Synthesis, Crystal Structure, Magnetic Properties, and Solution Study of the Complex μ-Oxalato-bis[aqua(1,4,7-triazacyclononane)nickel(II)] Nitrate Dihydrate†

Andrea Bencini, Antonio Bianchi,* and Paola Paoli
Dipartimento di Chimica, Università di Firenze, Via Maragliano 75/77, 50144 Firenze, Italy
Enrique García-España,* Miguel Julve,* and Victor Marcelino
Departament de Química Inorgánica, Universitat de Valencia, C/Dr. Moliner 50, 46100-Burjassot (Valencia), Spain

A new binuclear nickel(II) complex of formula $[Ni_2L^1_2(H_2O)_2(ox)][NO_3]_2{\cdot}2H_2O$, where L^1 and ox^{2-} refer to 1,4,7-triazacyclononane and oxalate anion respectively, has been synthesized and its crystal structure solved at room temperature. This compound crystallizes in the monoclinic system, space group $P2_1/c$, with a = 8.704(2), b = 7.344(5), c = 20.321(6) Å, β = 98.38(2)°, and Z = 2. The structure was refined to R' = 0.037. It consists of centrosymmetrical binuclear cations $[Ni_2L^1_2(H_2O)_2(ox)]^{2+}$ with water molecules of crystallization and nitrate counter ions. Each nickel atom is six-co-ordinated in an octahedral distorted *fac*-NiN_3O_3 arrangement: the Ni–N distances are in the range 2.059(5)—2.080(6) Å, and the Ni–O distances are 2.086(4) and 2.111(5) Å for oxalate and 2.120(5) Å for co-ordinated water. The oxalate joins two adjacent nickel atoms acting as a bis(bidentate) ligand. The C–C bond is perpendicular to the Ni ··· Ni vector giving two five-membered chelate rings. Magnetic susceptibility measurements in the temperature range 4.2—300 K show that the two nickel(II) ions of the binuclear unit are antiferromagnetically coupled with $J = -25.5$ cm^{-1} and g = 2.10, T_N being *ca.* 32 K. The electronic spectra, measured both in solution and in the solid state, allowed values of 977 and −135 cm^{-1} for the Racah parameter and the spin–orbit coupling constant, respectively, to be determined. The equilibrium constant relative to the addition of one ox^{2-} to the complex $[NiL^1]^{2+}$ has been determined potentiometrically in aqueous solution, log K = 3.26(1) (298.15 K and 0.1 mol dm^{-3} KNO_3). The enthalpy of this reaction has been measured by direct microcalorimetry. From the value obtained, $\Delta H^\ominus = -1.5(1)$ kcal mol^{-1}, a value of $T\Delta S^\ominus$ of 2.9 kcal mol^{-1} can be calculated. These parameters are interpreted and analysed taking into account previous data on analogous reactions for some tetra-azamacrocyclic nickel(II) complexes.

Although oxalato-bridged complexes have been known for many years[1–6] few crystal structures showing this binding feature of ox^{2-} have been determined by *X*-ray diffraction methods.[7–11] Tetra-azamacrocycles as well as bidentate and tridentate acyclic amines have been used as terminal ligands in order to avoid the formation of the one-dimensional nickel(II) oxalate chain. Variable-temperature magnetic susceptibility measurements of such oxalato-bridged complexes have revealed strong intramolecular antiferromagnetic coupling illustrating the great efficiency of oxalate in propagating electronic effects between two metal ions separated by more than 5 Å. It is now well known that the main factor governing the interaction between the two metallic centres in binuclear complexes with extended bridges is the overlap of the magnetic orbitals[12,13] which favours the antiferromagnetic interaction.

In the last few years, several complexes between the small tridentate ligand 1,4,7-triazacyclononane (L^1) or its *N*-methylated derivative and divalent and trivalent 3*d* transition metals have been reported.[14] As far as nickel(II) is concerned, several mononuclear complexes containing these ligands are known. However, to the best of our knowledge, the first example of binuclear nickel(II) complexes containing such ligands and extended bridges have been reported only recently.[15]

In the present paper we report on the synthesis, crystal structure, and spectroscopic and magnetic properties of the binuclear complex $[Ni_2L^1_2(H_2O)_2(ox)][NO_3]_2{\cdot}2H_2O$. In order to get further insight on the interaction between $[NiL^1]^{2+}$ and oxalate anion, we have also determined the thermodynamic parameters relative to this interaction in aqueous solution and compared them with previous data[9,11] on similar systems with tetra-azacycloalkanes.

Experimental

Materials.—1,4,7-Triazacyclononane (L^1) was prepared as described in the literature.[16] All other chemicals, nickel(II) nitrate hexahydrate, oxalic acid, and sodium oxalate were of Merck reagent grade and used as received. Solution and solid-state spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer.

Synthesis of $[Ni_2L^1_2(H_2O)_2(ox)][NO_3]_2{\cdot}2H_2O$.—This compound was prepared by adding sodium oxalate (0.05 mmol) dissolved in a minimum amount of water to an aqueous solution (30 cm^3) of $Ni(NO_3)_2{\cdot}6H_2O$ and L^1 (1 mmol). Blue prismatic crystals were obtained by slow evaporation of the resulting solution at room temperature (Found: C, 25.6; H, 5.8; N, 17.0. $C_{14}H_{38}N_8Ni_2O_{14}$ requires C, 25.5; H, 5.75; N, 16.95%).

Spectroscopic and Magnetic Measurements.—Diffuse reflec-

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: cal = 4.184 J.

Table 1. Summary of crystal data and data collection details

Formula	$C_{14}H_{38}N_8Ni_2O_{14}$
M	659.89
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	8.704(2)
b/Å	7.344(5)
c/Å	20.321(6)
β/°	98.38(2)
U/Å^3	1 285(4)
Z	2
D_c/g cm^{-3}	1.70
F(000)	694
μ(Mo-K_α)/cm^{-1}	15.16
Crystal size/mm	0.60 × 0.40 × 0.40
Scan width	0.80 + 0.35 tan θ
Scan type	ω—2Θ
Scan speed/° min^{-1}	4
Reflections collected	1 364
Independent reflections [$I > 3\sigma(I)$]	1 032
No. of parameters refined	175
R[a]	0.042
R'[b]	0.037
Weighting factor, w	$1/[\sigma(F)]^2$

[a] $\Sigma||F_o| - |F_c|/\Sigma|F_o|$. [b] $[\Sigma w_i(|F_o| - |F_c|)^2/\Sigma w_i|F_o|^2]^{\frac{1}{2}}$.

tance spectra were obtained by using the Nujol-mull technique in order to ensure the identity of species in solution and the solid state. Infrared spectra were recorded with a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets. Magnetic susceptibilities were measured by the Faraday method on polycrystalline samples over the temperature range 15—300 K by means of a pendulum-type apparatus[17] equipped with a helium cryostat. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Corrections for the diamagnetism of $[Ni_2L^1_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$ were estimated from Pascal's constants as -330×10^{-6} e.m. units mol^{-1} (1 e.m. unit = S.I. × $10^6/4\pi$). Magnetic susceptibility data were also corrected for temperature-independent paramagnetism (-100×10^{-6} e.m. units per Ni^{II}).

E.M.F. Measurements.—These were carried out in 0.1 mol dm^{-3} KNO_3 solution at 25 °C by using a titrating assembly that has been previously described.[18] The reference electrode was an Ag–AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen-concentration probe by titration of known amounts of HNO_3 with CO_2-free NaOH and determining the equivalent point by Gran's method,[19] which gives the standard potential of the cell, $E^{\ominus}$, and the ionic product of water K_w. The equilibria involving $[NiL^1]^{2+}$ and ox^{2-} were first investigated by titrating, with oxalic acid standard solutions, aqueous solutions of $[NiL^1]^{2+}$. These solutions were prepared, on the basis of reported stability constants,[14] such as to form just the species $[NiL^1]^{2+}$. Preliminary studies based on potentiometric titrations showed that no interaction occurred between oxalate and/or hydrogenoxalate and protonated forms of L^1 under the experimental conditions employed. The attainment of equilibrium in the complexation reactions was controlled by out-of-cell batchwise titrations. The complex $[NiL^1]^{2+}$ is stable enough toward acid dissociation to allow the performance of this type of measurements. The computer program SUPERQUAD[20] was used to determine the equilibrium constants. Although further measurements were carried out by titrating solutions of the solid complex $[Ni_2L^1_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$ with oxalic acid, just the constant relative to the formation of the mononuclear mixed-ligand species could be determined.

Microcalorimetry.—The enthalpy of the reaction between oxalate and $[NiL^1]^{2+}$ to yield the mixed-ligand mononuclear complex $[NiL^1(ox)]$ was determined by means of fully automatized equipment having a model 2277 Thermal Activity Monitor (Termometric AB) microcalorimeter. The system was programmed in order to follow batchwise titrations. In a typical experiment, 2 cm^3 of oxalate solution buffered at pH 9.6 with sodium tetraborate were placed in the calorimetric cell, and titrated with successive additions (volumes ranging from 40 to 100 μl) of an aqueous solution containing $[NiL^1]^{2+}$ solution also buffered at the same pH. All solutions were prepared so as to yield a final concentration of 0.1 mol dm^{-3} KNO_3. The thermal effect produced by each addition was recorded and subsequently corrected for the heats of dilution of the reacting solutions, by blank experiments. The heat evolution for the reaction of oxalate anion and $[NiL^1]^{2+}$ takes place within a few minutes. About twenty experimental points from four different experiments were used to calculate the enthalpy of this reaction. Taking into account the equilibrium constant, the composition of the solution after each addition was calculated in order to verify completion of the reaction.

Crystal Structure Determination and Refinement.—Diffraction data were collected at 298 K with an Enraf-Nonius CAD4 automated four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 73 Å). Crystal data and details of the data collection are given in Table 1. The unit-cell parameters and orientation matrix were determined from angular setting of 25 carefully centred reflections. 1 032 Reflections having $I > 3\sigma(I)$ were considered as independent and used in the structure analysis. They were corrected for Lorentz and polarization effects in the usual manner. The data set was empirically corrected for absorption effects once the structure had been solved. The structure was solved by using heavy-atom methods and successive Fourier syntheses. In all structure-factor calculations the atomic scattering factors were taken from ref. 21. The effect of anomalous dispersion was included for all non-hydrogen atoms. The values of f' and f'' used were those given in ref. 22. The structure was refined by least-square methods with anisotropic thermal parameters for all non-hydrogen atoms except those of the nitrate groups. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where the weights w were taken as $1/[\sigma(F_o)]^2$. The hydrogen atoms of the ligand were introduced in calculated positions; those of the water molecules of crystallization were found in a ΔF map, which did not give the hydrogens of the co-ordinated water molecules. The final values of R and R' are given in Table 1. The highest peak in the final Fourier difference map had an electron density of 0.5 e Å^{-3}. All the calculations were performed by an IBM Personal System/2 model 80 computer with SHELX 76[23] and ORTEP[24] programs. Final positional parameters for all non-hydrogen atoms are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

Description of the Structure of $[Ni_2L^1_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$.—The structure is made up of water molecules of crystallization, unco-ordinated nitrate anions, and $[Ni_2L^1_2(H_2O)_2(ox)]^{2+}$ binuclear cations having a symmetry centre at the midpoint of the C(1)–C(1^I) bond (I $1 - x$, $-y$, $1 - z$) of the oxalato bridge. The molecular geometry and the atom labelling

Table 2. Final atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for $[Ni_2L^1{}_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$

Atom	*X/a*	*Y/b*	*Z/c*
Ni	3 145(1)	2 483(2)	4 277(1)
N(1)	3 374(7)	5 160(8)	3 972(3)
N(2)	1 056(6)	2 584(10)	3 655(3)
N(3)	4 040(7)	1 866(8)	3 410(3)
N(4)	2 238(8)	313(10)	6 399(3)
O(1)	5 282(5)	2 333(8)	4 892(2)
O(2)	3 149(6)	−287(7)	4 555(3)
O(3)	2 101(5)	3 205(6)	5 120(2)
O(4)	954(6)	973(8)	6 246(3)
O(5)	3 360(6)	957(8)	6 166(3)
O(6)	2 412(6)	−970(8)	6 773(3)
O(7)	−1 053(9)	2 665(16)	4 846(4)
C(1)	5 613(9)	759(12)	5 093(4)
C(2)	1 911(9)	5 803(11)	3 570(4)
C(3)	568(8)	4 545(11)	3 659(4)
C(4)	4 721(9)	5 091(12)	3 603(4)
C(5)	4 541(9)	3 548(12)	3 101(4)
C(6)	2 744(9)	923(11)	2 992(4)
C(7)	1 244(9)	1 967(10)	2 979(4)

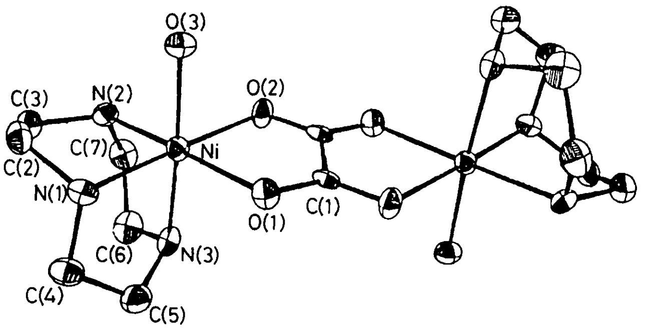

Figure 1. ORTEP drawing of the binuclear entity $[Ni_2L^1{}_2(H_2O)_2(ox)]^{2+}$ with the atom numbering scheme. Thermal ellipsoids are at the 50% probability level, and hydrogen atoms are not included

scheme for the cation are shown in Figure 1. The nickel co-ordination geometry is distorted octahedral with three nitrogen atoms from the facially co-ordinated tridentate amine and three oxygen atoms, one from a water molecule and the other two from the oxalato bridging ligand. The oxalate ion joins two adjacent co-ordination polyhedra with its oxygen atoms occupying two *cis* positions in both polyhedra. The nickel–nickel separation within the binuclear unit is 5.44 Å. Bond distances and angles involving non-hydrogen atoms are listed in Table 3. The three Ni–N bond lengths are within a narrow range [2.059(5)—2.080(6) Å] and are somewhat shorter than the average Ni–N bond distances found in other nickel(II) complexes with 1,4,7-triazacyclononane[25] and its *N*-methylated derivative.[15,26] As far as the Ni–O bond distances are concerned, the average Ni–O(oxalate) distance [2.098(18) Å] is very similar to that of Ni–O(water) [2.120(5) for Ni–O(3)]. Significant variations from the idealized orthogonal geometry are found within the five-membered chelate N–Ni–N chelate rings, the N–Ni–N angles ranging between 83.6(2) and 84.1(2)°, respectively. The O(1)–Ni–O(2) angle [79.8(2)°] is very similar to that found in other oxalato-bridged nickel(II) binuclear complexes.[7–11] However, it is smaller than the H_2O–Ni–OH_2 angle [87.1(2)°] in the complex *cis*-$[NiL^2(H_2O)_2]^{2+}$ (L^2 = 1,4,8,11-tetra-azacyclotetradecane).[27] This difference is due to the short bite distance of the oxalate ion [2.6 Å for O(1) ··· O(2)]. The N–C and C–C bond distances of co-ordinated L^1 compare favourably with the values in other nickel(II) complexes with this ligand and its *N*-methylated derivative. In particular the C–C bond lengths are shorter than the classical value of 1.54 Å. The oxalate ion is exactly planar, and the nickel(II) ion is 0.116 Å out of this plane. Bond distances and angles in the oxalate ion are in the expected range and very similar to those found in other oxalato-bridged nickel(II) binuclear complexes. The oxalate group in this compound is found to be symmetrical with a C–O distance of *ca.* 1.25 Å. However, for oxalic acid dihydrate the C–OH and C=O distances are 1.281 and 1.207 Å respectively.[28] Deprotonation and metal co-ordination of oxalate in complex formation are at the origin of such differences. The nitrate ion contributes to the packing by forming hydrogen bounds involving oxygen atoms and co-ordinated and unco-ordinated water molecules.

Table 3. Bond distances (Å) and angles (°) for $[Ni_2L^1{}_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$*

Nickel environment			
Ni–N(1)	2.080(6)	Ni–O(1)	2.086(4)
Ni–N(2)	2.059(5)	Ni–O(2)	2.111(5)
Ni–N(3)	2.078(6)	Ni–O(3)	2.120(5)
N(1)–Ni–N(2)	84.1(2)	O(1)–Ni–O(2)	79.8(2)
N(2)–Ni–O(3)	92.5(2)	O(1)–Ni–O(3)	88.8(2)
N(1)–Ni–O(3)	94.3(2)	O(2)–Ni–O(3)	90.5(2)
N(1)–Ni–N(3)	83.6(2)	O(2)–Ni–N(3)	91.7(2)
N(1)–Ni–O(1)	96.5(2)	O(2)–Ni–N(2)	99.5(2)
N(2)–Ni–N(3)	83.9(2)	O(1)–Ni–N(3)	94.8(2)
N(1)–Ni–O(2)	173.8(2)	O(1)–Ni–N(2)	178.5(2)
N(3)–Ni–O(3)	176.0(2)		
1,4,7-Triazacyclononane ligand			
N(1)–C(2)	1.487(9)	N(1)–C(11)	1.481(11)
C(2)–C(3)	1.521(11)	C(4)–C(5)	1.518(12)
N(2)–C(3)	1.502(11)	N(3)–C(5)	1.480(10)
N(2)–C(7)	1.480(10)	N(3)–C(6)	1.482(9)
C(7)–C(6)	1.511(11)		
Ni–N(1)–C(2)	110.6(4)	Ni–N(1)–C(4)	103.6(4)
N(1)–C(2)–C(3)	110.7(6)	N(1)–C(4)–C(5)	110.8(6)
C(2)–C(3)–N(2)	111.0(6)	C(4)–C(5)–N(3)	110.2(6)
C(3)–N(2)–C(7)	111.6(2)	C(5)–N(3)–C(6)	113.2(6)
N(2)–C(7)–C(6)	110.5(6)	N(3)–C(6)–C(7)	110.9(6)
Ni–N(3)–C(5)	110.4(5)	Ni–N(3)–C(6)	103.9(6)
Ni–N(2)–C(7)	110.7(4)	Ni–N(2)–C(3)	104.8(4)
C(2)–N(1)–C(4)	114.2(6)		
Oxalato bridge			
C(1)–O(1)	1.246(11)	C(1)–O(2^I)	1.253(9)
C(1)–C(1^I)	1.552(12)		
O(1)–C(1)–C(1^I)	117.9(7)	O(2)–C(1^I)–C(1)	116.4(7)
C(1)–O(1)–Ni	112.9(5)	C(1^I)–O(2)–Ni	112.8(5)
Nitrate anion			
N(4)–O(4)	1.216(9)	N(4)–O(5)	1.240(10)
N(4)–O(6)	1.206(9)		
O(4)–N(4)–O(5)	119.7(7)	O(4)–N(4)–O(6)	119.9(7)
O(5)–N(4)–O(6)	120.4(7)		

* Superscript I refers to the equivalent position $1 - x, -y, 1 - z$.

Electronic and I.r. Spectra.—The absorption spectrum of $[Ni_2L^1{}_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$ has been measured both in the solid state and aqueous solution. The spectra exhibit significant differences which can be attributed to dissociation of the binuclear complex into $[NiL^1(ox)]$ and $[NiL^1]^{2+}$ in solution (see thermodynamic study). Three spin-allowed transitions

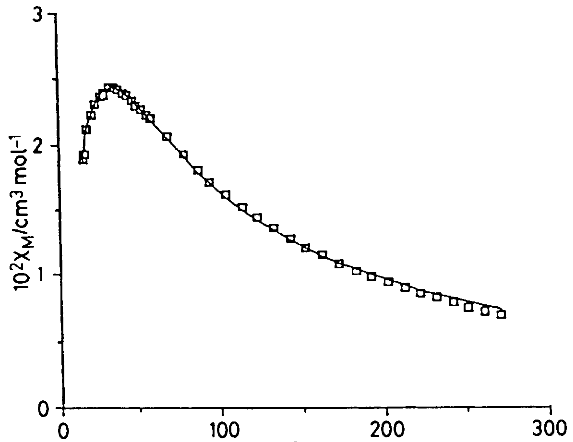

Figure 2. Thermal dependence of the molar magnetic susceptibility for $[Ni_2L^1{}_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$. Experimental data are represented by squares, whereas the solid line is the theoretical line obtained by least-squares fitting of all experimental points

from $3A_{2g}$ to $3T_{2g}$, $3T_{1g}$, and $3T_{1g}(P)$ are observed at 10 750 (ν_1), 17 700 (ν_2), and 26 600 (ν_3) cm^{-1}, respectively, in the reflectance spectra as expected for a d^8 configuration in a near-octahedral ligand field. The first band yields the octahedral splitting parameter of 10 750 cm^{-1}, a value very close to those reported for complexes $[NiL]^{2+}$ (L = a nine- to twelve-membered triazacyclic ligand) in aqueous solution.[29] For the octahedral case, by calculation in the strong-field coupling scheme with a d^8 configuration, the Racah parameter B is found to be 977 cm^{-1} which leads to a nephelauxetic ratio of 0.827 [considering that $15B$ has a value of 15 840 cm^{-1} for the gaseous ion (^3P) for Ni^{2+}]. With $g = 2.10$, obtained from the best fit of the magnetic susceptibility measurements (see below), and through the equation $g = 2 - 8/10Dq$, the spin–orbit coupling constant was calculated to be -135 cm^{-1} for the present compound. Compared with the free-ion value of -315 cm^{-1}, there is a marked reduction of about 57%. This fact is not uncommon for nickel complexes in distorted geometries.[30]

The i.r. spectra of $[Ni_2L^1{}_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$ displays the characteristic bands of the oxalate bridging ligand;[1,2] ν_{asym}(O–C–O) at 1 640vs, ν_{sym}(O–C–O) at 1 315w, and δ(O–C–O) at 795m cm^{-1} where vs, m, and w refer to very strong, medium, and weak respectively. Bands due to ionic nitrate[31] are located at 2 430w, 1 745w, 1 390vs, and 830w cm^{-1}. It should be noted that the i.r. spectra of nitrate-containing complexes are a useful tool to elucidate their stereochemistry. In particular Lever and Mantovani[32] have demonstrated the utility of the $\nu_1 + \nu_4$ (E',D_{3h}) combination band for structural purposes. This band which appears near 1 750 cm^{-1} together with the strong band at *ca.* 1 390 cm^{-1} [ν_3 (E',D_{3h})] support the presence of ionic nitrate as evidenced by the structure of $[Ni_2L^1{}_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$.

Magnetic Properties.—The temperature dependence of the molar magnetic susceptibility χ_M of $[Ni_2L^1{}_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$ is shown in Figure 2. The value at room temperature is in the range expected for two $S = 1$ states, and increases as the temperature is lowered until a maximum at *ca.* 32 K is reached, after which there is a rapid decrease. Such behaviour is characteristic of an antiferromagnetic interaction between the two single-ion triplet states with a small portion of non-coupled nickel(II) impurity. The data were fitted by means of least squares to the formula (1) where N, β, K, and g have their usual meanings. The parameter ρ represents the fraction of non coupled nickel(II) impurity. This expression results from the spin Hamiltonian ($\hat{H} = -J\hat{S}_A \cdot \hat{S}_B$) for an isotropic magnetic exchange with $\hat{S}_A = \hat{S}_B = 1$ without zero-field splitting, D. Although powder measurement is not ideal for a thorough analysis of $S = 1$ binuclear systems, the exchange parameter J is the dominant term in the spin Hamiltonian and hence is not influenced markedly by the value of D.[4] A least-squares fit of all the experimental points (solid line in Figure 2) leads to the following values: $J = -25.5$ cm^{-1}, $g = 2.10$, and $\rho = 0.043$. The agreement factor $R = \Sigma(\chi_{i,\text{exptl.}} - \chi_{i,\text{calc.}})^2/\Sigma(\chi_{i,\text{exptl.}})^2$ is 9.61×10^{-5}.

$$\chi_M = \frac{2N\beta^2g^2}{kT} \cdot \frac{\exp\dfrac{J}{kT} + J\exp\dfrac{3J}{kT}}{1 + 3\exp\dfrac{J}{kT} + J\exp\dfrac{3J}{kT}}(1 + \rho) + \frac{2N\beta^2g^2}{kT} \cdot \rho \qquad (1)$$

No polycrystalline powder spectrum could be detected e.p.r. because of the large zero-field splitting of the nickel(II) ions.

A relatively strong coupling through oxalate between nickel(II) ions separated by 5.44 Å is observed. This confirms the remarkable efficiency of bis(bidentate) oxalate-type ligands to transmit strong antiferromagnetic interaction between paramagnetic metal ions separated by more than 5 Å.[13,33] Such efficiency has its origin in the strong overlap between the xy-type magnetic orbitals centred on the metal ions [x and y being defined by the M–O(oxalate) bonds] through the symmetry-adapted molecular orbitals of the oxalate bridge.[34] The planarity of Ni(ox)Ni favours the overlapping and consequently the magnitude of the coupling. The d_{z^2} magnetic orbital of each nickel(II) ion in the binuclear unit also contributes to the exchange interaction. However, its overlapping with $2p$ orbitals of oxalate-oxygen atoms is much smaller than those of the d_{xy} ones because of their different symmetry. Consequently, a smaller contribution of the d_{z^2} exchange pathway has to be expected, the observed J value being mainly determined by that of d_{xy}.

The observed J value of $[Ni_2L^1{}_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$ (-25.5 cm^{-1}) is significantly smaller than that previously reported for $[Ni_2L^2{}_2(ox)][NO_3]_2$ (-39 cm^{-1}).[9] Such a difference can be understood on the basis of structural features. The NiN_3O_3 core in $[Ni_2L^1{}_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$ is much more distorted from the ideal octahedral symmetry than the NiN_4O_2 in $[Ni_2L^2{}_2(ox)][NO_3]_2$. This is due to the fact that L^1 only forms five-membered chelate rings when it co-ordinates to metal ions whereas in the case of L^2 the presence of five- and six-membered chelate rings reduces steric constraints. The Ni–O distances in $[Ni_2L^1{}_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$ [2.086(4) and 2.111(5) Å] are larger than the corresponding ones in the L^2 complex [2.071(4) and 2.069(4) Å]. Concerning the Ni_2(ox) binuclear unit, the nickel(II) ion is 0.116 Å out of the oxalate plane while in the L^2 complex it deviates by just 0.027 Å. The combination of both factors leads to a smaller spin density on oxalate-oxygen atoms in $[Ni_2L^1{}_2(H_2O)_2(ox)][NO_3]_2 \cdot 2H_2O$ yielding a lower J as has been observed.

Thermodynamic Study.—In Table 4 are presented the thermodynamic parameters corresponding to the addition of oxalate anion to $[NiL^1]^{2+}$ together with those previously reported[11] for the same reaction with the related complexes $[NiL^3]^{2+}$, $[NiL^4]^{2+}$, and $[NiL^2]^{2+}$ (L^3 = 1,4,7,10-tetra-azacyclododecane, L^4 = 1,7-dimethyl-1,4,7,10-tetra-azacyclododecane).

The reaction of $[NiL^1]^{2+}$ with oxalate anion is rapid, equilibrium being reached in the time-scale of a common potentiometric titration. This result is in accord with the calorimetric measurements since only few minutes were

Table 4. Thermodynamic parameters (kcal mol^{-1}) for the reaction of oxalate anion with $[NiL]^{2+}$ in 0.1 mol dm^{-3} KNO_3 solution at 25 °C

Reaction	$\Delta G^{\ominus}$	$\Delta H^{\ominus}$	$T\Delta S^{\ominus}$
$[NiL^1]^{2+}(aq) + ox^{2-}(aq)$	−4.4(1)[a,b]	−1.5(1)[b]	2.9[b]
$[NiL^3]^{2+}(aq) + ox^{2-}(aq)$	−5.6(1)[c]	−2.4(1)[c]	3.2[c]
$[NiL^4]^{2+}(aq) + ox^{2-}(aq)$	−5.7(1)[c]	−2.9(1)[c]	2.8[c]
$[NiL^2]^{2+}(aq) + ox^{2-}(aq)$	−3.8(1)[c]	−3.8(1)[c]	0.0[c]
cis-$[NiL^2]^{2+}(aq) + ox^{2-}(aq)$	−6.1	−2.6	3.5
trans-$[NiL^2]^{2+}(aq) + ox^{2-}(aq)$	−4.5	0.0	4.5
$[NiL^2]^{2+}(aq)$[d] $+ ox^{2-}(aq)$	−4.0	−5.4	−1.4

[a] Values in parentheses are standard deviations in the last significant figure. [b] This work. [c] Taken from ref. 11; $[NiL^2]^{2+}(aq)$ is mixture of planar (69%), *trans*-diaqua octahedral (29%), and *cis*-diaqua octahedral (2%) forms. [d] Planar form.

required for the calorimeter equilibration after the reaction started.

The formation of $[Ni_2L^1_2(ox)]^{2+}$ in aqueous solution was not detected under the experimental conditions used, similarly to what was found for $[NiL^3]^{2+}$ and $[NiL^4]^{2+}$[11] and in contrast with $[NiL^2]^{2+}$.[9] Even when $[Ni_2L^1_2(H_2O)(ox)][NO_3]_2\cdot 2H_2O$ was dissolved in water and titrated with oxalic acid the only species detected in solution was the mixed mononuclear complex $[NiL^1(ox)]$ [$\log K = 3.26(1)$]. This fact can be attributed to the expected very low constant for the equilibrium $[NiL^1(ox)] + [NiL^1]^{2+} \rightleftharpoons [Ni_2L^1_2(ox)]^{2+}$. The log *K* value for the corresponding reaction with L^2 is just 1.6, even though the constant for the addition of oxalate anion to *cis*-$[NiL^2]^{2+}$ is much higher ($\log K = 4.5$).[9]

The free-energy change, $\Delta G^{\ominus}$, associated with the reaction of $[NiL^1]^{2+}$ with oxalate anion is markedly smaller than corresponding values for the other complexes with *cis* arrangements: $[NiL^3]^{2+}$, $[NiL^4]^{2+}$, and *cis*-$[NiL^2]^{2+}$ (see Table 4). This decrease in the value of $\Delta G^{\ominus}$ is mainly due to a less favourable enthalpic term. Breaking of the hydrogen-bond network involving the co-ordinated water molecules and the nitrogen atoms of the macrocycle as well as steric constraints (see structure) when the substitution by oxalate takes place must be at the origin of this lower enthalpic contribution. The $T\Delta S^{\ominus}$ value, 2.9 kcal K^{-1} mol^{-1}, is similar to those found for the other *cis* complexes; in all four cases the main contribution to $T\Delta S^{\ominus}$ should be due to the release of two co-ordinated water molecules.

Acknowledgements

Financial support from the Spanish Comision Interministerial de Ciencia Y Tecnología [Proyecto PB (88-0490)] and from the Italian Ministero della Pubblica Istruzione is gratefully acknowledged.

References

1 N. F. Curtis, *J. Chem. Soc.*, 1963, 4109.
2 N. F. Curtis, *J. Chem. Soc. A*, 1968, 1415.
3 P. W. Ball and A. B. Blake, *J. Chem. Soc. A*, 1969, 1415.
4 M. D. Duggan, E. K. Barefield, and D. N. Hendrickson, *Inorg. Chem.*, 1973, **12**, 985.
5 J. F. Myers and N. J. Rose, *Inorg. Chem.*, 1973, **12**, 2074.
6 M. D. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1973, **12**, 1238.
7 N. W. Alcock, P. Moore, and H. A. A. Omar, *Acta Crystallogr., Sect. C*, 1987, **43**, 2074.
8 J. Ribas, M. Monfort, C. Diaz, and X. Solans, *An. Quim.*, 1988, **84B**, 186.
9 L. P. Battaglia, A. Bianchi, A. Bonamartini-Corradi, E. Garcia-España, M. Micheloni, and M. Julve, *Inorg. Chem.*, 1988, **27**, 4174.
10 M. I. Arriourta, R. Cortés, T. Rojo, and J. Via, *Eur. J. Solid State Inorg. Chem.*, 1989, **26**, 91.
11 A. Bencini, A. Bianchi, E. García-España, Y. Jeanin, M. Julve, V. Marcelino, and M. Philoche-Levisalles, *Inorg. Chem.*, 1990, **29**, 963.
12 'Magneto-Structural Correlations in Exchange Coupled Systems,' eds. R. D. Willet, D. Gatteschi, and O. Khan, NATO ASI Series C, Reidel, Dordrecht, 1983, vol. 140.
13 O. Khan, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 834.
14 P. Chaudhuri and K. Wieghardt, *Prog. Inorg. Chem.*, 1987, **35**, 329 and refs. therein.
15 P. Chaudhuri, M. Guttman, D. Ventur, K. Wieghardt, B. Nuber, and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 1985, 1618.
16 R. Yang and L. J. Zompa, *Inorg. Chem.*, 1976, **15**, 1499.
17 J. C. Bernier and P. Poix, *L'Actualité Chimique*, 1978, **2**, 78.
18 A. Bianchi, L. Bologni, P. Dapporto, M. Micheloni, and P. Paoletti, *Inorg. Chem.*, 1984, **23**, 1201.
19 G. Gran, *Analyst* (*London*), 1952, **77**, 661; F. J. Rossoti and H. Rossoti, *J. Chem. Educ.*, 1965, **42**, 375.
20 P. Gans, A. Sabatini, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.
21 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
22 Ref. 21, Table 2.3.2.
23 G. M. Sheldrick, SHELX 76, A Program for Crystal Structure Determination, Cambridge University Chemical Laboratory, Cambridge, 1976.
24 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.
25 L. J. Zompa and T. N. Margulis, *Inorg. Chim. Acta*, 1978, **28**, L157.
26 P. Chaudhuri, H. J. Kuppers, K. Wieghardt, S. Gehring, B. Nuber, and J. Weiss, *J. Chem. Soc., Dalton Trans.*, 1988, 1367.
27 E. K. Barefield, A. Bianchi, E. J. Billo, P. J. Connolly, P. Paoletti, J. S. Summers, and D. G. Van Derveer, *Inorg. Chem.*, 1986, **25**, 4197.
28 S. Shibata and M. Kimura, *Bull. Chem. Soc. Jpn.*, 1954, **27**, 485.
29 L. J. Zompa, *Inorg. Chem.*, 1978, **17**, 2531.
30 R. Brener, E. Ehrenfreund, H. Shechter, and J. Makowsvsky, *J. Phys. Chem. Solids*, 1977, **38**, 1023.
31 M. R. Rosenthal, *J. Chem. Educ.*, 1973, **50**, 331.
32 A. B. P. Lever and E. Mantovani, *Inorg. Chem.*, 1971, **10**, 817.
33 M. Verdaguer, O. Khan, M. Julve, and A. Gleizes, *New J. Chem.*, 1985, **9**, 325.
34 M. Verdaguer, M. Julve, A. Michalowicz, and O. Khan, *Inorg. Chem.*, 1983, **22**, 2624.

Received 6*th December* 1989; *Paper* 9/05216J