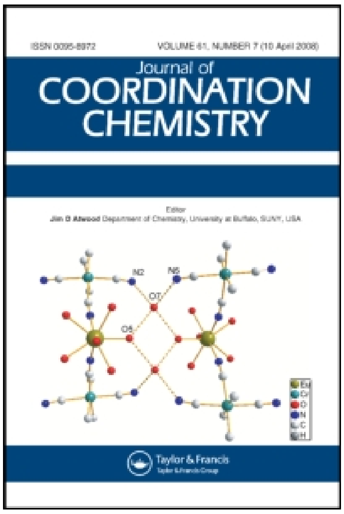

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Synthesis, Structure and Properties of an Oxalato-Bridged Dinuclear Nickel(II) Complex

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SYNTHESIS, STRUCTURE AND PROPERTIES OF AN OXALATO-BRIDGED DINUCLEAR NICKEL(II) COMPLEX

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A new dinuclear nickel(II) compound, $[Ni_2(TPA)2(\mu\text{-}C_2O_4)](H_2O)_{0.75}(ClO_4)_2$ [TPA = tris(2-pyridylmethyl) amine], was synthesized and characterized by electronic spectroscopy and X-ray methods. In the complex, the oxalate ion acts as a bis-bidentate ligand and the two Ni(II) ions are six coordinated with a distorted octahedral structure. The complex crystallizes in the triclinic space group $P\bar{1}$, with $a = 13.203(4)$, $b = 16.574(5)$, $c = 21.802(6)$ Å, $\alpha = 78.644(5)$, $\beta = 80.299(5)$, $\gamma = 72.446(5)^\circ$, $V = 4429$ Å^3, $Z = 2$; $R_1 = 0.0615$, $wR_2 = 0.1639$. In the temperature range 4–300 K, magnetic measurements show that the exchange interaction between the two metal ions is antiferromagnetic with $J = -18.74\,\text{cm}^{-1}$, $g = 2.10$.

Keywords: Dinuclear Ni(II) complex; Tris(2-pyridylmethyl)amine; Oxalate bridged; Magnetic properties

INTRODUCTION

Many important natural enzymes contain nickel, such as ureases [1], hydrogenases [2], and carbon monoxide dehydrogenases [3]. Structures and properties of appropriate nickel complexes are of importance in order to understand these biosystems and to develop models for their action. Nickel dimers bridged by oxalate ion are well known, and magnetic and spectroscopic properties of such complexes that have an N_4O_2 coordination environment have attracted much attention [4–8].

With tris(2-pyridylmethyl)amine (TPA) as terminal ligand and oxalate ion as bridging ligand, we have synthesized a novel complex containing a binuclear nickel center. The aim of this study was to characterize the nickel-oxalato dimer and compare its structure and properties with compounds that have a similar coordination environment.

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EXPERIMENTAL

Materials and Compound Preparation

TPA · $3HClO_4$ was synthesized according to a literature procedure [9]. All other starting materials and organic solvents were purchased commercially and used without further purification.

$[Ni_2(TPA)_2(\mu\text{-}C_2O_4)](H_2O)_{0.75}(ClO_4)_2$

TPA · $3HClO_4$ (0.1 mmol) was dissolved in 10 mL of methanol, followed by the addition of the proper amount of triethylamine. $Ni(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol) and dipotassium oxalate (0.05 mmol) were added to the resulting solution. This solution was stirred for 30 min and then allowed to stand at room temperature. After some 25 days, purple crystals suitable for X-ray analysis were obtained. IR (KBr, cm^{-1}): 1648(s), 1610(m), 1575(w), 1485(w), 1445(m), 1350(w), 1310(w), 1150(w), 1090(s), 1029(m), 800(w), 770(m). Anal. Calc. for $C_{76}H_{75}Cl_4N_{16}Ni_4O_{25.5}$ (%): C, 45.71; H, 3.78 N, 11.22. Found: C, 45.61; H, 3.83; N, 11.30.

Crystallographic Studies

A crystal of $[Ni_2(TPA)_2(\mu\text{-}C_2O_4)](H_2O)_{0.75}(ClO_4)_2$ was mounted on a Bruker Smart 1000 X-ray diffractometer. Determination of unit cell parameters and data collection were performed using Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined on F^2. By full-matrix least-squares methods using SHELXTL version 5.0. Hydrogen atoms were treated as riding on their attached atoms, refined and placed at calculated positions. Crystal parameters and details of the data collection and refinement are listed in Table I.

RESULTS AND DISCUSSION

Crystal Structure of $[Ni_2(TPA)_2(\mu\text{-}C_2O_4)](H_2O)_{0.75}(ClO_4)_2$

The structure and atom numbering scheme of $[Ni_2(TPA)_2(\mu\text{-}C_2O_4)](H_2O)_{0.75}(ClO_4)_2$, together with the packing structure are shown in Fig. 1. The dinuclear cation consists of two $[Ni(TPA)]^{2+}$ units bridged by a bis-bidentate oxalate anion, and is centrosymmetric. The intramolecular Ni···Ni distance (5.347 Å) is short compared to those in $[(NiL)_2(\mu\text{-ox})](ClO_4)_2$ (5.516 Å) [6], $Ni(TAA)ClO_4) \cdot 0.5\,H_2O$ (5.412 Å) [7], *cis*-$[(Ni_2\text{-}(cyclam)_2(\mu\text{-ox})](NO_3)_2$ (5.395 Å) [10], and *cis*-$[Ni_2(Me_2cyclen)_2(\mu\text{-ox})](ClO_4)_2 \cdot 2H_2O$ (5.465 Å) [11]. Bond distances between Ni(1) and nitrogen atoms lie in the range of 2.059(5)–2.089(5) Å, while the Ni(1)–O(1) and Ni(1)–O(2A) bonds are 2.10(4) and 2.026(4) Å, relatively shorter than those in similar complexes, owing to the larger O(1)–Ni(1)–O(2) angle [81.52(16)°]. The basal plane positions are occupied by two nitrogen atoms [N(2), N(4)] and O(1), O(2) from oxalate, and the Ni(1) atom lies in this plane. Axial positions are filled with nitrogen atoms from pyridine [N(1), N(3)], and the resultant bond angle [N(1)–Ni(1)–N(3)] is 162.0(2)°. The angles N(3)–Ni(1)–N(2) [93.9(2)°], N(3)–Ni(1)–N(4) [82.1(2)°], N(3)–Ni(1)–O(1) [88.17(18)°] and

TABLE I Crystallographic data and processing parameters for $[Ni_2(TPA)_2(\mu\text{-}C_2O_4)](H_2O)_{0.75}(ClO_4)_2$

Empirical formula	$C_{76}H_{75}Cl_4N_{16}Ni_4O_{25.5}$
Formula weight	1997.16
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P_{\bar{1}}$
Unit cell dimensions	$a = 13.203(4)$ Å $\alpha = 78.644(5)°$ $b = 16.574(5)$ Å $\beta = 80.299(5)°$ $c = 21.802(6)$ Å $\gamma = 72.446(5)°$
Volume	4429(2) $Å^3$
Z, Calculated density	2, 1.498 Mg/m^3
Absorption coefficient	1.041 mm^{-1}
F (000)	2054
Crystal size	$0.35 \times 0.30 \times 0.10$ mm
Theta range for data collection	1.79 to 23.32°
Limiting indices	$-14 \leq h \leq 14$, $-18 \leq k \leq 8$, $-23 \leq l \leq 24$
Reflections collected/unique	15450/12721[R(int) = 0.0306]
Completeness to $\theta = 23.32$	99.1%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9030 and 0.7120
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12721/0/1130
Goodness-of-fit on F^2	0.977
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0615$, $wR2 = 0.1639$
R indices (all data)	$R1 = 0.1113$, $wR2 = 0.2029$
Largest diff. peak and hole	0.703 and -0.545 e $Å^{-3}$

N(3)–Ni(1)–O(2) [97.8(2)°] deviate somewhat from idealized octahedral geometry. Thus Ni(II) lies in a distorted octahedral coordination environment.

Figure 1A indicates that hydrogen bonds exist between O(25) (water) and O(2) (2.892 Å), O(25) and O(20) (perchlorate) (3.412 Å). An extended hydrogen-bond network shown in Fig. 1B. The perchlorate group plays an important role for lining adjacent groups. Significant bond parameters are given in Table II.

Electronic Spectra

Electronic absorption spectra for DMF solutions of the complex were recorded at room temperature, with maxima at 18 939, 11 160 and 6983 cm^{-1}assigned to $^3T_{1g}(P) \leftarrow {}^3A_{2g}$, $^3T_{1g} \leftarrow {}^3A_{2g}$ and $^3T_{1g} \leftarrow {}^3A_{2g}$ transitions, respectively [11,12]. The first two peaks are assumed to be ν_3 and ν_2 of Ni(II) in the octahedral field and we calculate [13] values of ν_1 (6821 cm^{-1}), Dq (682 cm^{-1}) and B (642 cm^{-1}). The ν_1 (10Dq) value is equal to the energy of the first spin-allowed transition, and a close agreement (2.3%) was shown between experiment (6983 cm^{-1}) and the calculated value. The parameter B is known as the electronic repulsion parameter (Racah parameter), and the nephelauxetic ratio ($\beta = B_{\text{complex}}/B_{\text{free ion}}$) [14] is 0.62, indicating the relatively larger delocalization of the metal electrons. The value of β is similar to values for other octahedral Ni(II) complexes such as *uns*-*cis*-$[Ni(1,3\text{-pdda})(H_2O)_2)$ (0.69) and *uns*-*cis*-$[Ni(eddp)\text{-}(H_2O)_2] \cdot H_2O$ (0.66) [15], but is smaller than for $\{[(tacn)Ni(H_2O)]_2(\mu\text{-}C_2O_4)\}I_2 \cdot 2H_2O$ (0.94) and $\{[(tacn)Ni(H_2O)]_2(\mu\text{-}C_2O_4)\}(ClO_4) \cdot 2H_2O$ (0.94) [8]. This indicates more effective orbital overlap between metal ions and ligand atoms.

The ratio of ν_2/ν_1 for the complex is 1.60, while the ratio for regular octahedral Ni(II) is 1.8. Compared with other complexes, $(\mu\text{-SeCN})_2[Ni(dpt)(SeCN)_2]_2$ (1.77),

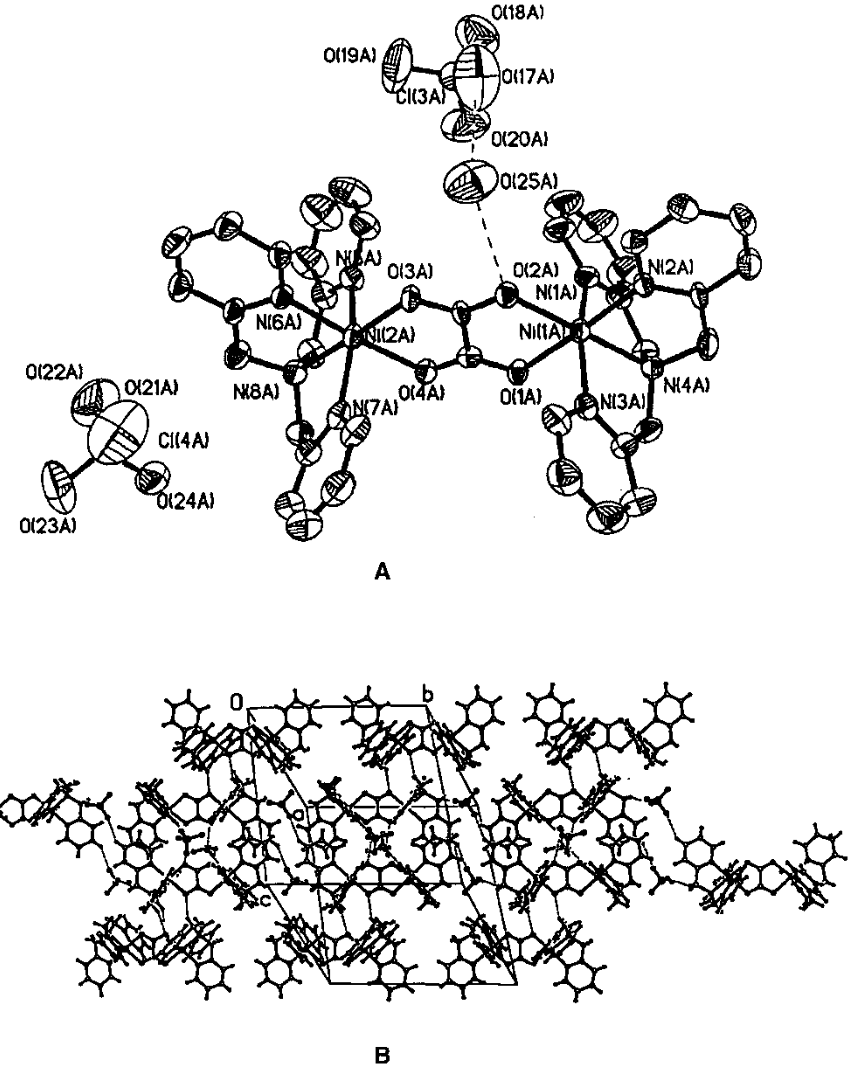

FIGURE 1 A, Diagram of $[Ni_2(TPA)_2(\mu\text{-}C_2O_4)](H_2O)_{0.75}(ClO_4)_2$ with the atom numbering scheme; B, packing in the cell.

TABLE II Selected bond distances (Å) and angles (°) for $[Ni_2(TPA)_2(\mu\text{-}C_2O_4)](H_2O)_{0.75}(ClO_4)_2$

Ni(1)–O(2)	2.026(4)	Ni(1)–N(2)	2.059(5)
Ni(1)–N(3)	2.069(5)	Ni(1)–N(1)	2.076(5)
Ni(1)–N(4)	2.089(5)	Ni(1)–O(1)	2.101(4)
O(1)–C(19)	1.247(7)	O(2)–C(20)	1.242(7)
O(2)–Ni(1)–N(2)	97.44(18)	O(2)–Ni(1)–N(3)	97.8(2)
N(2)–Ni(1)–N(3)	93.9(2)	O(2)–Ni(1)–N(1)	98.3(2)
N(2)–Ni(1)–N(1)	92.1(2)	N(3)–Ni(1)–N(1)	162.0(2)
O(2)–Ni(1)–N(4)	178.92(19)	N(2)–Ni(1)–N(4)	83.64(19)
N(3)–Ni(1)–N(4)	82.1(2)	N(1)–Ni(1)–N(4)	81.7(2)
O(2)–Ni(1)–O(1)	81.52(16)	N(2)–Ni(1)–O(1)	177.76(18)
N(3)–Ni(1)–O(1)	88.17(18)	N(1)–Ni(1)–O(1)	86.08(19)
N(4)–Ni(1)–O(1)	97.40(17)		

(μ-SeCN)$_2$[Ni(aepn)(SeCN)$_2$]$_2$ (1.76) and (μ-SeCN)$_2$[Ni(medien)(SeCN)$_2$]$_2$ (1.73) [16], this value is indicative of more distorted octahedral geometry.

Magnetic Properties

The magnetic susceptibility of the complex was measured in the temperature range 4–300 K using a SQUID magnetometer. The variable-temperature magnetic moments and magnetic susceptibilities are shown in Fig. 2. Oxalate is efficient in propagating antiferromagnetic interactions between two paramagnetic centers. The μ_{eff} value at room temperature (300 K) is 3.96 BM, consistent with a spin-only system. When temperature is lowered, the magnetic moment decreases to 0.35 BM at 4.77 K. This indicates antiferromagnetic interaction of the two nickel atoms. In order to quantitatively understand the magnitude of the spin-exchange interaction, magnetic data of the complex were fitted to be susceptibility equation (1).

$$\chi_M = 2Ng^2\beta^2/k(T-4.4)\{[5+\exp(-4J/kT)]/5+3\exp(-4J/kT)+\exp(-6J/kT)\} \times (1-\rho)+4Ng^2\beta^2\rho/3kT, \tag{1}$$

where J is the exchange coupling parameter and ρ represents the fraction of non-coupled nickel(II) impurities. The least-squares fitting results for the experimental data give $J = -18.74\,\text{cm}^{-1}$, $g = 2.10$, $\rho = 1.50\times10^{-4}$, and the agreement factor defined by $R\left[R=\sum(\chi i_{\text{obs}}-\chi i_{\text{cald}})^2/\sum(\chi i_{\text{obs}})^2\right]$ is equal to 2.12×10^{-6}.

The J value of the title complex is comparable with that of [NiL)$_2$(μ-ox)](ClO$_4$)$_2$ ($-13.8\,\text{cm}^{-1}$) [6] and Ni(TAA)(ClO$_4$)$\cdot$0.5ox ($-14.4\,\text{cm}^{-1}$) [7], indicating a relatively weak coupling through the bridging ligand.

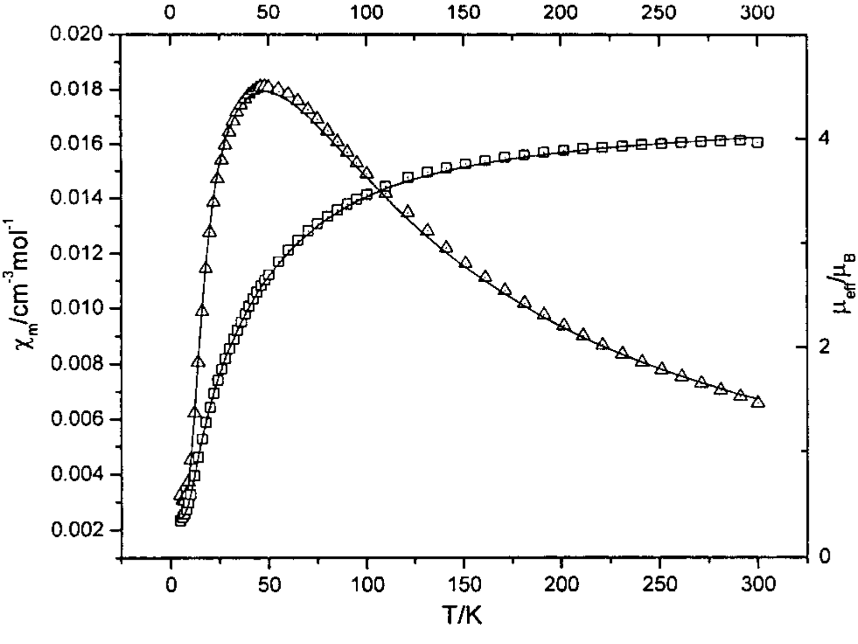

FIGURE 2 Temperature variation of magnetic susceptibility and magnetic moment *vs* temperature curves for [Ni$_2$(TPA)$_2$(μ-C$_2$O$_4$)](H$_2$O)$_{0.75}$(ClO$_4$)$_2$.

Acknowledgments

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Supplementary Data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 198718. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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