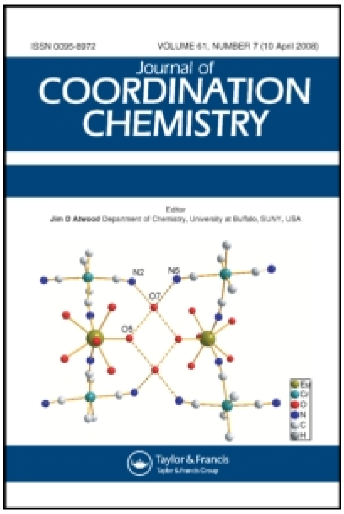

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Synthesis, Crystal Structure and Magnetic Properties of an Oxalato-Bridged Dinickel(II) Complex Containing A MacrocyClic Ligand

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF AN OXALATO-BRIDGED DINICKEL(II) COMPLEX CONTAINING A MACROCYCLIC LIGAND

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A new binuclear nickel(II) complex $[Ni(\mu\text{-}C_2O_4)(\textit{rac}\text{-cth})_2](ClO_4)_2$ [*rac*-cth = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane] has been prepared and its structure determined. It consists of centrosymmetric $[Ni(\mu\text{-}C_2O_4)(\textit{rac}\text{-cth})_2]^{2+}$ cations separated by perchlorate anions, with a centre of symmetry lying in the middle of the C–C bond of the bis-bidentate oxalate bridge. The tetraazamacrocycle adopts a folded conformation around the nickel atom, which is six coordinated in a distorted octahedral arrangement. Variable temperature magnetic susceptibility measurements (4–300 K) suggest a moderate intramolecular antiferromagnetic interaction between the metal ions ($J = -34.0\,\mathrm{cm}^{-1}$, $g = 2.07$)

Keywords: Macrocyclic ligands; Binuclear nickel(II) complexes; Crystal structure; Magnetic properties

INTRODUCTION

Polymetallic complexes with extended bridged structures are of current interest due to their novel magnetic properties [1]. The oxalate ion has proven to be an appropriate bridging unit to design magnetic materials

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and many oxalato-bridged complexes have been reported [2–4]. However, as far as oxalato-bridged nickel(II) complexes are concerned, only a few crystal structures containing macrocyclic ligands have been determined by X-ray diffraction methods (macrocyclic ligands = 1,4,8,11-tetraazacyclotetradecane [5], 1,7-dimethyl-1,4,7,10-tetracyclododecane [6] and 1,4,7-triazacyclononane [7]). It is well-known that variations in the structural features of the macrocyclic ligands induce important changes in the chemical properties of their metal complexes. With this fact in mind, we describe here the synthesis and characterization of a new complex $[Ni(\mu\text{-}C_2O_4)(\textit{rac}\text{-cth})_2](ClO_4)_2$ [*rac*-cth = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane].

EXPERIMENTAL

Materials and Synthesis

All starting materials were of analytical grade. The species *cis*-$K[Cr(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ [8] and $[Ni(\textit{rac}\text{-cth})](ClO_4)_2$ [9] were prepared as described elsewhere. The complex was prepared by mixing an aqueous solution of *cis*-$K[Cr(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ (0.1 mmol) and $[Ni(\textit{rac}\text{-cth})](ClO_4)_2$ (0.2 mmol) in acetonitrile with stirring; the resulting precipitate was separated by filtration. *Anal.* Found: C, 42.2; H, 7.8; N, 11.39. Calc. for $C_{34}H_{72}Cl_2N_8Ni_2O_{12}$: C, 42.0; H, 7.5; N, 11.5%. Blue single crystals suitable for an X-ray investigation were obtained by slow evaporation of the filtrate at room temperature.

Physical Measurements

C, H and N were determined on a Perkin-Elmer 240 C instrument. IR spectra were recorded using KBr discs on a Shimadzu IR-408 spectrophotometer in the 4000–600 cm^{-1} region. Electronic spectra in acetonitrile were recorded on a Shimadzu UV-2101PC scanning spectrophotometer. The X-band EPR spectrum of a powdered sample was recorded on a Bruker ER 200 D-SRC spectrometer at room temperature. 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 the constituent atoms [10].

X-ray Crystallography

Determination of the unit cell and data collection was performed on a BRUKER SMART 1000 diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 293(2) K with crystal size $0.5 \times 0.5 \times 0.3$ mm. A total of 4698 [*Rint* = 0.0222] independent reflections were collected by the ω-2θ scan technique in the range $2.02^\circ \leq \theta \leq 26.04^\circ$. Empirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods and refined by the full-matrix least-squares technique on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [11]. Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. The final refinement including hydrogen atoms converged to R values of $R = 0.036$, $Rw = 0.101$. The weight, $w = 1/[\sigma^2(F_o^2) + 0.0608P^2 + 2.8419P]$ where $P = (F_o^2 + 2F_c^2)/3$. Final atomic coordinates for all non-hydrogen atoms and equivalent thermal parameters are listed in Table I. Selected bond lengths and angles are presented in Table II.

Crystal Data

$C_{34}H_{72}Cl_2N_8Ni_2O_{12}$, $M = 973.32$, orthorhombic, *Pbca*, $a = 14.9858(12)$, $b = 15.2135(12)$, $c = 20.1194(15)$ Å, $V = 4587.0(6)$ Å^3, $Z = 4$, $F(000) = 2072$, $D_c = 1.409$ g cm^{-3}, $\mu = 1.001$ mm^{-1}.

RESULTS AND DISCUSSION

Preparation of [Ni(μ-C_2O_4)(*rac*-cth)$_2$](ClO_4)$_2$

It has been reported that the electrophilic attack of the Cu(bpy)^2 complex on the coordinated oxalate ion in *cis*-K[Cr(C_2O_4)$_2$(H_2O)$_2$] $\cdot$ 2H_2O produces the dicopper(II) complex [Cu_2(μ-C_2O_4)(bpy)$_2$(H_2O)$_2$(NO_3)$_2$], and a reasonable mechanism was proposed [12,13]. In the present study, the formation of the dinickel(II) complex most likely arises from a similar mechanism given in Scheme 1. That is, electrophilic attack of the Ni(*rac*-cth)$^{2+}$ complex on the coordinated oxalate ion in *cis*-K[Cr(C_2O_4)$_2$(H_2O)$_2$] $\cdot$ 2H_2O results in the formation of the binuclear species [Ni(μ-C_2O_4)(*rac*-cth)$_2$](ClO_4)$_2$].

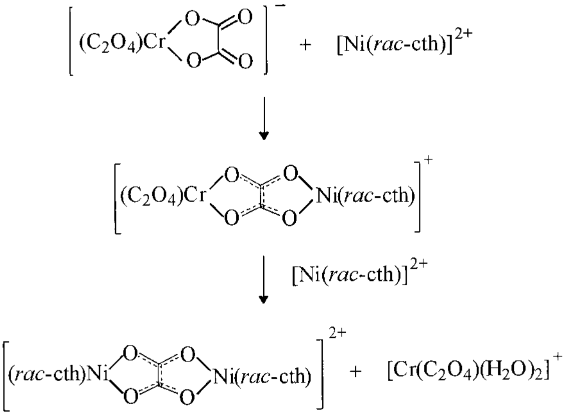
TABLE I Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$\times 10^3$) for $[\mathrm{Ni}(\mu\text{-}\mathrm{C_2O_4})(\mathit{rac}\text{-}\mathrm{cth})_2](\mathrm{ClO_4})_2$

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}
Ni(1)	6264(1)	1089(1)	4488(1)	31(1)
O(1)	6151(1)	−137(1)	4950(1)	39(1)
O(2)	4891(1)	1041(1)	4646(1)	38(1)
C(1)	4637(1)	343(1)	4913(1)	32(1)
N(1)	6299(1)	432(2)	3527(1)	43(1)
C(2)	5775(2)	775(2)	2943(1)	49(1)
C(3)	5923(2)	1768(2)	2863(1)	50(1)
C(4)	5581(2)	2382(2)	3401(1)	47(1)
N(2)	6140(1)	2317(1)	4012(1)	36(1)
C(5)	5813(2)	2902(2)	4539(1)	47(1)
C(6)	6399(2)	2818(2)	5142(1)	50(1)
N(3)	6390(1)	1907(1)	5390(1)	39(1)
C(7)	7091(2)	1736(2)	5910(1)	50(1)
C(8)	7984(2)	1548(2)	5574(1)	51(1)
C(9)	8056(2)	730(2)	5141(2)	47(1)
N(4)	7651(1)	892(1)	4477(1)	40(1)
C(10)	7775(2)	151(2)	4011(2)	52(1)
C(11)	7266(2)	325(2)	3384(2)	56(1)
C(12)	6052(3)	326(2)	2286(2)	72(1)
C(13)	4797(2)	564(2)	3064(2)	61(1)
C(14)	5555(3)	3321(2)	3122(2)	80(1)
C(15)	6769(2)	957(2)	6324(2)	69(1)
C(16)	7217(2)	2529(3)	6376(2)	72(1)
C(17)	9031(2)	452(2)	5102(2)	75(1)
Cl(1)	8886(1)	2747(1)	3533(1)	61(1)
O(3)	9288(4)	1974(3)	3687(4)	231(3)
O(4)	8646(4)	2650(6)	2904(2)	257(4)
O(5)	8145(2)	2877(2)	3933(2)	125(1)
O(6)	9509(2)	3424(2)	3590(2)	110(1)

TABLE II Selected bond lengths (Å) and angles (deg) for the complex

Ni(1)–O(2)	2.0842(16)	Ni(1)–N(3)	2.210(2)
Ni(1)–O(1)	2.0915(16)	O(1)–C(1)$^{\#1}$	1.253(3)
Ni(1)–N(4)	2.099(2)	O(2)–C(1)	1.249(3)
Ni(1)–N(2)	2.1072 (19)	C(1)–O(1)$^{\#1}$	1.253(3)
Ni(1)–N(1)	2.176(2)	C(1)–C(1)$^{\#1}$	1.549(4)
O(2)–Ni(1)–O(1)	79.67(6)	O(2)–Ni(1)–N(3)	88.74(7)
O(2)–Ni(1)–N(4)	166.89(8)	O(1)–Ni(1)–N(3)	98.26(7)
O(1)–Ni(1)–N(4)	87.54(7)	N(4)–Ni(1)–N(3)	90.28(8)
O(2)–Ni(1)–N(2)	90.75(7)	N(2)–Ni(1)–N(3)	83.17(8)
O(1)–Ni(1)–N(2)	170.26(7)	N(1)–Ni(1)–N(3)	170.56(8)
N(4)–Ni(1)–N(2)	102.11(8)	C(1)$^{\#1}$–O(1)–Ni(1)	113.42(14)
O(2)–Ni(1)–N(1)	98.24(7)	C(1)–O(2)–Ni(1)	113.37(14)
O(1)–Ni(1)–N(1)	89.28(8)	O(2)–C(1)–O(1)$^{\#1}$	126.5(2)
N(4)–Ni(1)–N(1)	84.35(8)	O(2)–C(1)–C(1)$^{\#1}$	117.1(2)
N(2)–Ni(1)–N(1)	90.35(8)	O(1)$^{\#1}$–C(1)–C(1)$^{\#1}$	116.4(2)

Symmetry transformations used to generate equivalent atoms: $^{\#1}-x+1,\ -y,\ -z+1$.



SCHEME 1 A representation of the mechanism of electrophilic attack of Ni(*rac*-cth)$^{2+}$ on $[Cr(C_2O_4)_2(H_2O)_2]^-$.

Spectroscopic Characterization

The infrared spectrum shows bands characteristic of the bridging oxalato ligand [14,15] (ν_{asym}(O–C–O)s at *ca* 1640 vs, ν_{sym}(O–C–O) at *ca* 1310w and δ(O–C–O) at *ca* 790m cm^{-1} where vs, m, and w refer to very strong, medium, and weak, respectively), a very sharp medium intensity band at 3225–3250 cm^{-1} and a broad strong band at *ca* 1080 cm^{-1} characteristic of the NH group in *rac*-cth [16] and perchlorate ions respectively. The electronic spectrum of the complex in acetonitrile solution is typical of an octahedral nickel(II) complex [17], exhibiting the three spin-allowed transitions from $^3A_{2g}$ to $^3T_{2g}$, $^3T_{1g}$, and $^3T_{2g}(P)$ with maxima at *ca* 10500 (ν_1, $\varepsilon = 70\,M^{-1}cm^{-1}$), 17100 ($\nu_2$, $\varepsilon = 79\,M^{-1}cm^{-1}$) and 27400 cm^{-1} ($\nu_3$, $\varepsilon = 141\,M^{-1}cm^{-1}$). According to the ligand field theory [18], $10\,Dq$, B and ν_3 can be obtained by using two observed bands (ν_2 and ν_3); $10\,Dq = 10800\,cm^{-1}$, $B = 806\,cm^{-1}$, $\nu_1(calc) = 10800\,cm^{-1}$. The observed ν_1 frequency is consistent with the calculated value, indicating that the assignments are reasonable. The nephelauxetic ratio, $\beta = B_{complex}/B_{free} = 0.76$ (considering $B = 1056\,cm^{-1}$ for the gaseous ion (^3P) Ni^{2+}) shows moderately strong covalent bonding of nickel in the complex. It also exhibits a shoulder at 12500 cm^{-1}, which could be attributed to the spin-forbidden A_{2g}-E_g transition in O_h symmetry. The ν_1 band in the near-infrared region is diagnostic of *cis* coordination, that is, the tetraamine is folded in order to accommodate the oxalate ligand [5]. The X-band polycrystalline powder EPR spectrum of the complex does not exhibit any signal due to the large zero-field splitting of the nickel(II) ions [5].

Description of the Structure of [Ni(μ-C_2O_4)(*rac*-cth)$_2$](ClO$_4$)$_2$]

A perspective view of the cation [Ni(μ-C_2O_4)(*rac*-cth)$_2$]$^{2-}$ with the atom labelling scheme is shown in Fig. 1. The structure consists of centrosymmetric [Ni(μ-C_2O_4)(*rac*-cth)$_2$]$^{2+}$ cations separated by perchlorate anions, with a centre of symmetry lying in the middle of the C–C bond of the bis-bidentate oxalate bridge. The tetraazamacrocycle adopts a folded conformation around the nickel atoms. Each Ni(II) ion is in a $4+2$ environment. The basal plane consists of two oxygen atoms from the oxalate group and two nitrogen atoms from *rac*-cth, whereas the apical positions are occupied by the other two nitrogen atoms from *rac*-cth. The oxalate ion is symmetrically coordinated in the plane with Ni–O average distances 2.088 Å. The in-plane Ni–N bond distances average 2.103 Å and the axial Ni–N bond distance is 2.193 Å. Thus, the coordination geometry around the nickel ion can be described as a distorted octahedron.

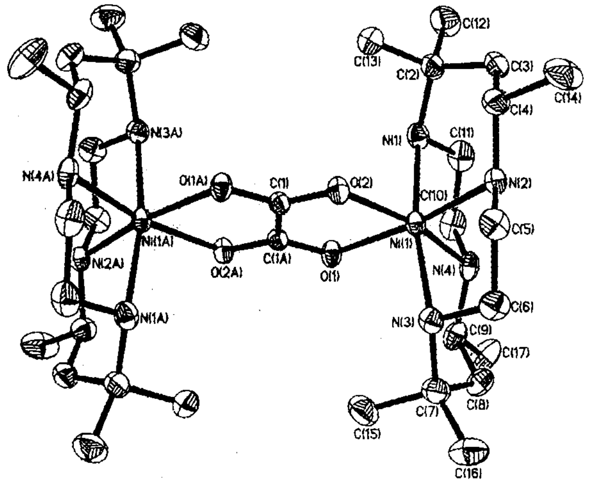


FIGURE 1 Perspective view of the [Ni(μ-C_2O_4)(*rac*-cth)$_2$]$^{2+}$ cation with the atom labelling scheme.

Magnetic Properties

The magnetic behaviour of the complex is shown in Fig. 2 in the form of a $\chi_m T$ *vs* T plot (χ_m being the magnetic susceptibility for a binuclear nickel(II) unit). The $\chi_m T$ value ($1.93\,\mathrm{cm^3\,mol^{-1}\,K}$) at 299.19 K is slightly lower than the spin-only value ($2.00\,\mathrm{cm^3\,mol^{-1}\,K}$) expected for the uncoupled dinickel(II) unit. The experimental value decreases upon cooling, indicating an intramolecular antiferromagnetic interaction between two single-ion triplet states. As the ground state of nickel(II) in a octahedral environment is orbitally nondegenerate, the intramolecular exchange interaction can be represented by the isotropic spin Hamiltonian $\hat{H} = -J\hat{S}_A \cdot \hat{S}_B$. where J is the exchange integral and $S_A = S_B = 1$ (local spins); χ_m may be expressed as

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

where N_α is the temperature-independent paramagnetism, assumed to be $-200\times10^{-6}\,\mathrm{cm^3\,mol^{-1}}$ for two nickel(II) ions.

The zero-field splitting, D, has not been considered because it has been shown that the zero-field splitting, D, does not change the position of the maximum of χ_m *vs* T curve. Since it is known this position determines the value of J, the effect of D on the magnetic behaviour can be neglected due to the large stabilization of the singlet ground state [19].

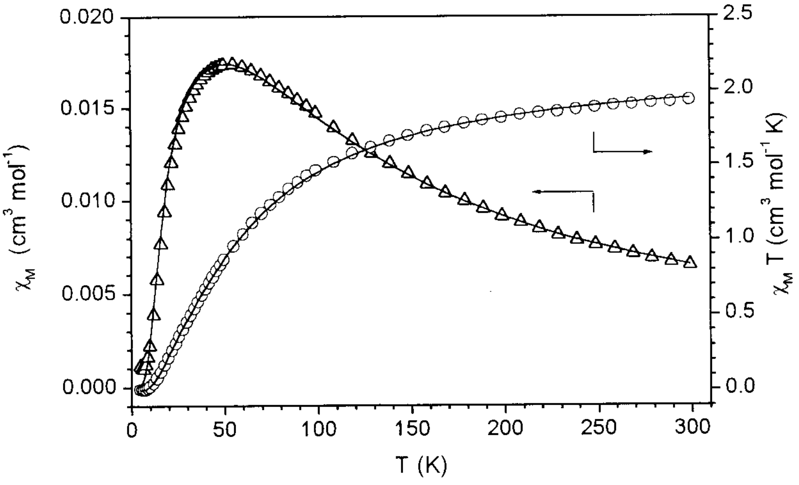


FIGURE 2 The χ_m *vs* T and $\chi_m T$ *vs* T plots for the complex.

TABLE III Magnetic parameters (J in cm^{-1}) for binuclear nickel(II)–oxalato systems

Compounda	*J*	*g*	*Ref*
NiN_4ox environment			
(μ-ox)[Ni(cyclam)]$_2$(ClO_4)$_2$	−39.0	2.33	5
(μ-ox)[Ni(cyclen)]$_2$(NO_3)$_2$	−35.0	2.30	6
(μ-ox)[Ni(Me_2cyclen)]$_2$(ClO_4)$_2$	−34.0	2.15	6
(μ-ox)[Ni(*meso*-tetd)]$_2$(ClO_4)$_2$	−36.8	2.19	19
(μ-ox)[Ni(*rac*-cth)]$_2$(ClO_4)$_2$	−34.0	2.07	this work
(μ-ox)[Ni(232-tet)]$_2$(ClO_4)$_2$	−32.1	2.22	20
(μ-ox)[Ni(trine)]$_2$(ClO_4)$_2$	−35.2	2.20	19
NiN_3Oox environment			
(μ-ox)[Ni(L)(H_2O)]$_2$(NO_3)$_2$	−25.5	2.10	7
(μ-ox)[Ni(dpt)(H_2O)]$_2$(ClO_4)$_2$	−24.7	2.32	21
(μ-ox)[Ni(Medpt)(H_2O)]$_2$(ClO_4)$_2$	−21.6	2.24	21
(μ-ox)[Ni(ept)(H_2O)]$_2$(ClO_4)$_2$	−24.4	2.06	22

[a] Referenced ligands are: (cyclam) 1,4,8,11-tetraazacyclotetradecane, (cyclen) 1,4,7,10-tetracyclododecane, (Me_2cyclen) 1,7-dimethyl-1,4,7,10-tetracyclododecane, (*meso*-tetd) 5,7,7,12,12,14-hexamethyl-1,4-8,11-tetra-azacyclotetradecane, (232-tet) *N,N*′-bis(2-aminoethyl)-1,3-propanediamine, (trien) triethylenetetramine, (L) 1,4,7-triazacyclononane, (dpt) bis-(3-aminopropy10amine, (Medpt) 3,3′-diamino-*N*-methyl-dipropylamine, (ept) *N*-(2-aminoethyl)-1,3-propanediamine.

Least-square fitting of all experimental data leads to J and g values of $-34.0\,cm^{-1}$ and 2.07 with the agreement factor $R=\sum(\chi_m T_{obsd}-\chi_m T_{cacld})^2/\sum(\chi_m T_{obsd})^2=2.0\times10^{-4}$. The moderately antiferromagnetic coupling observed is due to overlap between the x^2–y^2-type magnetic orbitals centred on the metal ions (x and y are defined by the M-O(oxalate) bonds) through the symmetry-adapted molecular orbitals of the oxalate bridge. The J value is mainly determined by the contribution of the $d_{x^2-y^2}$ exchange pathway; a smaller contribution of the d_{z^2} exchange pathway has to be expected for its overlapping with $2p$ orbitals of oxalate–oxygen atoms is much smaller than those of the $d_{x^2-y^2}$ ones. The observed J value of $34.0\,cm^{-1}$ is similar to that for NiN_4ox oxalato dimers, where the peripheral ligands are two bidentate or one tetradentate amine, but significantly larger than that for NiN_3Oox oxalato dimers, where O usually stands for H_2O [20–22] (Table III lists the magnetic parameters (J in cm^{-1}) for selected dinuclear nickel(II)–oxalato complexes). It may depend on decreasing electronegativity of peripheral ligand when an O-atom of a water molecule is substituted by an N-amine atom [21].

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