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RESONANCE RAMAN STUDIES OF A DIOXY-TETRAAZA-NICKEL COMPLEX CONTAINING A COFACIAL DIMERIC STRUCTURE

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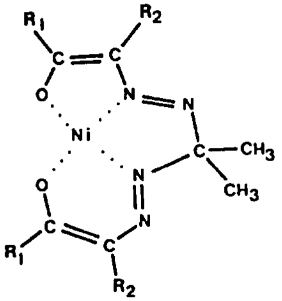
ABSTRACT

The electronic absorption and resonance Raman (rR) spectra of a planar Ni(II) N_2O_2-core complex were measured in solution as well in the solid state. Excitation within the contour of the first CT transition produced rR enhancement mainly of internal ligand vibrations. In the solid state the electronic structure is dominated by the properties of a face-to-face dimer.

INTRODUCTION

The significant role of highly conjugated macrocyclic ligands in biological processes and in "molecular metals" suggests that highly conjugated synthetic macrocyclic ligand may confer unusual properties on coordinated metals as well. The cooperative functioning of pairs of metal atoms has attracted attention to dimeric complexes. Side-by-side dimers have received much attention. Face-to-face dimers are represented by dimeric porphyrins or dihydrooctaaza (14) annulene complexes. In an effort devotes to the syntheses of dimeric complexes in which the metal ion proximity is enforced by the ligands, we have studied the molecular and crystalline structure of several Dioxy-Tetraaza-Nickel complexes.



$R_1 = R_2 = C_6H_5$ noted Ni MMK

$R_1 = C_6H_5$, $R_2 = H$ noted Ni HMK

$R_1 = R_2 = CH_3$ noted Ni DMK

We report here a resonance Raman (rR) study of the planar Dioxy-Tetraaza-Nickel (II) complex Ni HMK, which exhibits a cofacial dimeric structure, in solution as

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well in the solid state to provide information on the electronic structure and the molecular interaction.

EXPERIMENTAL

The nickel (II) macroligand complexes Ni MMK, Ni HMK and Ni DMK were prepared by template reaction from monohydrazone derivatives and acetone according to the procedure previously described (ref. 1). The starting materials are : diphenyl glyoxal monohydrazone $R_1 = R_2 = C_6H_5$; phenyl glyoxal monohydrazone $R_1 = C_6H_5$, $R_2 = H$; biacetyl monohydrazone $R_1 = R_2 = CH_3$; nickel (II) acetate ; and acetone.

The ^1H, ^{13}C NMR spectra were obtained with a Bruker WP 80 spectrometer.

The infrared spectra were recorded at room temperature on a Bruker IFS 113 Fourier transform spectrometer with KBr disc or Nujol mull (4000 - 400 cm^{-1}) and polyethylene disc (400 - 50 cm^{-1}).

U.V. visible spectra were run at room temperature in chloroform solution or in the solid state using KBr pellets.

The Raman spectra were obtained at room temperature using a Dilor RTI instrument equipped for photon counting and accumulation of spectra. Seven lines (457.9, 465.8, 472.7, 476.5, 488.0, 501.7, 514.5 nm) of a Spectra-Physics Ar^+ laser and three lines (530.9, 568.2, and 647.1 nm) of a Spectra-Physics Kr^+ laser were used for the excitation. Solid samples were in the form of KBr pellets and K_2SO_4 was added as internal standard. Samples were rotated to avoid decomposition.

The Raman spectra of the static samples, small monocristal or concentrated solution were carried out with a Microdil 28 multichannel instrument equipped with photodiode array, using low power at sample. The same objective of a conventional optical microscope is used to focus the laser beam into a spot on the part of the sample to be analysed and to collect the scattered light at the focal point.

RESULTS

Structures

The ^1H NMR spectra of Ni DMK are in good agreement with a planar Cs symmetry in solution. Conventional ^1H and ^{13}C NMR spectra of Ni HMK and Ni MMK does not permit to obtained the molecular structure. However the AP test (ref. 2) gives a spectrum in accordance with a Cs symmetry as for Ni DMK.

In the solid state, if the molecular structures of Ni MMK and Ni HMK are analogous and close to Cs symmetry, the crystalline arrangements are very different. Indeed in Ni MMK (ref. 3), the closest intermolecular distance are 3.39 Å between two carbon atoms of the pheny group, the closest Ni-Ni distance is 5.586 Å and too great for metal-metal interaction. The crystalline structure of Ni HMK (ref.4) consists of discreet centrosymmetric dimeric moieties containing a cofacial bimolecular association with a Ni-Ni distance of 3.303 Å. The displacement of the Ni atoms from the N_2O_2 donor atom plane toward on another indicates a reasonably weak Ni-Ni bond.

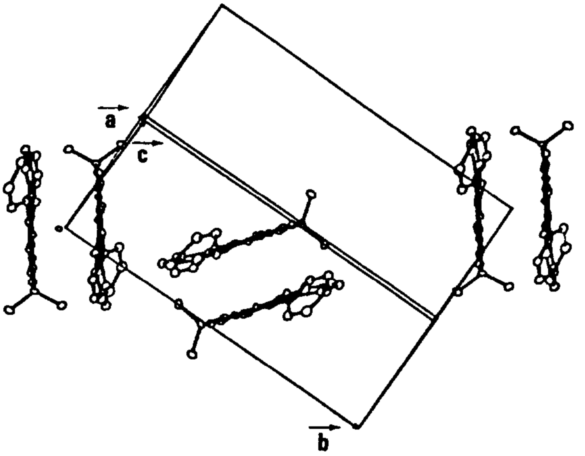

Fig. 1 : Structure of Ni HMK

Infrared (i.r.) and Raman (R) spectra (λ_0 = 647.1 nm)

A comparison between the solid state spectra of Ni HMK and the spectra recorded in solution, where the dimeric structure is not present, suggests that most fundamentals are scarcely perturbed by the dimeric interaction and makes reasonable the use of an approximate model with Cs symmetry.

The vibrations of Ni HMK can be classified in three groups : vibration modes of the phenyl and methyl groups, modes of the chelate ring and nickel-ligand modes. The in-plane aromatic CH stretching fundamentals are assigned to the group of weak bands between 3100 and 3000 cm^{-1}, the azomethinic C-H stretching modes can be assigned at the same wavenumbers. The ir and R bands around 1600 and 1000 cm^{-1} are assigned to stretching modes of the phenyl groups. The medium bands in the range 1300-1400 cm^{-1} is relevant to C-H deformation modes of CH$_3$ group. The ir and R bands at 1475, 1440 and 1335 cm^{-1} are tentitatively attributed to the skeletal stretching modes ν C---N, ν C---C and ν N---N of the macroligand. The intense ir band at 1150 cm^{-1} is attributed to the C-O stretching mode. The bands at 450 and 250 cm^{-1} are assigned to the ν Ni-O and ν Ni-N vibration respectively.

Resonance Raman (rR) spectra

Raman spectra (1700-500 cm^{-1}) recorded with different exciting radiations within the contour of the first electronic transition are carried out in solution as well in the solid state. The electronic spectrum together with excitation profiles of some Raman modes for Ni HMK in the solid state are shown in figure 2.

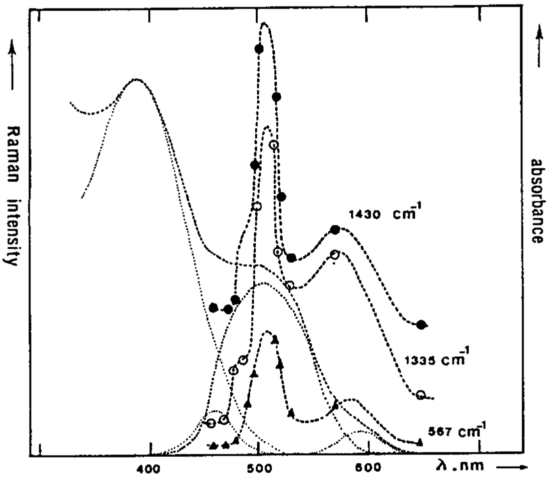

Fig. 2 : Excitation profiles and electronic spectrum of Ni HMK.

All of the Raman peaks observed in the r R spectra are polarized (I / I//≈0.3) demonstrating that only the Raman scattering due to the symmetric vibrations is apprecially resonance enhanced. We thus conclude that Franck-Condon effects (A term of the Albrecht equation) are mainly responsible for the observed r R results while any contribution of a vibronic coupling (B term) must be negligeable. The electronic spectrum is assigned to a charge transfer metal-ligand on the basis of the resonance profiles. These profiles in the solid state exhibit maxima about 30 mn lower than the corresponding profiles in solution and a supplementary maximum attributed to electronic interaction between the two adjacent molecules in the solid state.

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