Dinuclear nickel(II) complexes of a series of dinucleating macrocycles with similar or dissimilar coordination sites: synthesis, structure and physicochemical property

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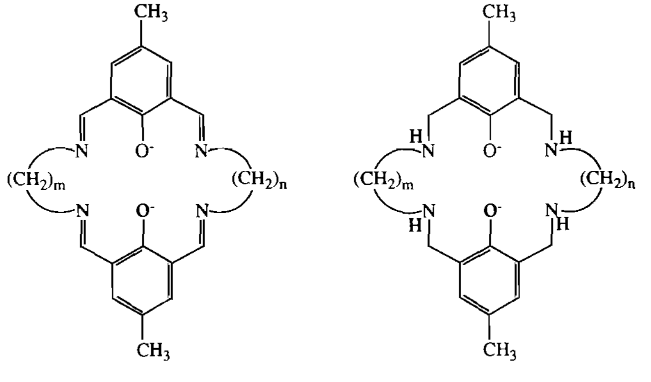
Abstract

The dinucleating macrocycles $H_2(L^{m,n})$ containing two 2,6-di(aminomethyl)-4-methylphenol entities combined through two alkane chains, $-(CH_2)_m-$ ($m=2$, 3) and $-(CH_2)_n-$ ($n=2$, 3, 4, 5), at the amine nitrogens, form nickel(II) complexes of the general formula $[Ni_2(L^{m,n})(OAc)_2]$ ($(m,n)=(2,2)$, (2,4), (2,5), (3,3)) and $[Ni_2(L^{2,3})(OAc)(NCS)(CH_3OH)]$. $[Ni_2(L^{2,2})(OAc)_2]\cdot 10H_2O$ crystallizes in the triclinic system of space group $P\bar{1}$ with $a=9.983(2)$, $b=12.832(2)$, $c=7.932(1)$ Å, $\alpha=101.29(1)$, $\beta=101.08(2)$, $\gamma=106.57(2)°$, $V=921.1(3)$ Å^3 and $Z=1$. The refinement converges with $R=5.65$ and $R_w=5.89\%$ based on 2308 reflections with $|F_o|>3\sigma(|F_o|)$. The macrocycle adopts a folded conformation and each nickel has a *cis*-β octahedral geometry with the N_2O_2 donor set of the macrocycle and two oxygens of a bidentate acetate group. The Ni–Ni separation bridged by two phenolic oxygens is 3.004 Å and the Ni–O–Ni angle is 95.6°. Cryomagnetic properties (4.2–300 K) of the complexes are well reproduced based on the spin Hamiltonian $\mathcal{H}=-2JS_1\cdot S_2-D(S_{z1}{}^2-S_{z2}{}^2)$ with a positive exchange integral ($J=+10.1$ to $+2.1$ cm^{-1}) and a negative zero-field splitting parameter ($D=-0.53$ to -2.40 cm^{-1}). Each complex shows two reduction waves and two oxidation waves attributable to the metal centers.

Introduction

Dinucleating macrocycles of type I (Scheme 1) have been obtained for various (m,n) sets of the lateral chains and extensively used for studies on homo- and heterodinuclear complexes and mixed-valence complexes [1–8], but analogous macrocycles fully saturated at azomethine linkages (type II) have received much less attention. A type II macrocycle with $m=n=3$ was first synthesized by Mandal *et al.* and used for studies on dinuclear copper(II) complexes [9, 10]. The synthesis of type II macrocycles with a fairly wide range of (m,n) sets of the lateral chains was performed recently in our laboratory by the reduction of type I macrocycles obtained as Cu_2Pb complexes [11]. In the previous study we reported the synthesis and property of dinuclear Cu_2(II,II) and Cu_2(I,II) complexes of type II macrocycles with (m,n)=(2,3), (2,4), (2,5), (3,3) and (3,4) [11]. Based on studies using unsaturated (type I) [1–8], half-saturated [12–14] and saturated (type II) macrocycles [9–11, 15–17], it is suggested that the saturation of the azomethine linkages has a significant effect upon the stereochemistry and physicochemical properties of dinuclear copper complexes. Very recently Nag and coworkers studied a dinuclear nickel(II) complex of a type II macrocycle with $m=n=3$ [15–17]. However, nickel complexes of type II macrocycles with other (m,n) sets have not been studied.



I II

Scheme 1.

In this study we have prepared dinuclear nickel(II) complexes of type II macrocyles of a fairly wide range

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of (*m*,*n*) sets of the lateral chains, hoping to examine the effects of the saturation of the azomethine linkages and the ring size of the macrocycles upon the stereochemistry and physicochemical properties of dinuclear nickel(II) complexes. For this purpose a new macrocycle with $(m,n)=(2,2)$ was first prepared in this study. Type I and type II macrocycles are abbreviated as $H_2(R^{m,n})$ and $H_2(L^{m,n})$, respectively, hereafter. Two types of dinuclear nickel(II) complexes, $[Ni_2(L^{m,n})(OAc)_2](solv)_x$ ($L^{m,n}=L^{2,2}, L^{2,4}, L^{2,5}, L^{3,3}$; OAc = CH_3COO^-; solv = H_2O or CH_3OH) and $[Ni_2(L^{2,3})(OAc)(NCS)(CH_3OH)]$, were obtained and their magnetic, spectral and electrochemical properties are reported together with the single crystal X-ray structure analysis of $[Ni_2(L^{2,2})(OAc)_2]\cdot 10H_2O$.

Experimental

Physical measurements

Elemental analyses of carbon, hydrogen and nitrogen were obtained from the Element Analysis Service Center at Kyushu University. Analyses of Ni were made on a Shimadzu AA-660 atomic absorption/flame emission spectrophotometer. IR spectra were recorded on a JASCO IR-810 spectrometer on KBr disks or Nujol mulls. Electronic spectra were recorded on a Shimadzu MPS-2000 spectrometer. 400 MHz ^1H NMR spectra were measured with a JEOL JNM-GX 400 spectrometer in $CDCl_3$, using tetramethylsilane as the internal standard. Mass spectra were recorded on a Hitachi M-60 mass spectrometer. Magnetic susceptibilities of powder samples were measured using a HOXAN HSM-D SQUID susceptometer in the temperature range 4.2–100 K and a Faraday balance in the temperature range 80–300 K. Calibrations were made with $Mn(NH_4)_2(SO_4)_2\cdot 6H_2O$ for the SQUID susceptometer and with $[Ni(en)_3]S_2O_3$ for the Faraday balance [18]. Diamagnetic corrections were made with Pascal's constants [19]. Effective magnetic moments were calculated by the equation $\mu_{eff}=2.828[(\chi_A-N\alpha)\times T]^{1/2}$, where χ_A is the molar magnetic susceptibility per Ni corrected for diamagnetism of the constituting atoms and $N\alpha$ is the temperature-independent paramagnetism. Cyclic voltammograms (CV) were recorded on an apparatus comprising an HA-501 potentiostat/galvanostat, an HB-104 function generator and an HF-201 coulomb/amperehour meter of Hokuto Denko Ltd. A three-electrode cell was used for CV measurements in which the working electrode was either a glassy carbon or a platinum electrode, the counter electrode was a platinum coil, and the reference electrode was a saturated calomel electrode. Tetrabutylammonium perchlorate was used as the supporting electrolyte. Controlled-potential electrolyses were performed on the same instrument using a platinum net as the working electrode.

Materials

Tetrabutylammonium perchlorate used as the supporting electrolyte in electrochemical measurements was purchased from Nakarai Chem. Co. and recrystallized twice from a mixture of ethyl acetate and hexane. Dimethyl sulfoxide and dichloromethane for electrochemical measurements were dried by distillation from CaH_2 and stored over molecular sieves. All other chemicals and solvents were of reagent grade and were used as received. The macrocycles $H_2(L^{m,n})$ ($(m,n)=(2,3)$, (2,4), (2,5), (3,3)) were prepared as reported previously [11].

Preparations

$H_2(L^{2,2})$

A mixture of 2,6-diformyl-4-methylphenol [20] (1.0 g, 6.1 mmol), lead(II) perchlorate trihydrate (2.8 g, 6.1 mmol) and triethylamine (0.7 g) in methanol (50 cm^3) was refluxed. A methanol solution (50 cm^3) of ethylenediamine (0.37 g, 6.1 mmol) was added dropwise, and the mixture was refluxed for 1 h and allowed to stand at room temperature to give $Pb_2(R^{2,2})(ClO_4)_2$ CH_3OH as yellow microcrystals. They were separated, washed successively with methanol and ether, and dried *in vacuo*. The yield was 2.9 g (47%). *Anal.* Found: C, 27.46; H, 2.58; N, 5.44. Calc. for $C_{23}H_{26}N_4O_{11}Cl_2Pb_2$: C, 27.09; H, 2.57; N, 5.49%.

Finely ground $Pb_2(R^{2,2})(ClO_4)_2\cdot CH_3OH$ (5.38 g, 5.3 mmol) was suspended in methanol (200 cm^3). A portion of $NaBH_4$ (2.0 g) was added to the suspension and the mixture was stirred for 20 min at room temperature. The operation of the addition of $NaBH_4$ (2.0 g) and the stirring for 15 min at room temperature was repeated twice. The resulting colorless solution was evaporated to dryness, the residue was dissolved in water (200 cm^3), and the solution was made weakly acidic (pH 4) with dilute sulfuric acid. The resulting lead(II) sulfate was removed by filtration, and the filtrate was made alkaline with ammonia to pH 8–9 and then extracted with $CHCl_3$. The $CHCl_3$ extract was dried with anhydrous Na_2SO_4 and concentrated to *c.* 10 cm^3 under reduced pressure to give a colorless precipitate. It was separated, washed with a small amount of petroleum ether, and dried *in vacuo*. The yield was 1.67 g (82%); m.p. 191 °C. *Anal.* Found: C, 66.23; H, 7.96; N, 13.68. Calc. for $C_{22}H_{32}N_4O_4\cdot 1/8CHCl_3$: C, 66.15; H, 8.07; N, 14.03%. MS: *m*/*z* 384. ^1H NMR ($CDCl_3$): δ 2.20(s, 6H), 2.82(s, 8H), 3.81(s, 8H), 6.78(s, 4H).

$[Ni_2(L^{2,2})(OAc)_2]\cdot 10H_2O$ (1)

A solution of $H_2(L^{2,2})$ (0.39 g, 1 mmol) and nickel(II) acetate tetrahydrate (0.50 g, 2 mmol) in methanol (30 cm^3) was refluxed for 30 min. The reaction mixture was concentrated to *c.* 10 cm^3, diluted with water (10 cm^3) and allowed to stand at room temperature to give blue crystals. They were separated, washed successively with a small amount of methanol and ether, and dried *in vacuo*. The yield was 0.41 g (51%). *Anal.* Found: C, 39.32; H, 6.91; N, 7.05; Ni, 14.12. Calc. for $C_{26}H_{56}N_4Ni_2O_{16}$: C, 39.13; H, 7.07; N, 7.02; Ni, 14.70%.

[$Ni_2(L^{2,3})(OAc)(NCS)(CH_3OH)$] (2)

A solution of $H_2(L^{2,3})$ (0.40 g, 1 mmol) and nickel(II) acetate tetrahydrate (0.50 g, 2 mmol) in methanol (30 cm^3) was refluxed for 30 min. To the resulting green solution was added a methanol solution (10 cm^3) of NH_4SCN (0.08 g, 1 mmol), and the mixture was refluxed for 30 min to give green microcrystals. They were separated, washed successively with a small amount of methanol, and dried *in vacuo*. The yield was 0.05 g (16%). *Anal.* Found: C, 49.05; H, 5.83; N, 10.49; Ni, 17.61. Calc. for $C_{27}H_{39}N_5Ni_2O_5S$: C, 48.91; H, 5.93; N, 10.56; Ni, 17.70%.

[$Ni_2(L^{2,4})(OAc)_2$]·1/2H_2O (3)

This was obtained as blue crystals by the reaction of $H_2(L^{2,4})$ (0.41 g, 1 mmol) and nickel(II) acetate tetrahydrate (0.50 g, 2 mmol) in a way similar to that of **1** except that all the operations were carried out under argon by the use of a Schlenk apparatus. The yield was 0.24 g (37%). *Anal.* Found: C, 51.43; H, 6.47; N, 8.13; Ni, 18.17. Calc. for $C_{28}H_{41}N_4Ni_2O_{6\ 5}$: C, 51.34; H, 6.31; N, 8.55; Ni, 17.92%.

[$Ni_2(L^{2,5})(OAc)_2$]·H_2O (4)

This was obtained as blue crystals by the reaction of $H_2(L^{2,5})$ (0.43 g, 1 mmol) and nickel(II) acetate tetrahydrate (0.50 g, 2 mmol) in nearly the same way as that of **3**. The yield was 0.19 g (28%). *Anal.* Found: C, 51.42; H, 6.38; N, 7.77; Ni, 17.65. Calc. for $C_{29}H_{44}N_4Ni_2O_7$: C, 51.37; H, 6.54; N, 8.23; Ni, 17.31%.

[$Ni_2(L^{3,3})(OAc)_2$]·1/2CH_3OH (5)

This was obtained as blue crystals by the reaction of $H_2(L^{3,3})$ (0.41 g, 1 mmol) and nickel(II) acetate tetrahydrate (0.50 g, 2 mmol) in nearly the same way as that of **1**. The yield was 0.34 g (51%). *Anal.* Found: C, 51.51; H, 6.15; N, 8.48; Ni, 17.85. Calc. for $C_{28\ 5}H_{42}N_4Ni_2O_{6\ 5}$: C, 51.71; H, 6.39; N, 8.46; Ni, 17.73%.

X-ray structural analysis of [$Ni_2(L^{2,2})(OAc)_2$]·$10H_2O$ (1)

Single crystals of **1** were obtained when a dilute methanol solution of $Ni(OAc)_2·4H_2O$ and $H_2(L^{2,2})$ was allowed to stand for about 10 days at room temperature. A crystal with approximate dimensions 0.30×0.30×0.35 mm sealed in a glass tube was used for the X-ray diffraction study. Intensities and lattice parameters were obtained on a Rigaku AFC-5 automated four-circle diffractometer, using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) at 20 ± 1 °C. Lattice parameters and their estimated standard deviations were obtained from a least-squares fit to 25 2θ values in the range $28 < 2\theta < 33°$. Crystal data are summarized in Table 1. For the intensity data collections, the ω–2θ scan mode was used at a scan rate of 4° min^{-1}. The octant measured was $+h$, $\pm k$, $\pm l$. Three standard reflections were monitored every 100 reflections and showed no systematic decrease in the intensity. The intensity data were corrected for Lorentz and polarization factors, but not for absorption. 2308 independent reflections with $|F_o| > 3\sigma(|F_o|)$ in the range $2.5 \leqslant 2\theta \leqslant 50°$ were assumed to be observed.

TABLE 1 Crystal data for [$Ni_2(L^{2,2})(CH_3COO)_2$]·$10H_2O$

Formula	$C_{26}H_{56}N_4Ni_2O_{16}$
Color of crystal	blue
Formula weight	789.12
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.983(2)
b (Å)	12 832(2)
c (Å)	7 932(1)
α (°)	101.29(1)
β (°)	101.08(2)
γ (°)	106.57(2)
V (Å^3)	921.1(3)
Z	1
D_c (g cm^{-3})	1.439
μ(Mo Kα) (cm^{-1})	5.473
No. reflections	2308
R (%)	5 65
R_w (%)	5.89

The structure was solved by direct methods. Refinement was carried out by the block-diagonal least-squares method, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and equal weight ($w = 1/\sigma^2(F_o)$) was adopted for all reflections. Atomic scattering factors were taken from ref. 21. Hydrogen atoms were fixed at the calculated positions and were not refined. All the calculations were carried out on a FACOM M-1800/20 computer in the Computer Center of Kyushu University by the use of a local version [22] of the UNICS-III [23] and ORTEP [24] programs. The final agreement factors are given in Table 1. The final positional parameters of non-hydrogen atoms with their estimated standard deviations are listed in Table 2.

Results and discussion

Synthesis and general characterization

The unsaturated macrocycle $(R^{2,2})^{2-}$ has been reported previously as mononuclear and dinuclear cop-

TABLE 2 Final atomic coordinates for non-hydrogen atoms ($\times 10^4$) of $[Ni_2(L^{2,2})(OAc)_2]\cdot 10H_2O$ (1)

Atom	x	y	z	B_{eq} (Å^2)
Ni	1543(1)	749(1)	860(1)	1.89(2)
O	−264(5)	30(4)	1628(6)	1.96(15)
N(1)	2793(6)	1329(5)	3481(7)	2.28(20)
N(2)	−2284(6)	617(5)	−679(7)	2.36(21)
C(1)	−482(8)	785(6)	2862(9)	2.02(24)
C(2)	593(8)	1296(6)	4506(9)	2.24(25)
C(3)	407(8)	2047(6)	5846(9)	2.58(26)
C(4)	−836(8)	2357(6)	5653(10)	2.70(27)
C(5)	−1847(8)	1904(6)	4035(10)	2.45(26)
C(6)	−1725(7)	1119(6)	2631(9)	2.19(25)
C(7)	1943(8)	947(6)	4726(9)	2.38(25)
C(8)	3972(8)	853(7)	3432(9)	2.82(27)
C(9)	−1024(9)	3193(7)	7150(10)	3.68(31)
C(10)	−2894(8)	692(6)	892(9)	2.62(26)
C(11)	−3364(8)	419(6)	−2393(9)	2.99(29)
O(A1)	1309(5)	2359(4)	847(6)	2.90(18)
O(A2)	3161(5)	2002(4)	119(6)	3.05(18)
C(A1)	2518(8)	2695(6)	466(9)	2.93(27)
C(A2)	3144(10)	3893(6)	448(11)	4.25(33)
O(W1)	−458(6)	6182(4)	7025(7)	4.14(21)
O(W2)	5418(6)	2679(5)	−1515(8)	4.90(23)
O(W3)	4670(6)	3645(4)	5676(7)	4.56(22)
O(W4)	3090(6)	5127(5)	5566(8)	5.32(24)
O(W5)	7675(7)	3984(6)	1428(8)	6.71(29)

per(II) and nickel(II) complexes $[M(R^{2,2})]$ and $[M_2(R^{2,2})Cl_2]$ (M = Cu, Ni) [2]. In our preliminary studies for obtaining $H_2(L^{2,2})$, those complexes were reduced with various reagents but many difficulties arose in the separation of the reduced macrocycle from the reaction mixture. Eventually, a lead(II) complex of $(R^{2,2})^{2-}$, $Pb_2(R^{2,2})(ClO_4)_2\cdot CH_3OH$, was found to be a good starting material for $H_2(L^{2,2})$. In the reduction of this complex with $NaBH_4$ most of lead(II) ions were separated as metallic Pb and trace amounts of unreduced lead(II) ions were deposited as $PbSO_4$, and liberated $H_2(L^{2,2})$ was extracted with chloroform under mild alkaline conditions. The formation of $H_2(L^{2,2})$ was proved by mass spectra and 400 MHz ^{1}H NMR spectra (see 'Experimental').

The reaction of $H_2(L^{m,n})$ with $Ni(OAc)_2\cdot 4H_2O$ in a methanol–water mixture formed dinuclear nickel(II) complexes $[Ni_2(L^{m,n})(OAc)_2](solv)_x$ ($(m,n) = (2,2), (2,4), (2,5), (3,3)$; solv = H_2O, CH_3OH) as blue crystals. The corresponding complex of $(L^{2,3})^{2-}$ was not obtained. Instead, $[Ni_2(L^{2,3})(OAc)(NCS)(CH_3OH)]$ was obtained as green microcrystals when $H_2(L^{2,3})$, $Ni(OAc)_2\cdot 4H_2O$ and NH_4SCN were reacted in a 1:2:1 molar ratio in methanol. The methanol molecule of this complex was not removed by evacuation. Complexes **1**–**5** each shows a ν(N–H) stretching vibration at 3200–3250 cm^{-1}. The antisymmetric and symmetric stretching modes of the acetate group, $\nu_a(COO^-)$ and $\nu_s(COO^-)$, are seen at 1610 and 1550 cm^{-1}, respectively. Such a small separation between the $\nu_a(COO^-)$ and $\nu_s(COO^-)$ modes suggests the bidentate function of the acetate group [25]. The IR spectrum of **2** shows ν(CS) and ν(CN) vibrations of the SCN^- group at 820 and 2080 cm^{-1}, respectively, which suggest coordination of the group to the Ni(II) ion through the N atom [26].

The electronic spectra of complexes **1**–**5** were measured in dmso, dmf and on powder samples The results are summarized in Table 3. All the complexes show three absorption bands near 370, 620 and 890 nm and a sharp band near 770 nm. The three broad bands may be attributed to spin-allowed d–d transitions of the pseudo-octahedral nickel(II) ion judged from their low extinction coefficients [17] The sharp band near 770 nm is assigned to a spin-forbidden d–d band. The marked spectral resemblance of **1**–**5** suggests coordination of the methanol molecule in $[Ni_2(L^{2,3})(OAc)(NCS)(CH_3OH)]$ (**2**). In this complex NCS^- and CH_3OH probably replace one of the bidentate acetate groups in $[Ni_2(L^{m,n})(OAc)_2$ (**1** and **3**–**5**).

Structure of $[Ni_2(L^{2,2})(OAc)_2]\cdot 10H_2O$ (1)

The ORTEP view of the essential part of complex **1** is shown in Fig. 1 together with the numbering system. The interatomic bond distances and angles relevant to the nickel coordination sphere are listed in Table 4.

The complex is centrosymmetric and composed of $(L^{2,2})^{2-}$, two Ni(II) ions and two acetate ions. Ten water molecules are free from coordination and captured in the crystal lattice. Two nickel(II) ions are bridged by two phenolic oxygen atoms The geometry about each nickel(II) ion is six-coordinate with two phenolic oxygens and two amino nitrogens of the macrocycle and two carboxylate oxygens of the chelating acetate group. The macrocycle assumes a folded conformation and each N_2O_2 donor set coordinates in a non-planar manner affording a *cis*-β octahedral geometry about each nickel(II) ion. The two Ni–O(phenolate) bond distances are 2.042(5) and 2.013(4) Å. The two Ni–N bond distances are 2.073(5) and 2.078(7) Å. The Ni–O(carboxylate) distances are 2.189(5) and 2.146(6) Å, which are slightly elongated relative to the other Ni–O and Ni–N bonds. The two nickel ions are separated by 3.005(2) Å and the Ni–O–Ni angle is significantly small (95.6(2)°). Because of the deformed conformation of the macrocycle the O–C1 bond is tilted by 94.6° from the least-squares plane defined by Ni, Ni′, O and O′.

The crystal structures of $[Ni_2(L^{3,3})(ClO_4)_2(CH_3OH)_2]$ [15], $[Ni_2(L^{3,3})(\mu\text{-}O_2CCH_2NH_3)(H_2O)_2](ClO_4)_2$ [16] and $[Ni_2(L^{3,3})(py)_2](ClO_4)_2$ [17] have been reported. In $[Ni_2(L^{3,3})(ClO_4)_2(CH_3OH)_2]$ and $[Ni_2(L^{3,3})(py)_2](ClO_4)_2$, the macrocycle $(L^{3,3})^{2-}$ assumes a nearly coplanar conformation with respect to the N_4O_2 donor atoms

TABLE 3. Electronic spectral data of **1**–**5**

Complex	λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1}))				Solvent
$[Ni_2(L^{2,2})(OAc)_2]\cdot 10H_2O$ (**1**)	368	611	789	899	powder
	365(584)	618(37)	795(24)	895(34)	dmso
	370(343)	603(31)	785(14)	893(27)	dmf
$[Ni_2(L^{2,3})(OAc)(NCS)(CH_3OH)]$ (**2**)	377	609	764	877	powder
	373(472)	616(26)	763(13)	879(15)	dmso
	365(177)	595(20)	750(16)	880(17)	dmf
$[Ni_2(L^{2,4})(OAc)_2]\cdot 1/2H_2O$ (**3**)	380	624	757	888	powder
	370(103)	616(15)	760(11)	880(18)	dmso
	375(151)	612(17)	740(13)	884(16)	dmf
$[Ni_2(L^{2,5})(OAc)_2]\cdot H_2O$ (**4**)	376	633	764	887	powder
	365(205)	647(11)	745(12)	886(11)	dmso
	370(113)	650(12)	743(15)	890(14)	dmf
$[Ni_2(L^{3,3})(OAc)_2]$ $1/2CH_3OH$ (**5**)	369	615	761	886	powder
	370(55)	617(12)	764(6)	885(10)	dmso
	371(61)	613(19)	765(7)	883(16)	dmf

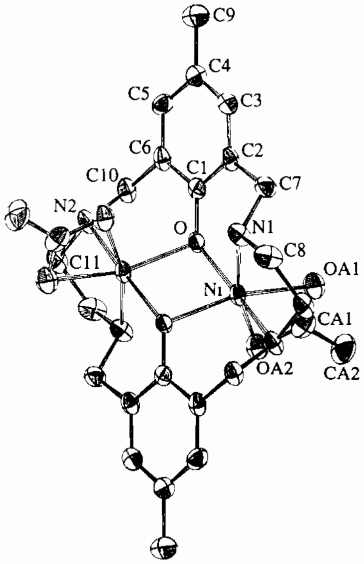

Fig. 1. ORTEP view of the essential part of $[Ni_2(L^{2,2})(OAc)_2]\cdot 10H_2O$ (**1**).

to afford an axially elongated octahedral geometry about each nickel(II) ion in the former and a square-pyramidal geometry in the latter. In those complexes the Ni–Ni distance is significantly long: 3.135 Å in the former and 3.206 Å in the latter. In $[Ni_2(L^{3,3})(\mu\text{-}O_2CCH_2NH_3)(H_2O)_2](ClO_4)_2$ the glycinate carboxyl group bridges the two nickel(II) ions so that the macrocycle is deformed from coplanar. The Ni–Ni separation in this complex is 3.066 Å.

The crystal structures of complexes of $(R^{3,3})^{2-}$ have been reported for Mn_2(II,II) [7c], Mn_2(II,III) [7c], Fe_2(II,II) [6d], Co_2(II,II) [4b], Co_2(II,III) [4c], Cu_2(II,II) [4d] and Cu_2(I,II) [6b]. In all these complexes the macrocycle is essentially coplanar.

TABLE 4. Selected bond distances and angles for $[Ni_2(L^{2,2})(CH_3COO)_2]$ $10H_2O$

Bond distances (Å)			
Ni–N1	2.073(5)	Ni–N2′	2.078(7)
Ni–O	2.042(5)	Ni–O′	2.013(4)
Ni–OA1	2.146(6)	Ni–OA2	2.189(5)
N1–C7	1.487(10)	N2–C10	1.487(10)
Ni- - -Ni′	3.005(2)		
Bond angles (°)			
N1–Ni–O	91.3(2)	N1–Ni–O′	172.0(2)
N2′–Ni–O	96.3(2)	N2′–Ni–O′	87.2(2)
N1–Ni–N2′	86.6(2)	O–Ni–O′	84.4(2)
OA1–Ni–OA2	60.4(2)	Ni–O–Ni	95.6(2)
N1–Ni–OA1	92.7(2)	O–Ni–OA1	99.4(2)
N2′–Ni–OA1	164.3(2)	O′–Ni–OA1	94.7(2)
N1–Ni–OA2	90.0(2)	O–Ni–OA2	159.7(2)
N2′–Ni–OA2	104.0(2)	O′–Ni–OA2	96.4(2)

Magnetic properties

The magnetic susceptibilities of **1**–**5** were measured in the temperature range 4.2–300 K. The temperature dependences of the magnetic susceptibility and effective magnetic moment of **1** are given in Fig. 2.

In all of the complexes, the effective magnetic moment, μ_{eff}, increases with lowering of temperature, reaches a maximum value (*c*. 3.7 μ_B/Ni) near 15 K, and then decreases below this temperature. Such a magnetic behavior suggests a ferromagnetic spin exchange between the two nickel(II) ions. The reduction in μ_{eff} at low temperature may be attributed to the zero-field splitting of the Ni(II) ion. Thus, magnetic analyses of the complexes were carried out based on the spin Hamiltonian $\mathscr{H} = -2JS_1 \cdot S_2 - D(S_{z1}{}^2 - S_{z2}{}^2)$, where D is the zero-field splitting parameter of the Ni(II) ion. The magnetic susceptibility expression based on this Ham-

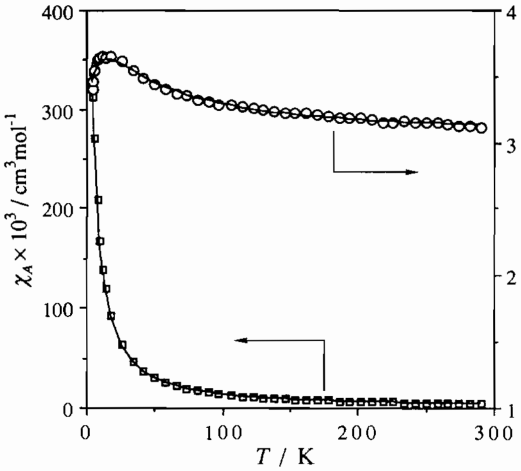

Fig. 2 χ_A vs. T and μ_{eff} vs. T plots of $[Ni_2(L^{2,2})(OAc)_2]\ 10H_2O$ (**1**).

iltonian has been derived by Ginsberg *et al.* [27]. We assume that the isotropic treatment is valid and the interdimer interaction is negligibly small. The magnetic susceptibility expression based on these assumptions is given by eqn. (1).

$$\chi_A = \frac{Ng^2\beta^2}{kT} \cdot \frac{1+\exp(A)+4\exp(B)}{2+2\exp(A)+2\exp(B)+\exp(C)+\exp(D)+\exp(E)} + N\alpha \tag{1}$$

$$A = 4J/kT$$

$$B = (4J+D)/kT$$

$$C = D/kT$$

$$D = [J-\sqrt{(3J+D)^2-8JD}]/kT$$

$$E = [J+\sqrt{(3J+D)^2-8JD}]/kT$$

where χ_A is the magnetic susceptibility per nickel, N is Avogadro's number, g is the Zeeman splitting parameter, β is the Bohr magneton, k is the Boltzman constant and T is the absolute temperature.

The cryomagnetic property of **1** could be well reproduced based on eqn. (1) as indicated by the solid curve in Fig. 2, using $J = +10.1$ cm^{-1}, $D = -0.90$ cm^{-1}, $g = 2.15$ and $N\alpha = 220 \times 10^{-6}$ cm^3 mol^{-1}. The discrepancy factor defined as $R(\chi) = [\Sigma(\chi_{obs}-\chi_{calc})^2/\Sigma(\chi_{obs})^2]^{1/2}$ was 0.021. Similarly, a good magnetic simulation was obtained for **2–5**. In these magnetic simulations $N\alpha$ is fixed at 220×10^{-6} cm^3 mol^{-1} [27–29]. The magnetic parameters determined for the present complexes are summarized in Table 5. The exchange integral J is positive for all the complexes, indicating that the magnetic interaction between the two nickel(II) ions is ferromagnetic.

TABLE 5 Magnetic parameters of **1–5**

Complex	g	J (cm^{-1})	D (cm^{-1})	$R(\chi)$
1	2.15	10.1	−0.90	0.021
2	2.18	6.6	−0.240	0.011
3	2.11	8.1	−0.53	0.023
4	2.10	7.6	−0.55	0.018
5	2.14	2.1	−2.30	0.008

$N\alpha$ is fixed at 220×10^{-6} cm^3 mol^{-1} for all the complexes [27–29].

Dinuclear nickel(II) complexes of $(L^{3,3})^{2-}$, $[Ni_2(L^{3,3})B_2](ClO_4)_2$ ($B = NH_3$, imidazole, pyridine or pyrazine) have been synthesized by Nanda *et al.* but they reported only the room-temperature magnetic moments of these complexes [16]. Their moments (per Ni) are rather small and some are smaller than the spin-only value 2.83 μ_B, suggesting an antiferromagnetic interaction between the nickel(II) ions. On the other hand, the magnetic interaction in $[Ni_2(L^{3,3})(\mu\text{-}O_2CCH_2NH_3)(H_2O)_2](ClO_4)_2$ is reported to be ferromagnetic [17].

Correlations between magnetic interaction and the bridging bond angle have been extensively studied for di-μ-hydroxodicopper(II) complexes [30, 31]. Antiferromagnetic interaction occurs when the Cu–O–Cu bridging angle is larger than 97.5° whereas ferromagnetic interaction occurs when the Cu–O–Cu angle is smaller than 97.5° [30, 31]. This criterion seems valid for dinuclear nickel(II) complexes since one of the magnetic orbitals of nickel(II) ($d_{x^2-y^2}$ when x and y axes are taken along the equatorial donor atoms) is the same as that of copper(II) and this orbital mainly contributes to magnetic interaction in dinuclear nickel(II) complexes. The ferromagnetic interaction in **1** ($J = +10.1$ cm^{-1}) and $[Ni_2(L^{3,3})(\mu\text{-}O_2CCH_2NH_3)(H_2O)_2](ClO_4)_2$ ($J > 0$) can be understood in view of their small Ni–O–Ni angles (95.6 and 93.8° (av.) respectively) [16]. The antiferromagnetic complexes $[Ni_2(L^{3,3})B_2](ClO_4)_2$ have a large Ni–O–Ni angle (105.7° for B = py) [17]. In related $[Ni_2(R^{3,3})Cl_2]$ the magnetic interaction is also antiferromagnetic ($J = -36$ cm^{-1}) probably due to a large Ni–O–Ni angle [7]. Some polynuclear nickel(II) complexes have been reported that show a ferromagnetic interaction; for example, $[Ni(acac)_3]_3$ (acac = acetylacetonato, ∠Ni–O–Ni = 78.3–89.3°, $J_{12} = J_{23} = +12.5$ cm^{-1}) [28], $[Ni(OMe)(salal)(EtOH)]_4$ (salal = salicylaldehydato, ∠Ni–O–Ni = *c.* 97.7°, $J = +7$ cm^{-1}) [32]. All of these complexes have the Ni–O–Ni angle smaller than 98°.

Electrochemistry

The electrochemical properties of complexes **1–5** were studied by cyclic voltammetry, in DMSO with a glassy

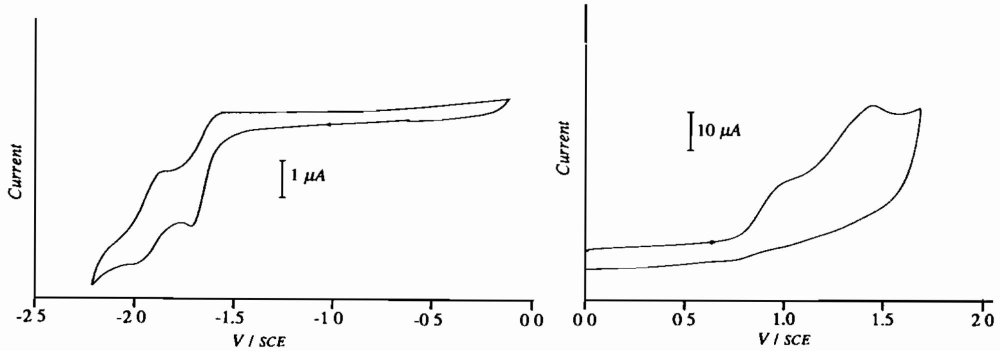

Fig. 3. Cyclic voltammograms of $[Ni_2(L^{2,2})(OAc)_2]$ $10H_2O$ (**1**) in DMSO for reduction (left) and CH_2Cl_2 for oxidation (right).

carbon working electrode for reduction and in CH_2Cl_2 with a platinum working electrode for oxidation. Cyclic voltammograms of **1** are given in Fig. 3.

In the sweep in negative potential range **1** shows two quasi-reversible waves at −1.63 and −1.92 V versus SCE. **2** also shows quasi-reversible waves at −1.62 and −1.89 V versus SCE. The two waves are assigned to the stepwise reduction of the metal centers [15]: $Ni_2(II,II) \rightarrow Ni_2(I,II) \rightarrow Ni_2(I,I)$. For **3**, **4** and **5** the two waves appearing at −1.6 to −1.9 V versus SCE were irreversible and poorly resolved. Das and Nag [15] reported that $[Ni_2(L^{3,3})(ClO_4)_2(CH_3OH)_2]$ exhibits two quasi-reversible reductions at higher potentials −1.32 and −1.65 V versus SCE in DMSO with a glassy carbon electrode. Thus, it appears that coordination of the acetate group destabilizes the nickel(I) state.

The stability of the mixed-valence $Ni_2(I,II)$ species, K_{con} can be determined electrochemically by the expression $\log K_{con} = \Delta E/0.0591$ (at 25 °C) [8a], where ΔE is the separation between the first and the second reduction potentials. Based on this equation the K_{con} values of **1** and **2** are evaluated at 8.1×10^4 and 3.7×10^4, respectively. Those values are smaller than 3.8×10^5 reported for $[Ni_2(L^{3,3})(ClO_4)_2(CH_3OH)_2]$ [15].

In the sweep at positive potential range complexes **1**–**4** show two irreversible waves in the region +0.7 to +1.4 V, where only the anodic peaks are barely resolved. The two waves are assigned to the oxidations at the metal centers [15]: $Ni_2(II,II) \rightarrow Ni_2(II,III) \rightarrow Ni_2(III,III)$. On the other hand, the two oxidations of $[Ni_2(L^{3,3})(OAc)_2]$ (**5**) are quasi-reversible and appear at +0.84 and +1.03 V versus SCE. The corresponding oxidation waves of $[Ni_2(L^{3,3})(ClO_4)_2(CH_3OH)_2]$ are found at +0.94 and +1.08 V versus SCE in acetonitrile with a platinum electrode. The K_{con} for the $Ni_2(II,III)$ species of **5** is evaluated at 1.6×10^3 which is slightly larger than 2.3×10^2 of $[Ni_2(L^{3,3})(ClO_4)_2(CH_3OH)_2]$ [15].

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