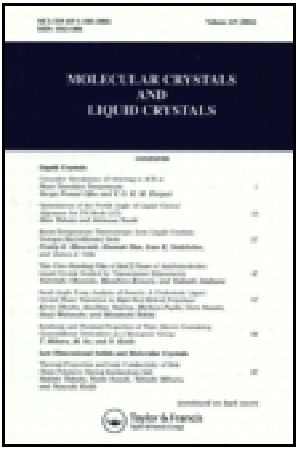

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Dinuclear Phenoxo-Bridged Nickel(II) Complexes of Macrocyclic Ligands with Cyano Groups Laterally Introduced on a Conjugated System within the Ligands

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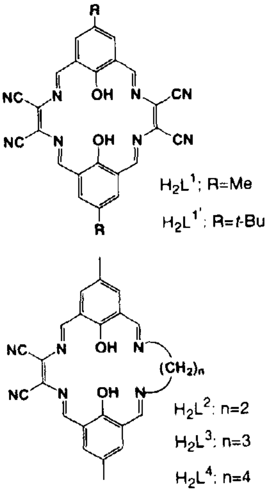
Diphenoxo-bridged dinuclear nickel(II) complexes of macrocyclic ligands having two cyano groups laterally introduced on a π-conjugated system within the ligands have been prepared and characterized. The reaction solvent DMF is coordinated to the nickel(II) ions to cause them high spin state. The antiferromagnetic interaction (J = ca. $-10\ \mathrm{cm}^{-1}$) was observed between the nickel(II) ions.

Keywords: dinuclear nickel(II) complex; macrocyclic ligand; π-conjugated system; cyano groups

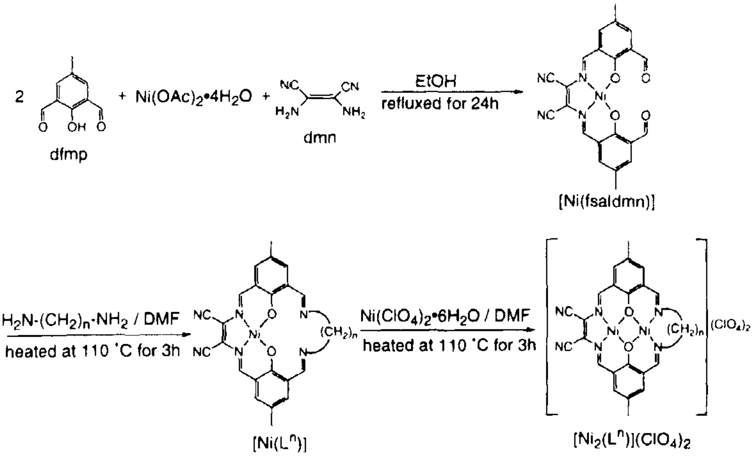
INTRODUCTION

There have been numerous reports on multinuclear complexes with macrocyclic ligands derived from condensation reaction of 2,6-diformyl-4-alkylphenol and diamine.[1] However, only a few dinuclear complexes of macrocyclic ligands with electron-withdrawing groups laterally introduced on a π-conjugated system within the ligands have been known.[2] Thompson et al. have prepared dinuclear copper(II) complexes of marcocyclic ligands (HL^1 and $H_2L^{1'}$ (see Scheme 1)) having electron-withdrawing cyano groups on the conjugated systems using diaminomaleonitrile (dmn) in combination with the dialdehydes 2,6-diformyl-4-methylphenol (dfmp) and 2,6-diformyl-4-*t*-butylphenol (dfbp).[3] The obtained dinuclear complexes showed a reduction in antiferromagnetic coupling between the copper(II) ions through the phenoxo-bridgings by the introduction of the CN groups. Although we tried to prepare dinuclear nickel(II) complexes of the ligands, we could not succeed in isolating the complexes. Because the mononuclear complex of the ligand H_2L^1 could be obtained, it has been considered that the central holes within the ligands are not large enough for accommodating two nickel(II) ions.



Scheme 1

In this study, the dinucleating ligands H_2L^2, H_2L^3 and H_2L^4 (Scheme 1) have been newly prepared and employed to produce the dinuclear nickel(II) complexes with the expectation that the enlarged hole size would make the dinuclear complexation possible. The complexes were prepared stepwise as shown in Scheme 2. We could not obtain the dinuclear complex of H_2L^2 probably due to the hole size problem as in the case of H_2L^1.



Scheme 2

EXPERIMENTAL

Preparations

[Ni(fsaldmn)] $Ni(OAc)_2{\bullet}2H_2O$ (5 mmol) and dfmp (10 mmol) were dissolved together in ethanol (50 cm^3), and the mixture was refluxed for 10 min., forming greenish yellow solution. The ethanol solution (20 cm^3) of dmn (5 mmol) was added dropwise to the mixture, being refluxed for 24 h. A bluish green precipitate formed was collected by filtration, washed with ethanol, and dried over P_2O_5 under vacuum (yield 96 %). Anal. Found C, 57.32; H, 3.15; N, 12.31%. Calcd for $C_{22}H_{14}N_4NiO_4$: C, 57.81; H, 3.09; N, 12.26%.

$[NiL^n]{\bullet}mH_2O$, n=2—4 [Ni(fsaldmn)] (0.88 mmol) was dissolved in DMF (50 cm^3), and to this was added dropwise the diamine (0.88 mmol). The DMF solution was heated at ca. 110 °C with stirring for 3 h. The resultant solution was evaporated to ca. 10 cm^3 and to this was added ethanol to give a brown precipitate, which was filtered off, washed with ethanol, and dried over P_2O_5 under vacuum (yield 80—90 %). Anal. $[NiL^2]{\bullet}2H_2O$; Found C, 55.47; H, 3.93; N, 16.39%. Calcd for $C_{24}H_{22}N_6NiO_4$: C, 55.73; H, 4.28; N, 16.25%. $[NiL^3]{\bullet}2.5H_2O$; Found C, 55.36; H, 4.25; N, 15.47%. Calcd for $C_{25}H_{25}N_6NiO_{4.5}$: C, 55.59; H, 4.66; N, 15.56%. $[NiL^4]{\bullet}2.5H_2O$; Anal. Found C, 55.98; H, 4.51; N, 15.63%. Calcd for $C_{26}H_{27}N_6NiO_{4.5}$: C, 56.34; H, 4.91; N, 15.16%.

$[Ni_2L^n](ClO_4)_2{\bullet}3DMF$, n=3 and 4 The equimolar amounts (0.58 mmol for $[Ni_2L^3](ClO_4)_2$ and 0.60 mmol for $[Ni_2L^4](ClO_4)_2$) of $[NiL^n]$ and $Ni(ClO_4)_2{\bullet}6H_2O$ were dissolved in DMF (100 cm^3) and heated at ca. 110 °C for 3 h. The resultant solution was evaporated to ca. 10 cm^3 and to this was added ethanol to give a brown precipitate, which was filtered off, washed with ethanol, and dried over P_2O_5 under vacuum (yield 60—70 %). Anal. $[Ni_2L^3(ClO_4)_2]{\bullet}3DMF$; Found C, 42.22; H, 3.89; N, 12.52 %. Calcd for $C_{34}H_{41}Cl_2N_9Ni_2O_{13}$: C, 42.01; H, 4.25; N, 12.96 %. $[Ni_2L^4](ClO_4)_2{\bullet}3DMF$; Found C, 43.09; H, 4.13; N, 12.22%. Calcd for $C_{35}H_{43}Cl_2N_9Ni_2O_{13}$: C, 42.63; H, 4.40; N, 12.78%.

Measurements

Infrared spectra were recorded as Nujol mulls using a Mattson Polaris FT-IR instrument. Magnetic susceptibilities were measured by a Faraday method and corrected for diamagnetism of constituent atoms using Pascal's constants.[4]

RESULTS AND DISCUSSION

The dinuclear complexes $[Ni_2L^1](ClO_4)_2$ could not be obtained by the 2:2:2 reaction of $Ni(ClO_4)_2{\cdot}6H_2O$, dfmp, and dmn. Alternatively, we tried to prepare the dinuclear complexes according to Scheme 2. The 2:1 condensation reaction of dfmp and dmn in the presence of nickel(II) ion proceeded to give the mononuclear complex [Ni(fsaldmn)], the structure of which was determined by the X-ray structure analysis for the one recrystallized from pyridine (FIGURE 1).[5] The nickel(II) ion adopts octahedral configuration with axial coordination of pyridine other than equatorial coordination by fsaldmn. The structural feature of the ligand moiety is almost the same as that of [Cu(saldmn)(DMSO)].[6]

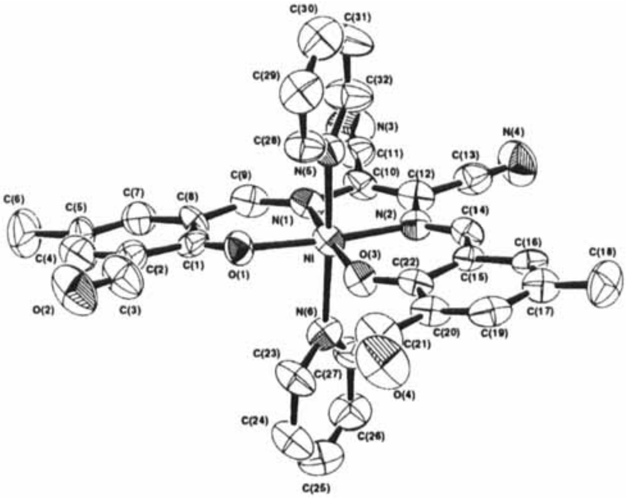


FIGURE 1 ORTEP view of $[Ni(fsaldmn)(py)_2]$. Selected bond distances (l/Å) and angles (ϕ/°) are Ni-O(1) 1.978(8), Ni-O(3) 1.999(8), Ni-N(1) 2.048(9), Ni-N(2) 2.015(9), Ni-N(5) 2.156(9), Ni-N(6) 2.137(9), O(1)-Ni-N(2) 172.1(4), O(3)-Ni-N(1) 172.8(4), N(5)-Ni-N(6) 173.4(5).

The dinuclear complexes $[Ni_2L^n](ClO_4)_2$ (n=3 and 4) were synthesized through mononuclear complexes $[NiL^n]$ (n=3 and 4). However, we could not obtain $[Ni_2L^2](ClO_4)_2$ through the corresponding mononuclear complex. The elemental analysis revealed that the metal insertion was not sufficient similarly to the result of the 2:2:2 reaction of $Ni(ClO_4)_2{\cdot}6H_2O$, dfmp, and dmn. Our repeated efforts to complete the metal insertion have been all in vain so far. It is considered that the central holes of the ligand H_2L^2 are also too small to accommodate two nickel ions.

The IR spectra of the dinuclear complexes show no NH stretching band. The bands coming from the C≡N vibration appear at 2224 cm^{-1}($[Ni_2L^3](ClO_4)_2\cdot 3DMF$) and 2222 cm^{-1} ($Ni_2L^4](ClO_4)_2\cdot 3DMF$). The presence of ClO_4^- ions free from coordination is confirmed by predominant single bands around 1100 cm^{-1} for both the complexes. Strong absorptions at 1643 cm^{-1} of the complexes could be assigned as the stretching band of the C=N double bonds within the ligands, which is probably superposed with that of the C=O bond of DMF molecules judging from the relative intensities.

The room temperature magnetic moments (per nickel atom) of the dinuclear complexes are 2.63 BM ($[Ni_2L^3](ClO_4)_2\cdot 3DMF$) and 2.86 BM($[Ni_2L^4](ClO_4)_2\cdot 3DMF$), the nickel(II) ion being assumed to be a high spin state. The DMF molecules could take part in axial coordination to the metal ions. The magnetic susceptibilities were measured in the temperature range 80—300 K (FIGURE 2). The magnetic moments

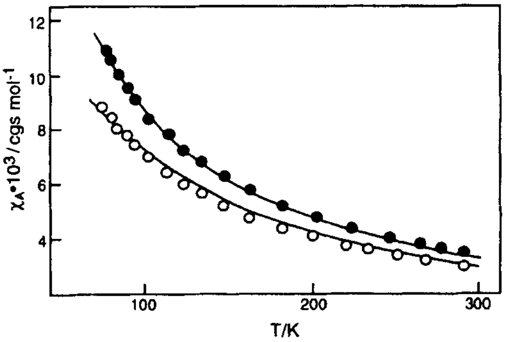


FIGURE 2 Temperature variation of magnetic susceptibility of $[Ni_2L^3](ClO_4)_2\cdot 3DMF$ (O) and $[Ni_2L^4](ClO_4)_2\cdot 3DMF$ (●). Solid curves are drawn with the parameters $g=1.97$, $J=-13$ cm^{-1}, and $N\alpha=50\times10^{-6}$ cgs mol^{-1} for $[Ni_2L^3](ClO_4)_2\cdot 3DMF$ and $g=2.00$, $J=-7.5$ cm^{-1}, $N\alpha=100\times10^{-6}$ cgs mol^{-1} for $[Ni_2L^4](ClO_4)_2\cdot 3DMF$.

decrease with lowering of temperature (2.33 BM at 80.7 K ($[Ni_2L^3](ClO_4)_2\cdot 3DMF$) and 2.57 BM at 81.3 K ($[Ni_2L^4](ClO_4)_2\cdot 3DMF$), which indicates that antiferromagnetic interaction is operative between the nickel(II) ions. The data were analyzed by the Van Vleck equation based on the Heisenberg model (H=-2JS_1•S_2). The magnetic coupling constants J were estimated as –13 cm^{-1} ([Ni_2L^3](ClO_4)$_2$•3DMF) and –7.5 cm^{-1} ([Ni_2L^4](ClO_4)$_2$•3DMF). These values are small compared with previously reported dinuclear high-spin nickel(II) complexes with Schiff-base macrocyclic ligands (J=-23—-36 cm^{-1}).[7] This might be explained with the electron-withdrawing effect of the CN groups on the magnetic interaction as has been reported on the dinuclear copper(II) complexes of the Schiff-base macrocyclic ligands.[3]

In this study, we successfully obtained the dinuclear nickel (II) complexes of macrocyclic ligands having two cyano groups on a lateral π-conjugated system within the ligands. We regard the dinuclear complexes as precursors to increase multinuclearity by further coordination of the CN groups to the other metal ions or conversion of the CN groups to the other coordinating groups like imino nitrogen. Such study is in progress in our laboratories.

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