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Synthesis, Crystal Structure, Magnetic Properties, and Thermodynamic and Electrochemical Studies of the Binuclear Complex (μ-Oxalato)bis[(1,4,8,11-tetraazacyclotetradecane)nickel(II)] Nitrate

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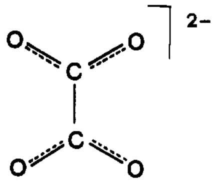
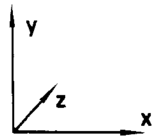
A new binuclear nickel(II) complex of formula $[Ni_2(cyclam)_2ox](NO_3)_2$ (**1**) (cyclam = 1,4,8,11-tetraazacyclotetradecane and ox^{2-} = oxalate dianion) has been synthesized and its crystal structure solved at room temperature. This compound crystallizes in the orthorhombic system, space group *Pbca*, with $a = 15.817$ (5) Å, $b = 12.845$ (3) Å, $c = 16.069$ (3) Å, $Z = 8$, and $R = 0.0363$. Its structure consists of centrosymmetrical μ-oxalato nickel(II) binuclear units with noncoordinated nitrate anions. The tetraaza macrocycle shows the *RRRR* set of nitrogen configuration, and each nickel is six-coordinated in an octahedral distorted arrangement: the Ni-N distances are in the range 2.087 (5)-2.101 (5) Å, and the Ni-O(ox) distances are 2.071 (4) and 2.069 (4) Å. The oxalate ion joins two adjacent coordination polyhedra, acting as a bisbidentate ligand. The two nickel(II) ions are antiferromagnetically coupled with $J = -39$ cm^{-1} (J being the parameter of the exchange Hamiltonian $\hat{H} = -J\hat{S}_A\hat{S}_B$). The stability constants of the equilibria $[Ni(cyclam)]^{2+} + ox^{2-} \rightleftharpoons [Ni(cyclam)ox]$ (log K = 2.8 (1)) and $[Ni(cyclam)ox] + [Ni(cyclam)]^{2+} \rightleftharpoons [Ni_2(cyclam)_2ox]^{2+}$ (log K = 1.6 (1)) have been determined spectrophotometrically in aqueous solution. An electrochemical study of **1** in nonaqueous solvents has revealed a higher stability for the mixed-valence complex (Ni^{II}-Ni^{III}) with regard to the mixture of the univalent complexes (Ni^{II}-Ni^{II}) and (Ni^{III}-Ni^{III}). The free energy change related to the comproportionation equilibrium (Ni^{II}-Ni^{II}) + (Ni^{III}-Ni^{III}) $\rightleftharpoons$ 2(Ni^{II}-Ni^{III}) ($-\Delta G°_C$ = 4.84 kcal mol^{-1} in DMF and 3.92 kcal mol^{-1} in DMSO) has been determined by cyclic voltammetry.

Introduction

Dimetallic macrocyclic complexes represent a helpful tool in the study of metal-metal interactions. In order to obtain binuclear macrocyclic complexes, three main synthetic strategies have been followed: (i) synthesis of large macrocycles or macrobicycles able to incorporate two metal ions,[2] (ii) synthesis of bis(macrocycles)[3,4] and (iii) use of chelating agents bridging two macrocyclic units.[5-7] Each metal center can interact with the other one, directly, by electrostatic forces or chemical bonding, and indirectly, via electronic delocalization through the macrocyclic framework or bridging ligands. This can lead, on account of the structure of the binuclear complex, to unusual chemical and physicochemical properties related to its magnetic, electrochemical, and thermodynamic behavior. In this paper we report the synthesis of the complex $[Ni_2(cyclam)_2ox](NO_3)_2$ (**1**) (cyclam = 1,4,7,11-tetraazacyclotetradecane and ox^2 = oxalate anion), in which the oxalate anion acts as a bridging bisbidentate ligand and the macrocycle adopts a folded conformation as shown by single-crystal X-ray analysis. It is well-known that the bisbidentate oxalate ligand is particularly able to propagate electronic effects when the *xy*-type exchange pathway is operative.[8]





The large antiferromagnetic coupling often observed in oxalato-bridged compounds is due to the strong overlap between the *xy*-type magnetic orbitals centered on each metal ion and delocalized toward the oxygen atoms of the oxalato bridge.[9] Such a situation is found in copper(II)[10] and nickel(II)[7] binuclear species. However, as far as we know, it is the first time that the ability of the oxalate ligand to couple two nickel(II) ions is discussed in terms of a full structural determination.[11] The stability constants related to the formation equilibria

$$[Ni(cyclam)]^{2+} + ox^{2-} \rightleftharpoons [Ni(cyclam)ox] \quad (1)$$

$$[Ni(cyclam)ox] + [Ni(cyclam)]^{2+} \rightleftharpoons [Ni_2(cyclam)_2ox]^{2+} \quad (2)$$

have been determined in aqueous solution by spectrophotometric measurements. The electrochemical behavior of the binuclear nickel(II) complex in nonaqueous media reveals the high stability induced by the oxalato bridge of the mixed-valence complex $[Ni^{II}(cyclam)(ox)Ni^{III}(cyclam)]^{3+}$ compared with that of the univalent complex mixture $[Ni^{II}_2(cyclam)_2ox]^{2+}$ + $[Ni^{III}_2(cyclam)_2ox]^{4+}$. The free energy change involved in the comproportionation equilibrium

$$[Ni^{II}_2(cyclam)_2ox]^{2+} + [Ni^{III}_2(cyclam)_2ox]^{4+} \rightleftharpoons 2[Ni^{II}(cyclam)(ox)Ni^{III}(cyclam)]^{3+} \quad (3)$$

has been determined by voltammetric measurements.

Experimental Section

Materials. Nickel(II) nitrate hexahydrate, oxalic acid dihydrate, potassium nitrate, and lithium hydroxide monohydrate were of Merck reagent grade and were used as received. The sodium salt of *p*-toluenesulfonic acid used as supporting electrolyte in the electrochemical study was recrystallized twice from an acetone/methanol mixture and dried under vacuum. Ferrocene was purified by sublimation prior to use. *cis*-$[Ni(cyclam)(CH_3SO_3)_2]$ has been synthesized by adapting the procedure described in ref 34. Satisfactory C, H, N analysis for this compound was obtained. The solvents DMF and DMSO were purified according to literature procedures.[12]

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(11) (a) An account of an unpublished structure is given in ref 7. (b) Very recently the crystal structure of $[(L)Ni(\mu\text{-}ox)Ni(L)](ClO_4)_2$ (L = 3,7,11-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1-(17),13,15-triene) has been reported: Alcock, N. W.; Moore, P.; Omar, H. A. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *C43*(11), 2074-6.

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Table I. Crystallographic Data for $[Ni_2(cyclam)_2ox](NO_3)_2$

chem formula	$C_{22}H_{48}N_{10}Ni_2O_{10}$
a, Å	15.817 (5)
b, Å	12.845 (3)
c, Å	16.069 (3)
V, Å^3	3265 (1)
Z	8
fw	730.10
space group	*Pbca*
T, °C	20
λ, Å	0.710 73
ρ_{obsd}, g·cm^{-3}	1.51
ρ_{calcd}, g·cm^{-1}	1.485
μ, cm^{-1}	12.21
$R = \sum\|(\Delta F)\|/\sum\|F_o\|$	0.0363
$R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$	0.0415
k, g ($w = k/[\sigma^2(F_o) + gF_o^2]$)	2.00, 6.78 × 10^{-4}

Table II. Final Atomic Fractional Coordinates with Esd's in Parentheses for $[Ni_2(cyclam)_2ox](NO_3)_2$

atom	x/a	y/b	z/c
Ni	0.06734 (4)	0.15198 (5)	0.09501 (4)
O(1)	0.0691 (3)	−0.0087 (3)	0.0846 (3)
O(2)	−0.0115 (3)	0.1350 (3)	−0.0069 (3)
O(3)	0.1497 (4)	0.0343 (4)	−0.1360 (3)
O(4)	0.1864 (4)	0.1792 (4)	−0.1867 (4)
O(5)	0.1110 (4)	0.0716 (4)	−0.2598 (3)
N(1)	0.0572 (3)	0.3146 (4)	0.0854 (4)
N(2)	0.1735 (3)	0.1724 (4)	0.0185 (4)
N(3)	0.1426 (3)	0.1406 (4)	0.2013 (3)
N(4)	−0.0326 (3)	0.1469 (4)	0.1806 (3)
N(5)	0.1494 (3)	0.0961 (4)	−0.1952 (4)
C(1)	0.1087 (5)	0.3422 (5)	0.0121 (1)
C(2)	0.1906 (5)	0.2852 (6)	0.0146 (6)
C(3)	0.2483 (5)	0.1094 (7)	0.0387 (5)
C(4)	0.2774 (5)	0.1191 (8)	0.1267 (6)
C(5)	0.2185 (5)	0.0770 (6)	0.1927 (5)
C(6)	0.0854 (5)	0.0994 (5)	0.2666 (4)
C(7)	0.0034 (5)	0.1592 (6)	0.2637 (5)
C(8)	−0.1052 (5)	0.2170 (6)	0.1644 (6)
C(9)	−0.0814 (5)	0.3292 (5)	0.1551 (6)
C(10)	−0.0295 (5)	0.03548 (5)	0.0790 (5)
C(11)	0.0236 (3)	−0.0410 (4)	0.0260 (3)

Synthesis of $[Ni_2(cyclam)_2(ox)](NO_3)_2$. A 0.5-mmol amount of lithium oxalate dissolved in a minimum amount of water was added to an aqueous suspension (50 cm^{-3}) of 1 mmol of cyclam and 1 mmol of nickel(II) nitrate hexahydrate. The solution, which was initially yellow, turned wine red after heating on a plate disk for 1 h with continuous stirring. Mauve single crystals of **1** suitable for X-ray analysis were obtained by slow evaporation of the resulting solution at room temperature. Anal. Calcd for $C_{22}H_{48}N_{10}O_{10}Ni_2$: C, 36.21; H, 6.60; N, 19.19. Found: C, 36.1; H, 6.8; N, 19.2.

Determination of the Structure and Refinement. Cell parameters and other relevant details are quoted in Table I. The dimensions of the cell were determined by diffractometry and then refined by using 15 accurately centered reflections; the structure was solved by Patterson and Fourier methods and refined by full-matrix least squares with anisotropic thermal parameters; the hydrogen atoms, locaed from a ΔF map, were isotropically introduced into the last refinement cycle, leading to an R factor of 0.0363. Five reflections (Table I) were excluded from the refinement as probably affected by extinction or counting errors. The final positional parameters for non-hydrogen atoms are listed in Table II; the atomic scattering factors, corrected for anomalous dispersion, were taken from ref 13. All the calculations were performed by using a GOULD 32/77 computer with SHELX-76,[14] ORTEP,[15] and PARST[16] programs.

Table III. Stability Constants for the System $[Ni(cyclam)]^{2+}/ox^{2-}$ Spectrophotometrically Determined in Water Solution (25 °C, 0.1 mol dm^{-3} KNO_3, 0.05 mol dm^{-1} Sodium Tetraborate (pH 9.6))

reacn	log K
$[Ni(cyclam)]^{2+} + ox^{2-}$	2.8 (1)[a–c]
$[Ni(cyclam)ox] + [Ni(cyclam)]^{2+}$	1.6 (1)[c]
2*cis*-$[Ni(cyclam)(H_2O)_2]^{2+} + ox^{2-}$	7.8
2*trans*-$[Ni(cyclam)(H_2O)_2]^{2+} + ox^{2-}$	5.5
2*square*-$[Ni(cyclam)]^{2+} + ox^{2-}$	4.7

[a] Values in parentheses are standard deviations in the last significant figure. [b] A value of log K related to this reaction was reported by Billo.[33] log K = 2.6 (2) in 0.1 mol dm^{-3} $NaClO_4$ at 25 °C. [c] $[Ni(cyclam)]^{2+}$ is a mixture of planar (69%), *trans*-diaquo octahedral (29%), and *cis*-diaquo octahedral (2%) forms.

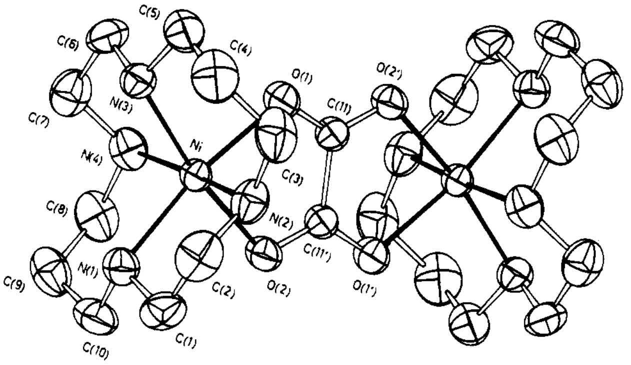

Figure 1. ORTEP drawing of the $[Ni_2(cyclam)_2ox]^{2+}$ dimeric cation.

Spectrophotometric Measurements. Infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets. The electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer equipped with 1-cm cells thermostated at 25 °C. Diffuse-reflectance spectra of **1** as Nujol mulls on filter paper were also recorded with the same apparatus. The stability constants for equilibria 1 and 2 have been determined by observing at 450 nm the formation of $[Ni(cyclam)]^{2+}$, which occurs in the reverse reactions in equilibria 1 and 2. Solutions of **1** with concentrations ranging from 10^{-3} to 10^{-2} mol dm^{-3} were prepared by dissolving the solid binuclear complex in 0.05 mol dm^{-3} tetraborate buffer (pH 9.6) containing the required quantities of KNO_3 to obtain a final 0.1 mol dm^{-3} nitrate concentration. The background solutions were previously thermostated at 25 °C. Equilibrium for (1) and (2) was reached after a few hours, as shown by monitoring the 450-nm absorbance of these complex solutions. The stability constants of these equilibria were determined, by treating the equilibrium absorbances with a new computer program derived from SUPERQUAD.[17] Their values are listed in Table III.

Electrochemical Measurements. Cyclic voltammetry was performed by using an Amel Model 552 potentiostat coupled with an Amel Model 862/A pen recorder. A classical three-electrode cell was used. The working electrode was a platinum disk, and the reference one, a saturated calomel electrode connected to the cell through a salt bridge composed of a 0.1 mol dm^{-3} KCl water solution, in contact with the calomel electrode, and a 0.1 mol dm^{-3} sodium *p*-toluenesulfonate solution in the same solvents of the sample media (DMF and DMSO), in contact with the cell solution. The salt-bridge solutions and the cell were separated by Corning fine glass frits. All solutions were deaerated with dry nitrogen for at least 15 min prior to obtaining the voltammograms. The potentials reported are referred to the saturated calomel electrode, and no correction for the *iR* potential drop due to the solution resistance and/or liquid-junction potential has been used. The ferrocenium/ferrocene (Fc^+/Fc) couple was used as internal reference; this displays a one-electron reversible wave centered at 0.415 and 0.405 V in DMF and DMSO, respectively.

Magnetic Measurements. Magnetic susceptibility measurements were carried out on polycrystalline samples in the 5.2–288.5 K temperature

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Table IV. Bond Distances (Å) and Angles (deg) for $[Ni_2(cyclam)_2ox](NO_3)_2$[a]

Ni–O(1)	2.071 (4)	N(3)–C(6)	1.438 (9)
Ni–O(2)	2.069 (4)	C(6)–C(7)	1.508 (11)
Ni–N(1)	2.101 (5)	C(7)–N(4)	1.460 (9)
Ni–N(2)	2.097 (5)	N(4)–C(8)	1.482 (9)
Ni–N(3)	2.087 (5)	C(8)–C(9)	1.497 (10)
Ni–N(4)	2.096 (5)	C(9)–C(10)	1.510 (12)
N(1)–C(1)	1.475 (9)	C(10)–N(1)	1.469 (9)
C(1)–C(2)	1.489 (11)	C(11)–O(1)	1.257 (7)
C(2)–N(2)	1.476 (9)	C(11)–O(2^{i})	1.260 (6)
N(2)–C(3)	1.470 (10)	C(11)–C(11^{i})	1.536 (7)
C(3)–C(4)	1.492 (13)	N(5)–O(3)	1.240 (7)
C(4)–C(5)	1.512 (12)	N(5)–O(4)	1.224 (8)
C(5)–N(3)	1.460 (9)	N(5)–O(5)	1.243 (8)
N(1)–Ni–N(2)	83.9 (2)	N(3)–Ni–O(1)	89.4 (2)
N(1)–Ni–N(3)	100.0 (2)	N(4)–Ni–O(1)	91.8 (2)
N(1)–Ni–N(4)	91.2 (2)	N(4)–Ni–O(2)	93.5 (2)
N(1)–Ni–O(2)	90.1 (2)	O(1)–Ni–O(2)	80.7 (2)
N(2)–Ni–N(3)	91.8 (2)	N(1)–Ni–O(1)	170.5 (5)
N(2)–Ni–O(1)	93.8 (2)	N(2)–Ni–N(4)	172.8 (2)
N(2)–Ni–O(2)	91.8 (2)	N(3)–Ni–O(2)	169.7 (2)
N(3)–Ni–N(4)	83.7 (2)		
Ni–O(1)–C(11)	112.4 (3)	N(2)–C(3)–C(4)	114.2 (7)
Ni–O(2)–C(11^{i})	112.6 (4)	C(3)–C(4)–C(5)	116.4 (7)
Ni–N(1)–C(10)	115.2 (4)	C(4)–C(5)–N(3)	111.9 (7)
Ni–N(1)–C(1)	104.8 (4)	C(5)–N(3)–C(6)	111.6 (5)
Ni–N(2)–C(2)	107.2 (4)	N(3)–C(6)–C(7)	108.7 (6)
Ni–N(2)–C(3)	116.5 (5)	C(6)–C(7)–N(4)	108.0 (6)
Ni–N(3)–C(5)	115.5 (4)	C(7)–N(4)–C(8)	113.4 (6)
Ni–N(3)–C(6)	104.9 (4)	N(4)–C(8)–C(9)	114.1 (6)
Ni–N(4)–C(7)	107.6 (4)	C(8)–C(9)–C(10)	115.3 (6)
Ni–N(4)–C(8)	116.7 (5)	C(9)–C(10)–N(1)	112.0 (6)
C(10)–N(1)–C(1)	112.0 (5)	O(1)–C(11)–O(2^{i})	125.8 (5)
N(1)–C(1)–C(2)	110.0 (6)	O(1)–C(11)–C(11^{i})	117.3 (5)
C(1)–C(2)–N(2)	108.9 (6)	O(2)–C(11^{i})–C(11)	116.8 (5)
C(2)–N(2)–C(3)	113.7 (5)		

[a] $i = \bar{x}, \bar{y}, \bar{z}$.

range by means of a pendulum-type apparatus[18] equipped with a helium cryostat. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Corrections for the diamagnetism of complex **1** were estimated from Pascal constants as -382×10^{-6} cm^3 mol^{-1}.

Results and Discussion

Description of the Structure and Discussion. The structure consists of NO_3^- ions and *cis*-$[Ni_2(cyclam)_2ox]^{2+}$ dimeric cations having a symmetry center at the middle point of the C(11)–C(11^{i}) (i = *x*, *y*, *z*) bond of the bridging oxalate ion. The cyclam ligand is arranged in a manner similar to that found in *cis*-$[Ni(cyclam)(OH_2)_2]^{2+}$,[19] showing the *RRRR* set of nitrogen configurations (Figure 1). The oxalate ion joins two adjacent coordination polyhedra with its oxygen atoms occupying in both polyhedra two cis positions. The shortest Ni···Ni separation is 5.395 (2) Å. The coordination around the nickel(II) ion is distorted octahedral. The four Ni–N bonds (Table IV) are within a narrow range (2.087 (5)–2.101 (5) Å) and are comparable with the values found in *cis*-$[Ni(cyclam)(OH_2)_2]^{2+}$ (2.092 (2)–2.109 (2) Å), while the two Ni–O bond lengths, 2.069 (4) and 2.071 (4) Å, are shorter than the $Ni-OH_2$ bond lengths, 2.130 (1) and 2.140 (2) Å. The distortion of the octahedron is mostly evident from the angles around nickel: the N–Ni–N angles of the five-membered chelate rings, 83.9 (2) and 83.7 (2)°, are smaller than those of the six-membered 91.2 (2) and 91.8 (2)° ones. The largest value of 100.0 (2)° found for the N(1)–Ni–N(3) angle can be connected with the repulsive interactions between the H(1) and H(13) atoms (H(1)···H(13) = 2.64 (9) Å) and with their involvement in hydrogen bonds (Table V). A similar value of 99.4 (1)° was also found in the *cis*-diaquo complex. The O(1)–Ni–O(2) 80.7 (2)° angle is very different from the $H_2O-Ni-OH_2$ 87.2 (1)° one in the above quoted complex but is similar (78.9 (2)°) to that found in $[(L)Ni(\mu\text{-}ox)Ni(L)](ClO_4)_2$ (L = 3,7,11-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene).[11b] This difference could be explained by considering the short bite distance of the oxalate ion: O(1)···O(2) = 2.682 (6) Å. The N–C and C–C bond distances compare favorably with the values in other cyclam-like systems.[19,20] In particular the C–C bonds are shorter than the 1.54-Å classical value. The bond angles in the six-membered rings are systematically greater than those in the five-membered ones. This behavior is probably related to the different strain of these rings: a similar situation is shown in the above quoted complexes. The two six-membered chelate rings show the chair conformation, while the five-membered rings show the envelope one.[21] Bond lengths and angles in the oxalate ion are in the range expected and are very similar to those found in several oxalates.[9,22] The ion is exactly planar, and the nickel(II) ion is 0.027 (8) Å out of this plane. The nitrate ion contributes to the packing by forming hydrogen bonds involving all its oxygen atoms.

Table V. Hydrogen-Bonding System (Å, deg)[a]

N(2)–H(6)	N(2)···O(3)	H(6)···O(3)	N(2)–H(6)···O(3)
0.87 (6)	3.074 (7)	2.24 (6)	159 (5)
N(1)–H(1)	N(1)···(5^{i})	H(1)···O(5^{i})	N(1)–H(1)···O(5^{i})
0.85 (7)	3.007 (8)	2.20 (7)	160 (6)
N(3)–H(13)	N(3)···(4^{i})	H(13)···O(4^{i})	N(3)–H(13)···O(4^{i})
1.00 (6)	3.013 (8)	2.10 (6)	151 (5)
N(4)–H(18)	N(4)···O(3^{ii})	H(18)···O(3^{ii})	N(4)–H(18)···O(3^{ii})
0.96 (6)	3.060 (7)	2.17 (6)	154 (5)

[a] $i = x, {}^1/_2 - y, {}^1/_2 + z$; $ii = \bar{x}, \bar{y}, \bar{z}$.

Electronic and IR Spectra. The reflectance spectrum of **1** is typical of an octahedral nickel(II) complex,[23] exhibiting three maxima at 11 500, 18 500, and 29 400 cm^{-1} (Δ_0 = 11 500 cm^{-1}; nephelauxetic ratio β = 0.831). It also exhibits a shoulder at 12 650 cm^{-1}, which could be attributed to the spin-forbidden $A_{2g}-E_g$ transition in O_h symmetry. The ν_1 band[6,24] in the near-infrared region is diagnostic of cis coordination; that is, the tetraamine is folded in order to accommodate the oxalate ligand as shown in Figure 1.

The infrared spectrum of **1** displays the characteristic bands (cm^{-1}) of the oxalate bridging ligand:[5,25] ν_{as}(O–C–O) at 1650 vs; ν_s(O–C–O) at 1315 w, and δ(O–C–O) at 795 m, where vs, m, and w refer to very strong, medium, and weak intensities, respectively. The IR spectrum of the N–H stretching region consists of a single absorption of medium intensity that is slightly split into three peaks at 3180, 3200, and 3225 cm^{-1}. However, $Ni(cyclam)(X)_2$ complexes with a planar arrangement of the macrocycle allowing a trans disposition of X groups (X = Cl^-, ClO_4^-)[26] exhibit a well-resolved doublet (3220 m and 3260 m cm^{-1}) in this region. These features suggest that N–H stretching peaks could serve as diagnostic of cis or trans coordination. Bands of ionic nitrate[27] are located at 2430 w, 1390 s, and 830 w cm^{-1}.

Magnetic Properties. The molar magnetic susceptibility, χ_M, plotted versus temperature for complex **1** is shown in Figure 2.

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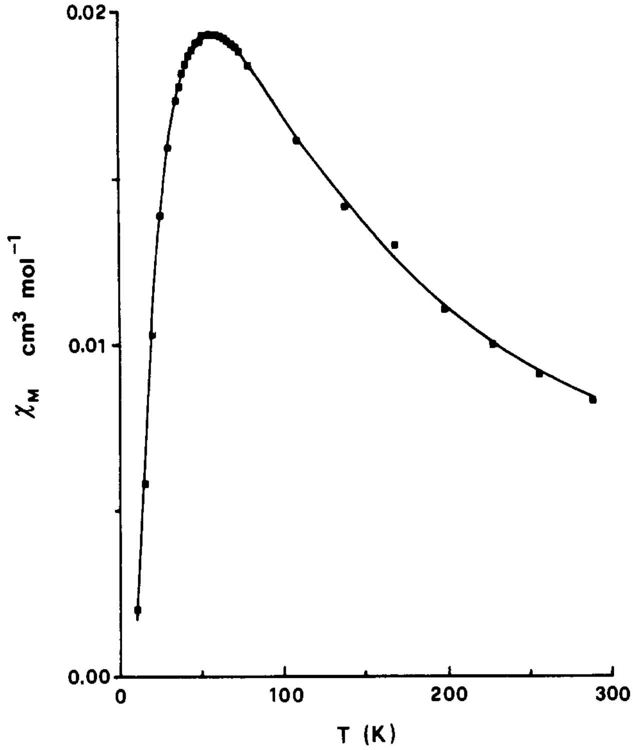


Figure 2. Molar paramagnetic susceptibility vs temperature curve for $[Ni_2(cyclam)_2ox](NO_3)_2$. Experimental points are represented by squares, whereas the solid line is the theoretical line obtained by least-squares fitting of all experimental points.

At room temperature, χ_M has the value expected for two $S = 1$ states. Upon sample cooling, χ_M first increases, reaching a maximum at 56.2 K, and then decreases markedly. This behavior is characteristic of an intramolecular antiferromagnetic interaction between the two single-ion triplet states, with a very small proportion ρ of noncoupled nickel(II) impurity. Representing the intramolecular magnetic interaction of **1** with the isotropic spin Hamiltonian $\hat{H} = -J\hat{S}_A\hat{S}_B$, where J is the cleavage integral and $S_A = S_B = 1$ (local spins), χ_M may be expressed as

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

In this expression N, β, k, and g have their usual meanings. The second term accounts for the noncoupled impurity, and the last term, $N\alpha$, is the temperature-independent paramagnetism, which is assumed to be -200×10^{-6} cm³ mol⁻¹ for two nickel(II) ions.

Although Ginsberg et al.[28] have also considered the effects of single-ion zero-field interactions on the magnetic susceptibility of Ni(II) binuclear complexes, Hendrickson et al.[7] 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. Owing to the large stabilization of the singlet ground state, the effect of the zero-field splitting on the magnetic behavior is expected to be negligible.

Least-squares fitting of all experimental data points leads to $J = -39$ cm⁻¹, $g = 2.33$, and $\rho = 0.01$, with an agreement factor $R = \sum(\chi_{exptl}(i) - \chi_{calcd}(i))^2/\sum(\chi_{exptl}(i))^2$ of 1.12×10^{-4}.

The X-band polycrystalline powder EPR spectrum of **1** does not exhibit any signal due to the large zero-field splitting of the nickel(II) ions.

Previously reported J values for μ-oxalato nickel(II) binuclear complexes such as $[Ni_2(trien)_2ox](ClO_4)_2$,[7] $[Ni_2(macro)_2ox](ClO_4)_2$,[7] $[Ni_2(en)_4ox](NO_3)_2$,[29] and $[Ni_2(dien)_2ox](NO_3)_2$[29] are very close to that for **1**.

When comparing J values for μ-oxalato copper(II) and μ-oxalato nickel(II) binuclear species, we must take into account the number of unpaired electrons on each magnetic center (1 for copper(II) and 2 for nickel(II)) and compare the $n^2|J|$ values.[30] We have

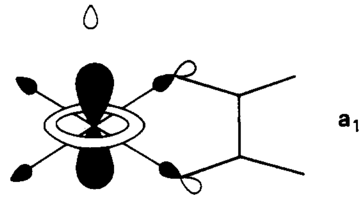
$$\begin{array}{ccc} J_{|Cu-Cu|} & > & 4J_{|Ni-Ni|} \\ 385.4\ \text{cm}^{-1} & & 156\ \text{cm}^{-1} \end{array}$$

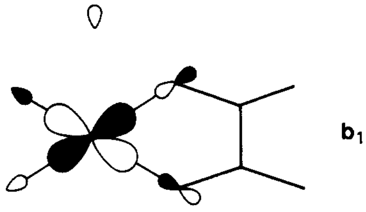
These values[31] show the special efficiency of copper(II) compared to that of nickel(II) to yield antiferromagnetic interactions: the M(II) – O(oxalato bridge) distance for copper(II) is shorter than the one observed for nickel(II) (1.98 and 2.07 Å, respectively), and the energies of the $d_{Cu(II)}$ orbitals are lower than those of nickel(II). The combination of these facts produces a larger spin-density delocalization on the bridge and consequently a larger J value for the d_{xy} exchange pathway. Moreover, the ferromagnetic contributions in a μ-oxalato copper(II) binuclear unit can be neglected, whereas they must be taken into account for the analogous nickel(II) binuclear unit. In order to evaluate them, J_{Cu-Cu} and J_{Ni-Ni} may be expressed as

$$J_{Cu-Cu} = J_{b_1b_1} = -385.4\ \text{cm}^{-1}$$

$$J_{Ni-Ni} = \tfrac{1}{4}(J_{b_1b_1} + J_{a_1a_1} + 2J_{a_1b_1}) = -39\ \text{cm}^{-1}$$

where a_1 and b_1 are the d_{z^2} and d_{xy} magnetic orbitals schematized as follows:





The supplementary equation $J_{Cu-Ni} = {}^1/_2(J_{b_1b_1} + J_{a_1b_1}) = -52.7$ cm⁻¹, where J_{Cu-Ni} corresponds to the exchange coupling between copper(II) and nickel(II) in the chain $CuNi(ox)_2{\cdot}4H_2O$,[32] enables us to estimate the set of parameters $J_{b_1b_1} = -385.4$ cm⁻¹, $J_{a_1a_1} = -330.6$ cm⁻¹, and $J_{a_1b_1} = 280$ cm⁻¹. Correct signs and good relative energies are obtained for them, but we are far from reality because, for instance, $J_{b_1b_1}$ is not invariant in this series of complexes. Furthermore, the $J_{a_1a_1}$ value seems too large when compared to the $J_{b_1b_1}$ value, considering the different nature of the a_1 and b_1 magnetic orbitals.

The knowledge of J_{CuNi} for a (μ-oxalato)copper(II)nickel(II) heterobinuclear complex with a diamine as terminal ligand on the copper(II) could improve the $J_{a_1a_1}$ and $J_{a_1b_1}$ values, but such a complex, as far as we know, has not yet been isolated.

Thermodynamic Study. The stability constants related to equilibria 1 and 2 have been determined spectrophotometrically by measuring the concentration of $[Ni(cyclam)]^{2+}$ produced in the consecutive dissociations of $[Ni_2(cyclam)_2ox]^{2+}$ and [Ni(cyclam)ox] in aqueous solutions of $[Ni_2(cyclam)_2ox)](NO_3)_2$ containing 0.1 mol dm⁻³ NO_3^- total concentration and buffered at

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pH 9.6 by 0.05 mol dm^{-3} sodium tetraborate.

The [Ni(cyclam)]$^{2+}$ cation exists in water solution as an equilibrium mixture of paramagnetic octahedral diaquo blue forms and a diamagnetic square yellow one.[33,34] The equilibrium composition of the mixture depends on the temperature and on the ionic strength of the solution, in the sense that increasing temperature and concentration of inert electrolyte promote the formation of the yellow species. Under our experimental conditions the molar absorptivity at 450 nm of the yellow form is 50 mol^{-1} dm^3 cm^{-1}, which corresponds to 69% square and 31% octahedral forms (29% *trans-* and 2% *cis*-diaquo).[34] Recently, it has been shown that [Ni(cyclam)]$^{2+}$ reacts with chelating ligands L such as ethylenediamine, glycinate, and oxalate to produce the [Ni(cyclam)L]$^{n+}$ mixed complexes (n = 0, 1, and 2 for L = ox^{2-}, gly$^-$, and en, respectively) in which the ligand adopts a folded configuration.[34] Releasing L, [Ni(cyclam)L]$^{n+}$ produces in solution the *cis*[Ni(cyclam)(H$_2$O)$_2$]$^{2+}$ species, which undergoes a folded-to-planar isomerization. The rate of isomerization has been determined over the pH range 1–10.[35] The reaction is acid- and base-catalyzed and reaches a rate minimum at pH 3, where the half-life is approximately 250 days; at pH 10 the process is rapid with a half-life of approximately 7 s.

As a consequence of the isolation of the binuclear compound [Ni$_2$(cyclam)$_2$ox](NO$_3$)$_2$, we have further investigated the possible formation of binuclear species in water solution. In a first attempt we tried to determine the stability constants related to equilibria 1 and 2 by observing at 450 nm the disappearance of planar [Ni(cyclam)]$^{2+}$, which takes place in the formation reactions. The forward reaction in equilibrium 2 was very slow, since the equilibrium absorbance of solutions in which the concentration ratio [[Ni(cyclam)]$^{2+}$]/[ox^{2-}] was close to or greater than 1 could not be reached over a period of many days. On the contrary, the equilibrium can be reached in few hours following the reverse reactions and therefore the stability constants determined (see Experimental Section and Table III). All our measurements were carried out at pH 9.6 (0.05 mol dm^{-3} sodium tetraborate buffer) in order to avoid protonation of oxalate anion and the sluggish folded-to-planar isomerization of released *cis*-[Ni(cyclam)(H$_2$O)$_2$]$^{2+}$.

The stability constant for equilibrium 1 had already been determined by Billo.[34] Although the salt he used as inert electrolyte was different (0.1 mol dm^{-3} NaClO$_4$) from ours, the value of the constant remains the same within experimental error. As expected, the stepwise stability constant for the formation of the binuclear species (see Table III) is smaller than that determined for equilibrium 1. Thus, under the equilibrium condition used by Billo[34] the amount of binuclear species was almost negligible.

Electrochemical Study. The oxidation properties of the [Ni$_2$(cyclam)$_2$ox]$^{2+}$ dimer have been studied by cyclic voltammetry in anhydrous DMF and DMSO solvents containing 0.1 mol dm^{-3} sodium *p*-toluenesulfonate as supporting electrolyte. All solutions were 5 × 10^{-4} mol dm^{-3} in the complex. Substantially, the cyclic voltammograms of [Ni$_2$(cyclam)$_2$ox]$^{2+}$ present the same shape in both solvents. In Figure 3a we have reported the voltammogram obtained in DMF over the potential range 0.0–1.1 V at a scan rate of 100 mV s^{-1}. The figure shows two consecutive oxidation peaks followed in the reverse scan by the corresponding reduction peaks that we ascribed to the two monoelectronic reversible reactions

$$[\mathrm{Ni^{II}(cyclam)(ox)Ni^{III}(cyclam)}]^{3+} + e^- \rightleftharpoons [\mathrm{Ni^{II}_2(cyclam)_2ox}]^{2+} \quad (4)$$

$$[\mathrm{Ni^{III}_2(cyclam)_2ox}]^{4+} + e^- \rightleftharpoons [\mathrm{Ni^{II}(cyclam)(ox)Ni^{III}(cyclam)}]^{3+} \quad (5)$$

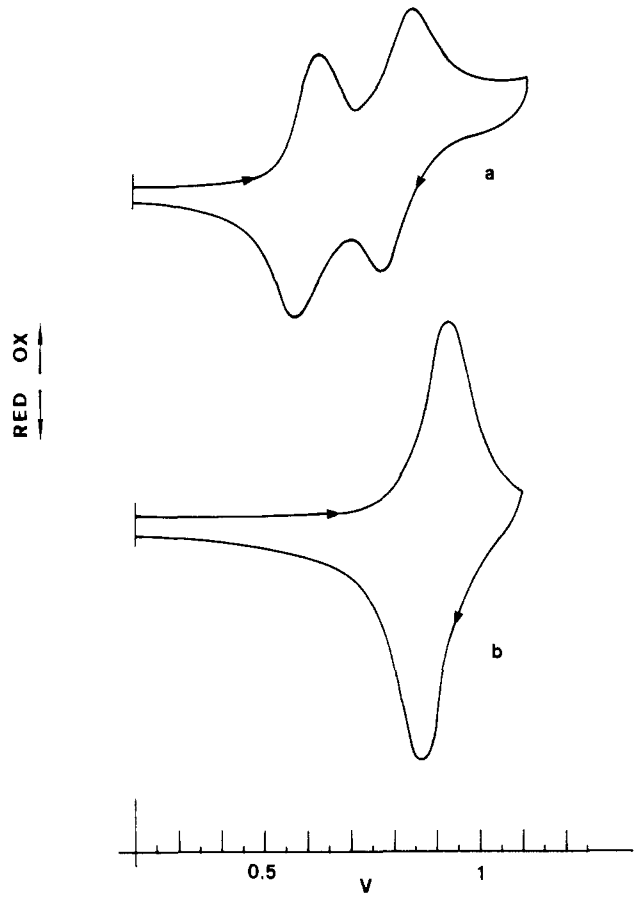

Figure 3. Cyclic voltammetric waves obtained for (a) [Ni$_2$(cyclam)$_2$ox](NO$_3$)$_2$ (5 × 10^{-4} mol dm^{-3} in DMF solution containing 0.1 mol dm^{-3} sodium *p*-toluenesulfonate) and (b) the sample in (a) after removal of the bridging oxalate ligand.

Table VI. Electrochemical Parameters for the Stepwise Oxidation of [Ni$_2$(cyclam)$_2$ox](NO$_3$)$_2$ in DMF and DMSO Solutions (0.1 mol dm^{-3} Sodium *p*-Toluenesulfonate at 25 °C; Potentials Reported in Volts versus SCE)

solvent	D^a	$E_{1/2}(1)^b$	$E_{1/2}(2)^c$	$\Delta E_{1/2}{}^d$	$E_{1/2}(\mathrm{M})^e$
DMF	36.7	0.560	0.770	0.210	0.840
DMSO	46.6	0.605	0.775	0.170	0.805

^{a} Dielectric constants at 25 °C. ^{b} Half-wave potentials associated with the redox process (4). ^{c} Half-wave potentials associated with the redox process (5). ^{d} $E_{1/2}(2) - E_{1/2}(1)$. ^{e} Half-wave potentials associated with the redox process involving the monomeric species produced by acidification of the [(Ni(cyclam)$_2$ox]$^{2+}$ solution.

The formation of the mixed-valence complex (Ni$^{\mathrm{II}}$–Ni$^{\mathrm{III}}$) occurs at $E_{1/2}(1)$ = 0.560 V, referred to the calomel electrode, while the oxidation of the (Ni$^{\mathrm{II}}$–Ni$^{\mathrm{III}}$) complex to produce the (Ni$^{\mathrm{III}}$–Ni$^{\mathrm{III}}$) one takes place at $E_{1/2}(2)$ = 0.770 V. The corresponding values obtained in anhydrous DMSO are 0.605 and 0.775 V (see Table VI). The binuclear complex dissociates by protonation of the oxalate bridge into monomeric units in which the macrocyclic ligand still maintains a folded configuration and the oxalate ligand has been replaced by solvent molecules. The visible spectrum of the new species is similar to that obtained for *cis*-[Ni(cyclam)(CH$_3$SO$_3$)$_2$] in DMF and DMSO, respectively. Also the electrochemical behavior of these new species is equal to that of *cis*-[Ni(cyclam)(CH$_3$SO$_3$)$_2$] in the same solvents. Figure 3b reproduces the voltammetric wave obtained after addition of an excess of methanesulfonic acid to the solution of the binuclear complex in DMF. The $E_{1/2}$(M) potentials of the mononuclear species are reported in Table VI. On the basis of these results, we can conclude that both the univalent (Ni$^{\mathrm{II}}$–Ni$^{\mathrm{II}}$) and (Ni$^{\mathrm{III}}$–Ni$^{\mathrm{III}}$) and the mixed-valence complexes do not dissociate appreciably in DMF and DMSO anhydrous solutions on the time scale of the voltammetric measurements. As expected on the basis of simple electrostatic interactions, the $E_{1/2}(1)$ value related to the oxidation state of the first metal center takes place at lower

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Table VII. Thermodynamic parameters for the Comproportionation Equilibrium in DMF and DMSO (0.1 mol dm^{-3} Sodium *p*-Toluenesulfonate at 25 °C)[a]

	K_c	$-\Delta G°_c$	$-\Delta G_{stat}$	$(-\Delta G_e) + (-\Delta G_r) + (-\Delta G_s)$
DMF	3.5×10^3	4.84	0.82	4.02
DMSO	7.5×10^2	3.92	0.82	3.10

[a] All ΔG values are reported in kcal mol^{-1}.

potential (Table VI) as the dielectric constant of the solvent decreases. The difference between $E_{1/2}(1)$ and $E_{1/2}(2)$ ($\Delta E_{1/2}$ in Table VI) cannot be easily predicted, depending on the stability of the mixed-valence complex $[\mathrm{Ni^{II}(cyclam)(ox)Ni^{III}(cyclam)}]^{3+}$ compared to that of the univalent metal complex mixture, to which some contributions can be ascribed.[36] The same contributions determine the free energy change $\Delta G°_c$ associated with the comproportionation equilibrium (3).

Comproportionation Equilibria. The stability constant associated with equilibrium 3 can be determined from the equation[37]

$$K_c = \exp((E°_2 - E°_1)F/RT) \qquad (6)$$

where $E°_1$ and $E°_2$ are the standard potentials related to the first and second oxidation steps of complex **1**. When these processes are reversible in nature, the $\Delta E_{1/2}$ value can accurately substitute the $E°_2 - E°_1$ difference and eq 6 becomes $K_c = \exp(\Delta E_{1/2}/25.69)$ at 298 K with $\Delta E_{1/2}$ given in millivolts. The free energy change $\Delta G°_c$ can be obtained from $\Delta G°_c = -RT \ln K_c$.

Four contributions have been identified in determining the magnitude of $\Delta G°_c$: (i) a statistic factor ($\Delta G_{stat} = -RT \ln 4$; 0.82 kcal mol^{-1} at 298 K) arising from the greater probability (by a factor of 4) of formation of the mixed-valence complex compared to that of the univalent mixture; (ii) an electrostatic factor (ΔG_e) due to the Coulombic interaction between the two metal centers; (iii) a contribution due to the electronic delocalization of the valence in the mixed-valence species (ΔG_r); (iv) a synergistic factor (ΔG_s) arising from the mutual stabilization between the bivalent and trivalent metal centers. In Table VII are reported the thermodynamic parameters for the comproportionation equilibrium (3) in DMF and DMSO. The values of the stability constant herein reported show that the mixed-valence species are very stable with respect to the rearrangement of the valence and that the stability decreases with the increase of the dielectric constant of the solvent. The decrease of the electrostatic interaction between the two metal centers, due to the increasing dielectric constant, lowers the value of ΔG_e; thus, K_c is greater in DMF than in DMSO.

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Registry No. **1**, 116633-72-8; $[\mathrm{Ni_2(cyclam)_2ox}]^{3+}$, 116633-73-9; $[\mathrm{Ni_2(cyclam)_2ox}]^{4+}$, 116633-74-0.

Supplementary Material Available: Listings of crystallographic data (Table S1), thermal parameters (Table S2), and hydrogen coordinates (Table S3) (3 pages); a listing of observed and calculated structure factors (Table S4) (12 pages). Ordering information is given on any current masthead page. A listing of experimental magnetic data is available from the authors on request.

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Structure of Tris(μ-3,5-diphenylpyrazolato-*N,N'*)tricopper(I). Structural Comparisons with the Silver(I) and Gold(I) Pyrazolate Trimers[†]

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Tris(μ-3,5-diphenylpyrazolato-*N,N'*)tricopper(I) was synthesized from CuCl and sodium 3,5-diphenylpyrazolate in the presence of 1 molar equiv of $AgNO_3$ and was characterized by single crystal X-ray analysis: triclinic, $P\bar{1}$ (No. 2), a = 13.036 (2) Å, b = 14.610 (2) Å, c = 11.674 (2) Å, α = 101.53 (1)°, β = 107.23 (1)°, γ = 100.07 (1)°, V = 2014.5 (6) Å^3, Z = 2. It consists of a nonplanar metallacycle containing a nine-membered Cu_3N_6 ring with long Cu–N bonds averaging 2.081 (7) Å. The Cu···Cu nonbonding distances average 3.339 (1) Å. A comparison of this complex with its isostructural silver and gold analogues showed an unexpected trend in the metal–nitrogen bond lengths with the Au–N bonds being especially short (1.98 Å).

Introduction

We have discussed recently[1] the syntheses and X-ray structures of the trimeric metallacyclic complexes $[\mathrm{M}(\mu\text{-}3,5\text{-}\mathrm{Ph_2pz})]_3$ (M = Ag$^{\mathrm{I}}$, Au$^{\mathrm{I}}$). Here we report the crystal structure of the isostructural $[\mathrm{Cu^I}(\mu\text{-}3,5\text{-}\mathrm{Ph_2pz})]_3$ (**1**), which completes the series of $[\mathrm{ML}]_3$ complexes for M = d^{10}, group 11 metal and L = 3,5-Ph$_2$pz. These complexes may serve as models for the study of the reactivity of trimetallic surfaces. They also relate to studies concerned with the communication among metal ions in biological systems through conjugated bridging ligands.

The ease of oxidation of Cu$^{\mathrm{I}}$ compounds and the commonality of 3- and 4-coordination are well established.[2] Consequently, structural data for 2-coordinate Cu$^{\mathrm{I}}$ complexes are scarce.[3] The short metal–metal contacts found in such complexes have been the focus of contradicting theoretical studies.[4,20] Stable Cu$^{\mathrm{I}}$ complexes N-bound to unsaturated ligands are of particular interest, as they may relate to the reduced form of the "type 1" site of Cu-containing proteins,[5] which show an unusually high Cu$^{\mathrm{II}}$/Cu$^{\mathrm{I}}$

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[†] Abbreviations: pzH = pyrazole; pz = pyrazolate anion; 3,5-Ph$_2$pz = 3,5-diphenylpyrazolate anion; 3,5-Me$_2$pz = 3,5-dimethylpyrazolate anion; 5-Mepz = 5-methylpyrazolate anion; pz(8) identifies a μ-3,5-diphenylpyrazolate ring by using the crystallographic numbering scheme of the carbon at the 4-position of that ring.

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