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Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
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To cite this Article Ōkawa, Hisashi , Aratake, Yuichiro , Motoda, Ken-Ichiro , Ohba, Masaaki , Sakiyama, Hiroshi and Matsumoto, Naohide(1996) 'Dinuclear nickel complexes of phenolbased dinucleating macrocycles: Synthesis, structure, and properties', Supramolecular Chemistry, 6: 3, 293 — 302

To link to this Article: DOI: 10.1080/10610279608032547

URL: http://dx.doi.org/10.1080/10610279608032547

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SUPRAMOLECULAR CHEMISTRY, Vol. 6, pp. 293–302
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Dinuclear nickel complexes of phenol-based dinucleating macrocycles: Synthesis, structure, and properties

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(Received June 13, 1994)

Dinuclear Ni_2(II,II) complexes with the formula $[Ni_2(R^{m,n})](ClO_4)_2$ ((m,n)= (2,2) (1), (2,3) (2), (2,4) (3)) have been obtained where $(R^{m,n})^{2-}$ denotes the macrocycles containing two 2,6-bis(iminomethyl)-4-methylphenolate entities combined through two lateral chains, $-(CH_2)_m-$ and $-(CH_2)_n-$, at the imino nitrogens. $[Ni_2(R^{2,2})](ClO_4)_2$ (1) crystallizes in the triclinic crystal system, space group $P\bar{1}$, with Z=1, a=8.396(2) Å, b= 10.021(2) Å, c=8.104(2) Å, α=109.56(2)°, β=99.40(2)°, γ=79.89(2)°, V=628.5(3) $Å^3$ and Z=1. The refinement converges with R=0.0384 and R_w=0.0415 for 2075 reflections with $|Fo| > 3\sigma(|Fo|)$. In the centrosymmetric $[Ni_2(R^{2,2})]^{2+}$, a pair of Ni(II) ions are bridged by two phenolic oxygens with the Ni···Ni separation of 2.801(1) Å. Each Ni assumes a planar configuration with Ni-O bond distances of 1.842(3) and 1.838(3) Å and Ni-N bond distances of 1.814(3) and 1.823(3) Å. In the solid state, 1 is diamagnetic ($S_1=S_2=0$) whereas $[Ni_2(R^{2,3})]-(ClO_4)_2$ (2) and $[Ni_2(R^{2,4})](ClO_4)_2$ (3) are of a mixed-spin ($S_1=0$, $S_2=1$). In DMSO and pyridine all the complexes assume high-spin ($S_1=S_2=1$). The Ni_2(II,II) complexes are electrochemically reduced in DMSO or pyridine to Ni_2(I,II) and Ni_2(I,I) complexes. The conproportionation constants of the Ni_2(I,II) complexes are determined to be 3.4×10^4-1.2×10^5 in DMSO and 1.6×10^3-2.6×10^5 in pyridine. The Ni_2(I,II) and Ni_2(I,I) complexes of 1–3 have been prepared by electrolysis in DMSO. The mixed-valent complexes of 1 and 2 are characterized by an intervalence (IV) transition band at 790 and ~700 nm, respectively, and belong to Class II using the classification of Robin and Day. The Ni_2(I,II) complex of 3 shows no IT band (Class I). The Ni_2(I,II) complexes of 1–3 show well-resolved ESR spectra due to the spin-coupled S_T = ½ ground-state. The Ni_2(I,I) complexes of 1–3 are all ESR- innocent probably due to the strong antiferromagnetic interaction.

INTRODUCTION

Recently dinuclear metal complexes have attracted much attention because of their unique physicochemical properties and unprecedented functions associated with metal-metal interactions and/or cooperative effects of metal ions[1–6] and as models for metallobiosites.[7] The use of dinucleating macrocycles in the study of dinuclear metal complexes has great advantages because of macrocyclic effects[8] to stabilize the dinuclear core structures. In particular, the macrocyclic effect to stabilize unusual oxidation states of metal ions[9] is well documented. Further, the properties and functions of dinuclear metal complexes may be modulated by the design of macrocycles.[9]

The macrocycles in Scheme 1 (abbreviated hereafter as $(R^{m,n})^{2-}$ where the superscripts m and n denote the number of methylenes in the lateral chains) have been obtained for various sets of lateral chains and used extensively for the studies of homo- and heterodinuclear metal complexes and mixed-spin complexes.[10–15] Dinuclear Ni_2(II,II) complexes of $(R^{2,2})^{2-}$, $(R^{2,3})^{2-}$, and $(R^{3,3})^{2-}$ have been obtained as chlorides,[10b,11b] but their solution chemistry was not studied because of the low solubility of the complexes in appropriate solvents. The lower oxidation states, Ni_2(I,II) and Ni_2(I,I), of dinuclear complexes are of great interest in their electronic nature and function. The nucleophilic reactivity of Ni(I) toward alkyl halides,[16] water,[17] carbon dioxide,[18] etc. are well known. In this study the dinuclear Ni_2(II,II) complexes with the formula $[Ni_2(R^{m,n})]-(ClO_4)_2$ ((m,n)=(2,2) (1), (2,3) (2), and (2,4) (3)) have been obtained and the crystal structure of $[Ni_2(R^{2,2})](ClO_4)_2$ (1) has been determined by X-ray crystallography. It was found that the complexes assume the low-spin ($S_1=S_2=0$: 1) or mixed-spin (S_1=O, $S_2=1$: 2 and 3) as solids but all the complexes assume the high-spin ($S_1=S_2=1$) in dimethyl sulfoxide (DMSO) or pyridine. The main emphasis is

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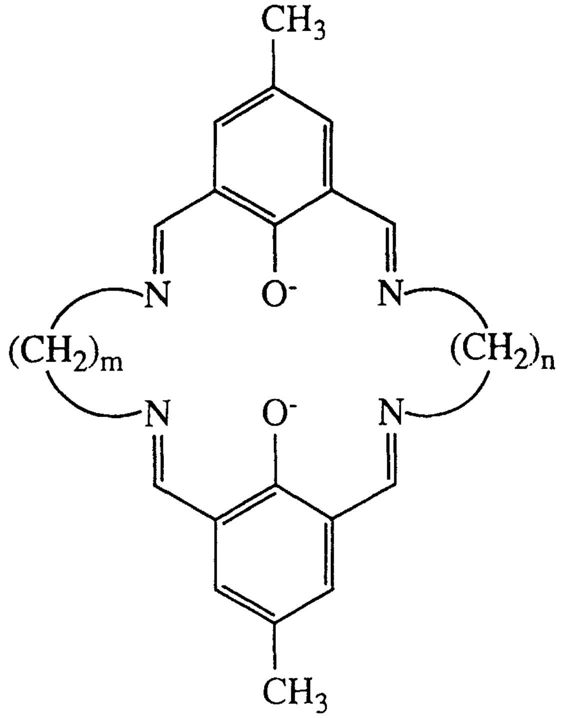

Scheme 1

placed on the Ni_2(I,II) and Ni_2(I,I) complexes provided in situ by electrolysis.

EXPERIMENTAL

Elemental analyses of C, H, and N were obtained at the Elemental Analysis Service Center of Kyushu University. Analyses of Ni, Cu, and Zn were made using a Shimadzu AA-660 atomic absorption/flame emission spectrophotometer. Infrared spectra were recorded using a JASCO IR-810 spectrometer in KBr disks or Nujol mulls. Molar conductances were measured at 1×10^{-3} M concentration in N,N-dimethylformamide (DMF) using a DKK AOL-10 conductivity meter at 20°C. Electronic spectra were recorded using a Shimadzu MPS-2000 spectrometer at room temperature. Magnetic susceptibilities of powder samples were measured on a Faraday balance in the temperature range of 80–300 K. The calibration of the apparatus was made with $[Ni(en)_3]S_2O_3$[19] and diamagnetic corrections were made with Pascal's constants.[20] Magnetic susceptibilities in solution were determined by the Evance method[21] in DMSO and pyridine, using a JEOL JNM-GX 400 spectrometer. Cyclic voltammograms were recorded on an apparatus comprised of a HA-501 potentiostat/galvanostat, a HB-104 function generator, and a HF-201 coulomb/amperehour meter from Hokuto Denko Ltd. A three-electrode cell was used to which were attached a glassy-carbon working electrode, a platinum-coil counter electrode, and a saturated calomel reference electrode. Tetra(n-butyl)ammonium perchlorate (TBAP) was used as the supporting electrolyte (**Caution!** TBAP may be explosive and should be handled with great care). Coulometry experiments were carried out using the same instrument with a platinum net as the working electrode. X-Band esr spectra were recorded using a JEOL JEX-FE3X esr spectrometer at liquid nitrogen temperature.

Preparation.N,N′-Bis(3-formyl-5-methylsalicylidene)-ethylenediaminatonickel(II), $[Pb\{Ni(R^{2,3})\}_2]$- $(ClO_4)_2$ and $[Pb\{Ni(R^{2,4})\}_2](ClO_4)_2$ were prepared using the literature methods.[10,22] **Caution!** These trinuclear perchlorate complexes and the dinuclear perchlorate complexes described below may be explosive and necessitate extreme caution in their handling.

$[Ni_2(R^{2,2})](ClO_4)_2$ (**1**). A mixture of N,N′-bis(3-formyl-5-methylsalicylidene)ethylenediaminatonickel-(II) (0.41 g, 1 mmol) and nickel(II) perchlorate hexahydrate (0.37 g, 1 mmol) in methanol was refluxed for 1 hour. A methanol solution (20 cm^3) of ethylenediamine (0.06 g, 1 mmol) was dropwise added,. and the mixture was refluxed for one hour to give orange crystals. They were separated by filtration, washed successively with methanol and ether, and dried in vacuo. Yield: 0.61 g (88 %). Anal. Calcd for $C_{22}H_{22}Cl_2N_4Ni_2O_{10}$: C, 38.26; H, 3.21; N, 8.11; Ni, 16.99. Found: C, 38.27; H 3.24; N, 8.14; Ni, 17.18. Selected IR data [ν/cm^{-1}] using KBr disks: 1620, ~1100. Molar conductance [Λ/Scm^{2}mol^{-1}] in DMF: 150.

$[Ni_2(R^{2,3})](ClO_4)_2 \cdot 3H_2O$ (**2**). A suspension of $[Pb\{Ni(R^{2,3})\}_2](ClO_4)_2$ (0.33 g, 0.25 mmol), nickel(II) sulfate hexahydrate (0.07 g, 0.25 mmol), and nickel(II) perchlorate hexahydrate (0.10 g, 0.25 mmol) in methanol (100 cm^3) was stirred for 12 hours at room temperature. The resulting $PbSO_4$ was separated by filtration and the filtrate was evaporated to dryness. The residue was extracted with acetonitrile (30 cm^3) and the extract was diffused with ether to give orange crystals. Yield: 0.30 g (79 %). Anal. Calcd for $C_{23}H_{30}Cl_2N_4Ni_2O_{13}$: C, 36.41: H, 3.99; N, 7.38; Ni, 15.47. Found: C, 36.68; H, 4.01; N, 7.58; Ni, 15.09. Selected IR data [ν/cm^{-1}] using KBr disks: 1630, 1620, ~1100. Molar conductance [Λ/Scm^{2}mol^{-1}] in DMF: 165.

$[Ni_2(R^{2,4})](ClO_4)_2 \cdot 0.5H_2O$ (**3**). This was obtained as orange crystals by the reaction of $[Pb\{Ni(R^{2,4})\}_2](ClO_4)_2$ (0.33 g, 0.25 mmol), nickel(II) sulfate hexahydrate (0.07 g, 0.25 mmol) and nickel(II) perchlorate hexahydrate (0.10 g, 0.25 mmol) using a method similar to that for **2**. Yield: 0.27 g (74 %). Anal. Calcd for $C_{24}H_{27}Cl_2N_4Ni_2O_{10.5}$: C, 39.61; H, 3.74; N, 7.70; Ni, 16.13. Found: C, 39.45; H, 3.91; N, 7.91; Ni, 15.81. Selected IR data [ν/cm^{-1}] using KBr disks: 1630, 1620,

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1100, 1090, 1065. Molar conductance [Λ/Scm^{2}mol^{-1}] in DMF: 170.

$[NiZn(R^{2,3})](ClO_4)_2$ (**4**). This was obtained as orange crystals by the reaction of $[Pb\{Ni(R^{2,3})\}_2](ClO_4)_2$ (0.33 g, 0.25 mmol), zinc(II) sulfate hexahydrate (0.08 g, 0.25 mmol) and zinc(II) perchlorate hexahydrate (0.09 g, 0.25 mmol) in a way similar to that for **2**. Yield: 0.29 g (82 %). Anal. Calcd for $C_{23}H_{24}Cl_2N_4NiO_{10}Zn$: C, 38.83; H, 3.40; N, 8.25; Zn, 9.19. Found: C, 38.75; H, 3.75; N, 7.63; Ni, 7.99; Zn, 9.21. Selected IR data [ν/cm^{-1}] using KBr disks: 1640, 1625, ~1100. Molar conductance [Λ/Scm^{2}mol^{-1}] in DMF: 150.

$[NiZn(R^{2,4})](ClO_4)_2$ (**5**). This was obtained as orange crystals by the reaction of $[Pb\{Ni(R^{2,4})\}_2](ClO4)_2$ (0.33 g, 0.25 mmol), zinc(II) sulfate hexahydrate (0.08 g, 0.25 mmol), and zinc(II) perchlorate hexahydrate (0.09g, 0.25 mmol) in methanol (100 cm^3). Yield: 0.28 g (77 %). Anal. Calcd for $C_{24}H_{26}Cl_2N_4NiO_{10}Zn$: C, 39.73; H, 3.61; N, 7.72; Ni, 8.09; Zn, 9.01. Found: C, 39.61; H, 3.84; N, 7.78; Ni, 8.05; Zn, 8.79. Selected IR data [ν/cm^{-1}] using KBr disks: 1640, 1620, ~1100. Molar conductance [Λ/Scm^{2}mol^{-1}] in DMF: 155.

Crystal structure analysis of $[Ni_2(R^{2,2})](ClO_4)_2$ (1). Single crystals of **1** were obtained by the slow diffusion of methanol into a DMF solution of **1**. A crystal with the approximate dimensions of 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 diffactometer using graphite-monochromatized Mo-Kα radiation (λ= 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 of $28° < 2\theta < 33°$. 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,±k,±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. A total of 2075 independent reflections with $|Fo| > 3\sigma(|Fo|)$ in the range $2.5° \leqq 2\theta \leqq 50°$ were assumed to be observed.

The structure was solved by direct methods. Refinement was carried out using the block-diagonal least-squares method, where the minimized function is $\Sigma w(|Fo| - k|Fc|)^2$ and weight ($w=1/\sigma^2(Fo)$) was adopted for all reflections. Atomic scattering factors were taken from Ref. 23. Hydrogen atoms were fixed at the calculated positions and were not refined. All the calculations were carried out using a FACOM M-1800/20 computer in the Computer Center of Kyushu University by the use of a local version[24] of the UNICS-III[25] and ORTEP[26] programs. The final agreement factors are given in Table 1. The final positional parameters of all non-hydrogen atoms with their estimated standard deviations are listed in Table 2.

Table 1 Crystal data for **1**.

Formula	$C_{22}H_{22}Cl_2N_4Ni_2O_{10}$
F.W.	690.72
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	8.396(2)
b/Å	10.021(2)
c/Å	8.104(2)
α/deg	109.56(2)
β/deg	99.40(2)
γ/deg	79.89(2)
V/Å^3	628.5(3)
Z	1
D_c/g cm^{-3}	1.825
μ (Mo Kα)/cm^{-1}	7.824
No. of reflection	2075
R /%	3.8
R_w /%	4.1

RESULTS AND DISCUSSION

Preparation and general property. The dinuclear Ni_2(II,II) chloride complexes, $[Ni_2(R^{2,2})]Cl_2$ and $[Ni_2(R^{2,3})]Cl_2$, were first synthesized in our laboratory through the mononuclear precursors $[Ni(R^{m,n})]$ ((m,n)= (2,2), (2,3)).[10] In this study, the perchlorate complex $[Ni_2(R^{2,2})](ClO_4)_2$ (**1**) was prepared in a similar way, without isolating the mononuclear precursor complex. For the preparation of $[Ni_2(R^{2,3})](ClO_4)_2$ (**2**) and $[Ni_2(R^{2,4})](ClO_4)_2$ (**3**), the modified template reaction[22] through the trinuclear precursors $[Pb\{Ni(R^{m,n})\}_2](ClO_4)_2$ was adopted. The conversion of $[Pb\{Ni(R^{m,n})\}_2](ClO_4)_2$

Table 2 Atomic positional parameters of non-hydrogen atoms of **1**

Atom	*x/a*	*y/b*	*z/c*
Ni	0.4230(1)	0.1374(1)	0.0803(1)
O	0.5572(3)	-0.0092(3)	0.1412(3)
N1	0.4111(4)	0.2534(3)	0.3055(4)
N2	0.2856(4)	0.2725(3)	0.0042(4)
C1	0.6418(5)	-0.0077(4)	0.2947(5)
C2	0.6157(5)	0.1091(4)	0.4446(5)
C3	0.7050(5)	0.1059(4)	0.6059(5)
C4	0.8185(5)	-0.0109(5)	0.6182(5)
C5	0.8424(5)	-0.1243(4)	0.4690(6)
C6	0.7553(5)	-0.1287(4)	0.3033(5)
C7	0.9129(6)	-0.0108(5)	0.7943(6)
C8	0.4977(5)	0.2333(4)	0.4438(5)
C9	0.2846(5)	0.3805(4)	0.3186(6)
C10	0.2682(5)	0.4116(4)	0.1444(5)
C11	0.2180(5)	0.2550(4)	-0.1549(5)
Cl	0.2327(1)	0.6304(1)	0.8140(2)
O1	0.3396(4)	0.5006(4)	0.7662(5)
O2	0.1004(4)	0.6168(4)	0.8909(6)
O3	0.3208(5)	0.7351(5)	0.9416(7)
O4	0.1828(6)	0.6763(5)	0.6655(6)

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to $[Ni_2(R^{m,n})](ClO_4)_2$ (**2** and **3**) was satisfactorily achieved when stoichiometric amounts of a trinuclear precursor, nickel(II) sulfate hexahydrate, and nickel(II) perchlorate hexahydrate were reacted in a methanol-acetonitrile mixture.[26] In this reaction, Pb(II) was deposited as $PbSO_4$ and the resulting Ni_2(II,II) complexes were isolated as the perchlorates in good yields. The reference complexes $[NiZn(R^{m,n})](ClO_4)_2$ ((m,n)=(2,3) (**4**), (2,4) (**5**)), with the Ni(II) ion at the site with the ethylene lateral chain and the Zn(II) ion at the site with the trimethylene or tetramethylene lateral chain were prepared in similar ways.

Complex **1** shows a ν(C=N) vibration at 1620 cm^{-1} whereas **2** and **3** show two ν(C=N) vibrations due to the asymmetric nature of the macrocycles $(R^{2,3})^{2-}$ and $(R^{2,4})^{2-}$ with respect to the two lateral chains. Similarly, two ν(C=N) vibrations are seen for **4** and **5**. The molar conductances of **1**–**5** in DMF fall in the range of 150–170 Scm^2mol^{-1} which are typical of 1:2 electrolytes in this solvent.[27]

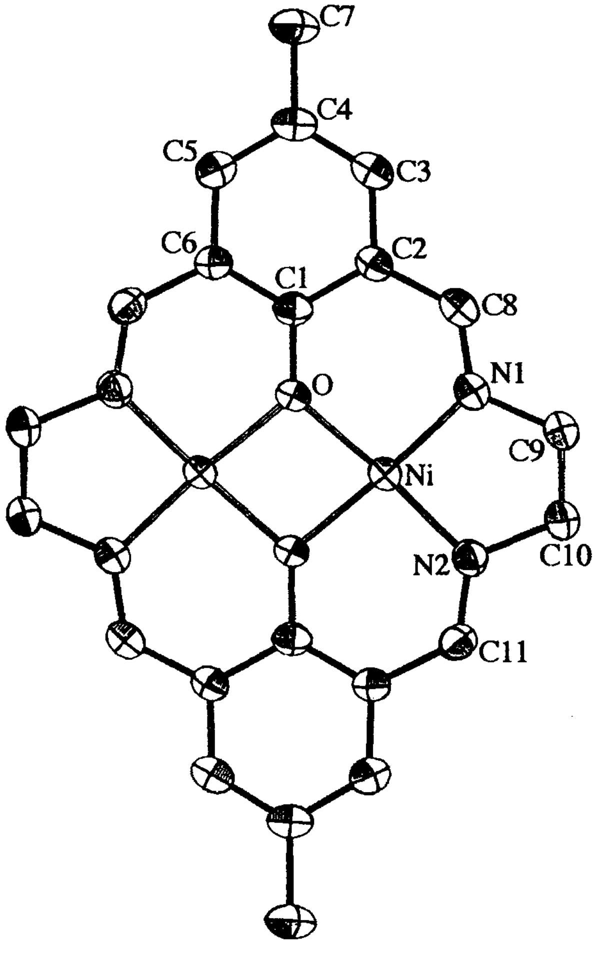

Figure 1 The ORTEP view of $[Ni_2(R^{2,2})]^{2+}$.

Table 3 Selected bond distances and angles of **1**.

Bond distances (Å)			
Ni-N1	1.814(3)	Ni-N2	1.823(3)
Ni-O	1.842(3)	Ni-O′	1.838(3)
Ni···Ni	2.801(1)		
Bond angles (deg°)			
Ni-O-Ni′	99.1(1)	N1-Ni-N2	89.1(1)
N1-Ni-O	94.9(1)	N2-Ni-O′	95.1(1)
O-Ni-O′	80.9(1)		

Crystal structure of $[Ni_2(R^{2,2})](ClO_4)_2$ (1). The first crystallographic evidence for the macrocycle $(R^{2,2})^{2-}$ has been obtained in this study. The ORTEP view of the essential part of **1** is shown in Fig. 1 together with the numbering scheme. The bond distances and angles relevant to the nickel coordination sphere are listed in Table 3.

The complex cation consists of $(R^{2,2})^{2-}$ and two Ni(II) ions. The Ni(II) ions reside within cavities to form a coplanar dinuclear core with an inversion center at the center of the cation. Two perchlorate ions are free from coordination, in accord with IR spectral data showing no split ν_3 perchlorate vibration. The two Ni(II) ions are bridged by two phenolic oxygens of the macrocycle with the Ni···Ni′ separation of 2.801(1) Å. The geometry about each Ni(II) ion is nearly planar with two phenolic oxygens and two imino nitrogens. The Ni-O bond distances are 1.842(3) and 1.838(3) Å and the Ni-N bond distances are 1.814(3) and 1.823(3) Å. Because of the short Ni···Ni separation, the Ni-O-Ni angle is very small (99.1(1)°).

The crystal structures of the dinuclear complexes of $(R^{3,3})^{2-}$ have been reported for Mn_2(II,II),[28] Mn_2(II,III),[28] Fe_2(II,II),[13d] Co_2(II,II),[11c] Co_2(II,III),[11d] Cu_2(II,II),[11e] and Cu_2(I,II).[13b] In these complexes, the dinuclear skeleton except for axial ligands can assume a nearly coplanar structure. When compared with these complexes, **1** has very short Ni-O and Ni-N bond distances that are favorable for the low-spin state of the Ni(II) ion. In the dinuclear nickel(II) complex $[Ni_2(L^{2,2})(CH_3COO)_2]10H_2O$[29] of the analogous macrocycle $(L^{2,2})^{2-}$ fully saturated at the azomethine linkages of $(R^{2,2})^{2-}$, the macrocycle assumes a folded non-planar configuration to provide a pseudo-octahedral surrounding about each Ni(II) together with a bidentate acetate group. Similar folded configurations are seen in the dinuclear complexes of $(L^{3,3})^{2-}$ (the analog saturated at the azomethine linkages of $(R^{3,3})^{2-}$).[30]

Spin-states in solid and solutions. Magnetic susceptibilities of **1**–**5** have been measured in solids and in solutions (DMSO and pyridine). Effective magnetic moments of the complexes are summarized in Table 4.

Table 4 Effective magnetic moments of **1–5**.

		on powder		*in dmso*	*in py*
Complex		*(82 K)*	*(290 K)*	*(300 K)*	*(295 K)*
$[Ni_2(R^{2,2})](ClO_4)_2$	**(1)**	dia.	dia.	3.00[b]	3.05[b]
$[Ni_2(R^{2,3})](ClO_4)_2 \cdot 3H_2O$	**(2)**	2.90[a]	3.07[a]	3.09[b]	3.07[b]
$[Ni_2(R^{2,4})](ClO_4)_2 \cdot 0.5H_2O$	**(3)**	2.94[a]	3.08[a]	3.10[b]	3.09[b]
$[NiZn(R^{2,3})](ClO_4)_2$	**(4)**	dia.	dia.	dia.	3.07
$[NiZn(R^{2,4})](ClO_4)_2$	**(5)**	dia.	dia.	dia.	3.08

[a]per molecule; [b]per Ni

In measurements on powdered samples, **1** is diamagnetic in accord with the planar configuration about the Ni(II) ion as proved by X-ray crystallography. Complexes **2** and **3** are paramagnetic with a room-temperature magnetic moment of 3.07 and 3.08 μ_B (per molecule), respectively. The moments are practically independent of temperature in the range of 82–300 K, clearly demonstrating that **2** and **3** are of the mixed-spin (S_1=0, S_2=1) in the solid. It is most likely that the Ni(II) at the site with the ethylene lateral chain is of low-spin whereas the Ni(II) at the site with the trimethylene or tetramethylene lateral chain is of high-spin. This is supported by the fact that the reference Ni(II)Zn(II) complexes **4** and **5** are diamagnetic. It should be mentioned that the two metal ions in $[Ni_2(R^{3,3})Cl_2]$ are of high-spin (S_1=S_2=1).[11a,13d]

In DMSO or pyridine, the complexes **1–3** have a magnetic moment ranging from 3.00 to 3.10 μ_B per Ni atom at room temperature. Evidently **1–3** are all of high-spin in these solvents, suggesting coordination of the solvent molecules to the Ni(II) ions. Interestingly, the Ni(II)Zn(II) complexes **4** and **5** remain diamagnetic in DMSO but become paramagnetic in pyridine (3.07 and 3.08 μ_B, respectively). The magnetic behavior of **1–5** in DMSO and pyridine reflect (1) the tendency of donation of the two solvents (pyridine is higher in donor number than DMSO[31]) and (2) the mutual effect of the neighboring metal ions upon donative solvation.

Electronic spectra of 1–5. All the complexes **1–5** show an intense absorption band at 370~380 nm (ϵ=11000~13000 dm^{3}mol^{-1}cm^{-1}) that is assigned to the π-π^* transition associated with the C=N bond.[32,33] In this study, we shall confine our attention to the visible absorption bands in the region of 400–900 nm. The spectral measurements have been made on powdered samples and in solution (DMSO or pyridine). The numerical data are summarized in Table 5 (see also Fig. 4).

The reflectance spectrum of **1** (low-spin) shows two bands at 505 and 580 nm, both of which can be attributed to the d-d transition bands of the planar low-spin Ni(II) ion.[34] The reflectance spectra of **2** and **3** (mixed-spin) differ from that of **1** and show three visible bands at 540–550, ~690, and 750 nm. The former band may be assigned to the low-spin Ni(II) and the latter two bands to the high-spin Ni(II). The Ni(II)Zn(II) complexes **4** and **5** show one absorption band at 550 nm.

In DMSO, **1** shows two absorption bands at 560 and ~650 nm. The solution spectrum differs from the reflectance spectrum in accord with the different spin-states, i.e., low-spin in solid state and high-spin in DMSO. **2** and **3** each shows three absorption bands near ~530, ~680, and ~770 nm in DMSO. The solution spectra of **4** and **5** in DMSO have one absorption band at 530 nm, demonstrating a planar configuration about the Ni(II) ion in this solvent. In pyridine, all the complexes **1–5** show four absorption bands in the visible region. It is plausible that in strongly donative pyridine all the complexes assume a similar geometry around each Ni(II), probably a distorted six-coordination with two pyridine molecules at the axial sites.

Electrochemical properties. Elecrochemical properties of the Ni_2(II,II) complexes **1–3** and the reference Ni(II)Zn(II) complexes **4** and **5** have been studied by cyclic voltammetry in DMSO and pyridine (see Figs. 2 and 3). The numerical data are summarized in Tables 6 and 7.

In the reduction, **1** shows two reversible or pseudo-reversible couples at -0.80 and -1.10 V (vs. SCE) in DMSO and two couples at -0.88 and -1.07 V in pyridine. They are assigned to the successive reductions at metal centers, Ni_2(II,II)/Ni_2(I,II) and Ni_2(I,II)/Ni_2(I,I), based

Table 5 Visible spectral data of **1–5** [λ/nm (ϵ/dm^{3}mol^{-1}cm^{-1})]

Complex	*on powder*	*in dmso*	*in pyridine*
1	505 580	560(110) 650(15)	500(330) 680(44) 810(26) 870(28)
2	540 680 750	525(130) 675(6) 760(4)	550(120) 670(20) 795(13) 859(17)
3	550 700 750	540(140) 680(10) 770(6)	550(140) 675(28) 800(20) 880(22)
4	550	530(120)	495(230) 660(18) 803(12) 880(11)
5	550	525(130)	495(150) 647(16) 804(9) 882(11)

Extinction coefficients per Ni.

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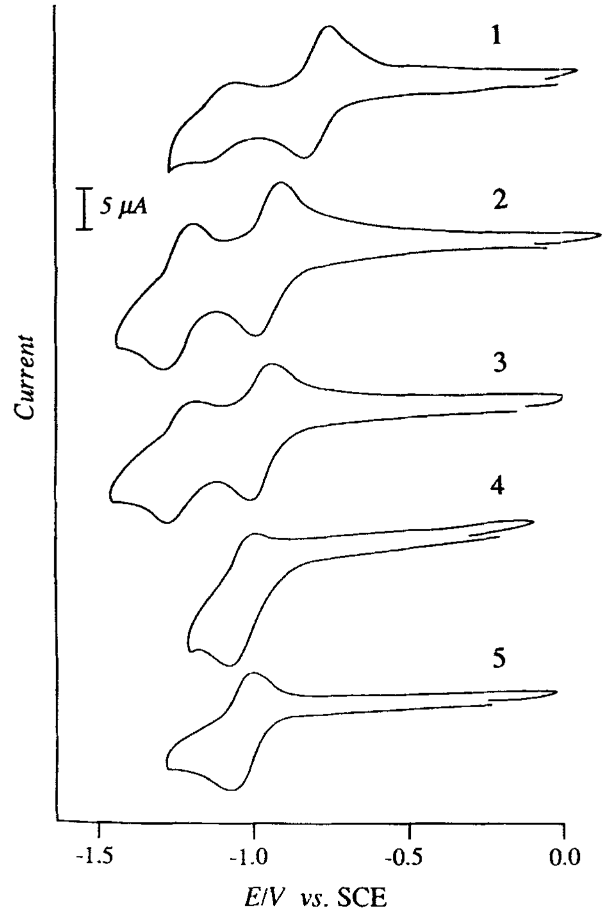

Figure 2 Cyclic voltammograms of **1–5** in DMSO.

on coulometry experiments. The corresponding waves of **2** and **3** appear at slightly lower potentials; ~-0.96 and ~-1.24 V in DMSO and ~-0.93 and ~-1.25 V in pyridine. It should be emphasized that the corresponding reductions of the analogous $[Ni_2(L^{m,n})]^{2+}$ complexes occur at significantly lower potentials (< -1.5 V).[29] Evidently, the Ni_2(I,II) and Ni_2(I,I) complexes are stabilized by the C=N groups. In the case of **2** and **3**, two Ni(II) ions are not equivalent as proved by the mixed-spin in the solid, but we can not specify the metal site reduced at the first reduction from the survey of the CV data. We have also noticed that **4** and **5** show a wave due to the Ni(II)Zn(II)/Ni(I)Zn(II) process at nearly the same potential in DMSO (-1.03 V) and in pyridine (-0.98 V), in spite of the different spin state in the two solvents.

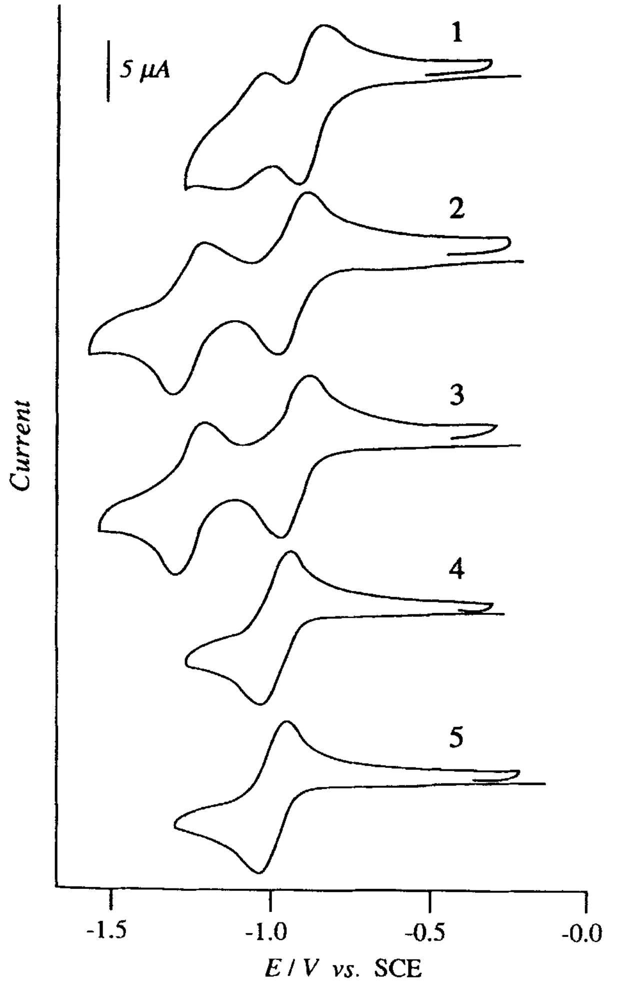

Figure 3 Cyclic voltammograms of **1–5** in pyridine.

In the oxidation in DMSO or pyridine, **1–5** showed no wave in the available potential. For the analogous $[Ni_2(L^{m,n})]^{2+}$ complexes, the metal-centered oxidation waves are observed near +0.7 ~+1.4 V.[29] Thus, the saturation at the C=N linkages of $(R^{m,n})^{2-}$ gives rise to the stabilization of the higher oxidation states of the dinuclear complexes.[15,30,35]

Ni_2(I,II) and Ni_2(I,I) complexes. The stability of the mixed-valent Ni_2(I,II) complexes is expressed by the conproportionation constant K_{con} for the equilibrium:

Ni_2(II,II) + Ni_2(I,I) = $2Ni_2$(I,II)

$K_{con}=[Ni_2(I,II)]^2/[Ni_2(II,II)][Ni_2(I,I)]$. The K_{con} values

Table 6 Electrochemical data of **1–5** [V vs. SCE] and conproportionation constants for Ni_2(I,II) complexes in dmso

Complex	*Ni_2(II,II)/Ni_2(I,II)*			*Ni_2(I,II)/Ni_2(I,I)*			*K_{con}*
	E_{pa}	E_{pc}	$E^1_{1/2}$	E_{pa}	E_{pc}	$E^2_{1/2}$	
1	-0.76	-0.83	-0.80	-1.07	-1.14	-1.10	1.2×10^5
2	-0.91	-0.98	-0.95	-1.20	-1.28	-1.24	8.1×10^4
3	-0.94	-1.00	-0.97	-1.20	-1.27	-1.24	3.7×10^4
4	-1.00	-1.06	-1.03				
5	-1.00	-1.06	-1.03				

Scan rate 100 m Vs^{-1}; galssy carbon electrode: $E_{1/2}=(E_{pc}+E_{pa})/2$.

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Table 7 Electrochemical data of **1–5** [V vs. SCE] and conproportionation constants for $Ni_2(I,II)$ complexes in pyridine

Complex	*$Ni_2(II,II)/Ni_2(I,II)$*			*$Ni_2(I,II)/Ni_2(I,I)$*			*K_{con}*
	E_{pa}	*E_{pc}*	*$E^1{}_{1/2}$*	*E_{pa}*	*E_{pc}*	*$E^2{}_{1/2}$*	
1	-0.85	-0.91	-0.88	-1.04	-1.10	-1.07	1.6×10^3
2	-0.90	-0.96	-0.93	-1.21	-1.28	-1.25	2.6×10^5
3	-0.89	-0.95	-0.92	-1.20	-1.27	-1.24	2.6×10^5
4	-0.95	-1.01	-0.98				
5	-0.95	-1.01	-0.98				

Scan rate 100 m Vs^{-1}; galssy carbon electrode; $E_{1/2}=(E_{pc}+E_{pa})/2$.

can be electrochemically obtained using the equation, $\log K_{con} = \Delta E_{1/2}/0.0591$ (at 25 °C) where $\Delta E_{1/2} = E^1{}_{1/2} - E^2{}_{1/2}$.[15] The K_{con} values of **1–3** have been determined by this method and the results are included in Tables 6 and 7. It is seen that in DMSO **1** is the most stable in the mixed-valent $Ni_2(I,II)$ state while in pyridine **2** and **3** are more stable than **1** in the mixed-valent state. These results suggest a significant solvation effect upon the stabilization of the mixed-valent complexes.

The $Ni_2(I,II)$ and $Ni_2(I,I)$ complexes of **1–3**, generated in situ in DMSO, were subjected to visible spectral and esr studies. The Ni(I)Zn(II) complexes of **4** and **5** were also studied for comparison. Relevant visible spectra are given in Figs. 4–6. The numerical data are summarized in Table 8.

It is generally seen that the visible band intensity increases in the order: $Ni_2(II,II) < Ni_2(I,II) < Ni_2(I,I)$. Because of this reason, the $Ni_2(I,II)$ complexes of **1–3** show simplified visible spectra in spite of the presence of a high-spin Ni(II) ion in each complex (see ESR spectral discussion given below). It should be pointed out that the spectral features of the $Ni_2(I,II)$ and $Ni_2(I,I)$ complexes of **1–3** and the Ni(I)Zn(II) complexes of **3–4**, on the whole, resemble each other, showing one or two bands in the visible region. This is rationalized by the visible spectral resemblance of planar d^8 and d^9 metal ions.[34] The visible bands found for the $Ni_2(I,I)$ and Ni(I)Zn(II) complexes are assigned to d-d transitions bands of the planar Ni(I) ion.[36b]

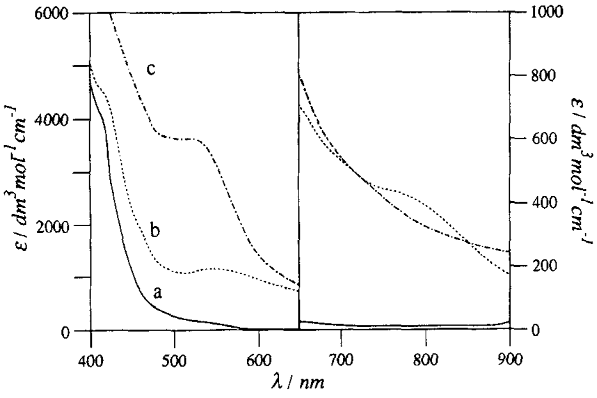

Figure 4 Electronic spectra of **1** (a) and its $Ni_2(I,II)$ (b) and $Ni_2(I,I)$ (c) complexes in DMSO.

The most noticeable characteristic in the visible spectrum of the $Ni_2(I,II)$ complex of **1** is the broad band with a moderate intensity (ca. 400 $dm^3mol^{-1}cm^{-1}$) at ~790 nm. This band is absent in both $Ni_2(II,II)$ (**1**) and its $Ni_2(I,I)$ complexes and can be assigned to the intervalence (IV) transition band in the mixed-valent state. According to Hush's theory,[36] the half-bandwidth ($\Delta\nu_{1/2}$) of IV band is correlated to the band maximum frequency ν_{max} as follows: $\Delta\nu_{1/2} = (2.31\nu_{max})^{1/2}$. Though the band near 790 nm is not well resolved, its half-bandwidth can be evaluated to be 4,000–6,000 cm^{-1} that agrees well with the calculated $\Delta\nu_{1/2}$ value (5400 cm^{-1}) by the above equation. We have also found that this band shifts to ~800 nm in pyridine and to ~810 nm in DMF. The solvent-dependence of the IV band is commonly known

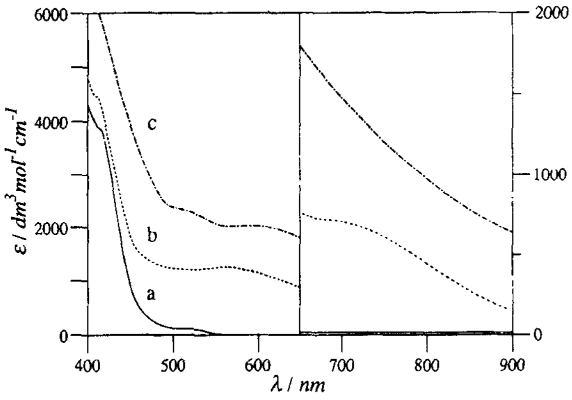

Figure 5 Electronic spectra of **2** (a) and its $Ni_2(I,II)$ (b) and $Ni_2(I,I)$ (c) complexes in DMSO.

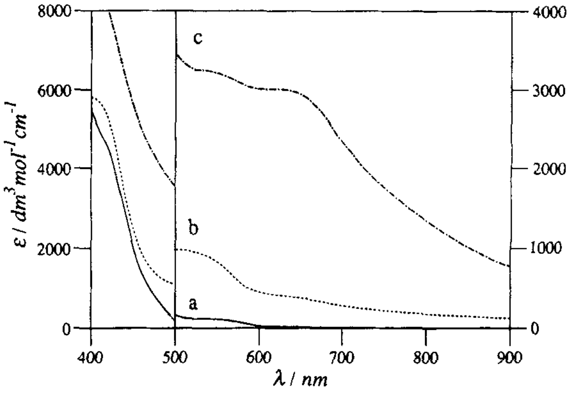

Figure 6 Electronic spectra of **3** (a) and its $Ni_2(I,II)$ (b) and $Ni_2(I,I)$ (c) complexes in DMSO.

Table 8 Visible spectral data of $Ni_2(I,II)$ and $Ni_2(I,I)$ complexes of **1–3** and Ni(I)Zn(II) complexes of **4–5** [λ/nm (ϵ/$dm^3mol^{-1}cm^{-1}$)]

Complex	*$Ni_2(I,II)$*		*$Ni_2(I,I)$*	
1	545(1100)	790(400)	530(3500)	
2	575(1000)	700(550)	520(2200)	600(2000)
3	540(880)	650(370)	540(3200)	640(2900)
			Ni(I)Zn(II)	
4			540(500)	650(140)
5			530(510)	650(150)

λ/nm (ϵ/$dm^3mol^{-1}cm^{-1}$)

and the trend observed for the $Ni_2(I,II)$ complex seems to follow Hush's theory:[36] $\nu_{max} \propto (1/n^2)-(1/D)$ (n is the refractive index and D is the dielectric constant of the solvent). The electron delocalization coefficient, α^2, can be calculated by the equation[37] $\alpha^2 = (4.25\times10^{-4}) \times \epsilon_{max}\Delta\nu_{1/2}/\nu_{max}r^2$, where r is the intermetal separation. The α^2 value for this complex is calculated to be 0.009 using r=2.8 Å, $\Delta\nu_{1/2}$= 5400 cm^{-1}, ν_{max}=12700 cm^{-1}, and ϵ=400 $dm^3mol^{-1}cm^{-1}$. Thus, the $Ni_2(I,II)$ complex of **1** belongs to Class II in the classification of Robin and Day.[37] The IV band of the $Ni_2(I,II)$ complex of **2** appears at a shorter wavelength (~700 nm) and is broadened due to the superposition on a d-d component near 650 nm. For this mixed-valent complex, a smaller α^2 value (<0.005) is estimated. The corresponding IV band is not resolved for the mixed-valent complex of **3**. A candidate is the discernible absorption band at 650 nm which, however, can be assigned to a d-d component of Ni(I), because the Ni(I)Zn(II) complexes of **4** and **5** also show an absorption band at 650 nm. It appears that the two Ni ions of **3** differ markedly in electronic nature, due to the different lateral chains $-(CH_2)_2-$ and $-(CH_2)_4-$, providing a spin-localized (Class I) $Ni_2(I,II)$ complex.

The $Ni_2(I,II)$ complexes of **1–3** and the Ni(I)Zn(II) complexes of **4** and **5** are all esr-active and show well-resolved esr signals at liquid nitrogen temperature. The relevant esr spectra are shown in Fig. 7.

The $Ni_2(I,II)$ complex of **1** shows a rhombic esr spectrum with signals at g_1=2.27, g_2=2.20, and g_3=2.05 (trace **a**). On the other hand, the esr spectra of the $Ni_2(I,II)$ complexes of **2** and **3** apparently have an axial pattern with $g_{//}$ ~2.35 and $g_\perp$~2.08 (trace **b**). The esr spectra of the Ni(I)Zn(II) complex of **4** and **5** are complicated and show three signals at g~2.35, ~2.27, and ~2.20 and a stronger signal at g~2.07 (trace **c**). Such a spectral feature is unexpected for planar Ni(I)[38] that usually shows an axial pattern of $g_{//}>g_\perp$. However, if we suppose that the spectra are the superposition of two sets of signals, A (g~2.36 and ~2.07 (axial)) and B (g~2.27, ~2.20, and ~2.05 (rhombic); the signal near g~2.05 is probably concealed by the g~2.07 signal of the former), the set A is indeed the axial pattern characteristic of d^9 metal ions. At this stage we only point out two possibilities as the origin for the rhombic signals (B); (1) the Ni(I)Zn(II) complexes exist as two species differing in solvation and hence in ground-state electronic configuration or (2) the rhombic signals (set B) originate from a contaminant formed on the electrode.

The well-resolved esr spectra of the $Ni_2(I,II)$ complexes of **1–3** at liquid nitrogen temperature suggest a strong antiferromagnetic spin-coupling between Ni(I)(S=½) and Ni(II)(S=1) ions. In fact, very large negative exchange integrals of -J=103 ~110 cm^{-1} (based on $H=-2JS_1\cdot S_2$) have been reported for the isoelectronic Cu(II)Ni(II) complexes of $(R^{3,3})^{2-}$ and related

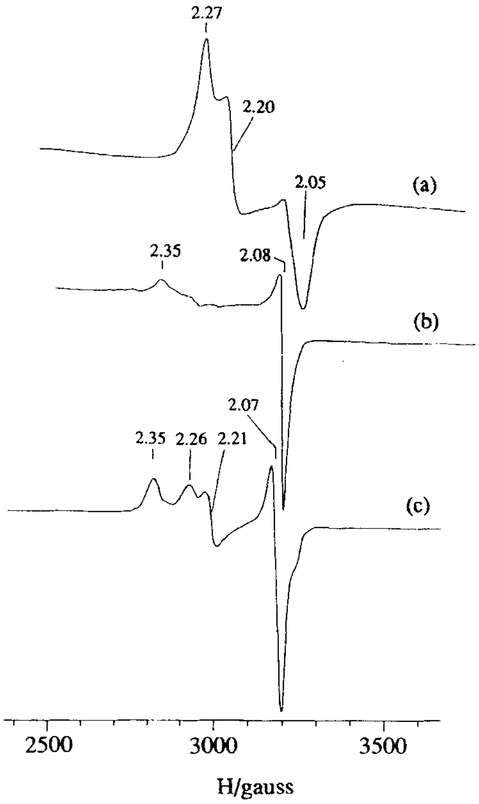

Figure 7 ESR spectra of $Ni_2(I,II)$ complexes of **1** and **2** (traces a and b respectively) and Ni(I)Zn(II) complex of **4** (c): in DMSO at liquid nitrogen temperature.

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ligands.[13e,39] Further, we have found a large negative exchange integral (-J=90 cm^{-1}) for [CuNi(R^{2,4})](ClO$_4$)$_2$·H$_2$O.[40] If we suppose a similar antiferromagnetic interaction for the Ni$_2$(I,II) complexes of **1–3**, the spin-quartet excited state is about 300 cm^{-1} (=3J) above the spin-doublet ground state. The energy separation is large enough to allow the thermal population only on the spin-doublet ground state at liquid nitrogen temperature. Based on the above discussion, we may conclude that the ESR spectra of the Ni$_2$(I,II) complexes certainly arise from the spin-doublet ground state (S_T=½).

The ESR spectral difference between the Ni$_2$(I,II) complex of **1** (rhombic) and those of **2** and **3** (axial) must reflect the different electronic nature of the mixed-valence complexes. The axial ESR spectra of the Ni$_2$(I,II) complexes of **2** and **3** indicate the valence-localization in the spin-coupled (S_T=½) ground state, giving a (S_1=½)–(S_2=0) system similar to the Ni(I)(S_1=½)–Zn(II)(S_2=0) of **4** and **5**. Evidently this is not the case of the Ni$_2$(I,II) complex of **1**. The rhombic pattern of trace **a** might indicate a partial valence-delocalization in the Ni$_2$(I,II) in frozen DMSO solution.

The Ni$_2$(I,I) complexes of **1–3** are esr-innocent. This is probably because of a strong antiferromagnetic interaction between a pair of Ni(I) (S=½) ions. Very large negative exchange integrals (-J=294~429 cm^{-1}) have been observed for the isoelectronic Cu$_2$(II,II) complexes of (R^{m,n})$^{2-}$.[28,41]

Supplementary material available. Positional and anisotropic thermal parameters, complete list of of bond distances and angles, and structure factors of [Ni$_2$(R^{2,2})](ClO$_4$)$_2$ (**1**).

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