it is difficult to attribute unambiguously and exclusively the Curie-Weiss behaviour of the present binuclear Ni(II) complex to any of the above effects. However, as far as the intramolecular magnetic exchange is concerned, we conclude that the interaction *via* the terephthalato bridge is very weak, if any. This suggests that there is no efficient orbital pathway for superexchange through the terephthalato bridge between two Ni(II) ions.

Acknowledgments

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