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Noncovalent Interactions in Metal Complexes. VI.[1] Bonding Interaction between Chelate π-System and Menthyl Group in Copper(II), Nickel(II), and Palladium(II) Complexes of 1-*l*-Menthyloxy-3-benzoylacetone

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Metal complexes, M(*l*-moba)$_2$(H$_2$O)$_n$ (M=Cu(II), n=0; Ni(II), n=2; Pd(II), n=0) and M(bpy)(*l*-moba)ClO$_4$ (M=Cu(II), Pd(II)), where H(*l*-moba) denotes 1-*l*-menthyloxy-3-benzoylacetone, have been synthesized and characterized by means of elemental analyses, NMR spectra, electronic spectra, and circular dichroism spectra. In the NMR spectra of H(*l*-moba), Pd(*l*-moba)$_2$, and Pd(bpy)(*l*-moba)ClO$_4$, the methylene protons adjacent to the *l*-menthyloxy group were observed as AB quartet. The chloroform solutions of Cu(*l*-moba)$_2$ and Cu(bpy)(*l*-moba)ClO$_4$ showed a positive CD band at 15500 and 16200 cm^{-1}, respectively. The chloroform solution of Ni(*l*-moba)$_2$(H$_2$O)$_2$ also showed a weak, positive CD band near 16000 cm^{-1}. When pyridine or *t*-butylamine was added to the chloroform solution of Cu(*l*-moba)$_2$, a negative CD appeared around 17000 cm^{-1} attributable to the five-coordinate species Cu(*l*-moba)$_2$B. On the other hand, with adding an amine to the chloroform solution of Ni(*l*-moba)$_2$(H$_2$O)$_2$, the 16000 cm^{-1} CD band decreased its intensity and finally disappeared. Similar trend was observed when alcohol, DMSO, or DMF was added to the chloroform solution of Ni(*l*-moba)$_2$(H$_2$O)$_2$. NMR and CD spectral results have been rationalized by assuming that the *l*-menthyl group interacts with the chelate ring of *l*-moba$^-$ and this interaction gives rise to a chirality around the metal ion.

Inter-ligand, noncovalent interactions which cause stereoselectivity and stereospecificity in metal complexes are of current interest, because of their importance in biological processes involving metal ion.[2–6] Recently we reported[2] that tris(1-*l*-menthyloxy-3-benzoylacetonato)M(III) complexes, M(*l*-moba)$_3$ (M=Co, Cr, and Mn), prefer the *cis*-Δ-configuration, and this was attributed to an inter-ligand CH/π-interaction between the *l*-menthyl group of the ligand and the phenyl group of the neighbouring ligand in the molecule; on the other hand, no CD induction was observed in the cases of Cu(*l*-moba)$_2$, Ni(*l*-moba)$_2$(H$_2$O)$_2$, Co(*l*-moba)$_2$(H$_2$O)$_2$, and Mn(*l*-moba)$_2$(H$_2$O)$_2$.

In this study, the CD spectra of Cu(*l*-moba)$_2$ and Ni(*l*-moba)$_2$(H$_2$O)$_2$ were reexamined in a highly concentrated chloroform solution, and it was noticed that these complexes show a weak CD band in the d-d band region. It is known that Cu(*l*-moba)$_2$ and Ni(*l*-moba)$_2$(H$_2$O)$_2$ take a square planar and a *trans*-octahedral configuration, respectively.[2] In these configurations, the phenyl group of the ligand is considerably separated from the *l*-menthyl group of the other ligand,and hence it is unlikely that there operates an inter-ligand, CH/π-interaction between these two groups. In this study, new metal complexes, Pd(*l*-moba)$_2$ and M(bpy)(*l*-moba)ClO$_4$ (M=Cu(II), Pd(II)), were prepared and the configurations of the complexes including Cu(*l*-moba)$_2$ and Ni(*l*-moba)$_2$(H$_2$O)$_2$ were examined by means of NMR, electronic absorption, and circular dichroism spectra, in a hope to clarify the mechanism how the *l*-menthyl group of the ligand invokes a chirality around the central metal ion.

Experimental

Preparations. Synthetic methods of H(*l*-moba) and its nickel(II) and copper(II) complexes, Ni(*l*-moba)$_2$(H$_2$O)$_2$ and Cu(*l*-moba)$_2$, are described in the preceding paper.[2] Benzyl *l*-menthyloxyacetate was synthesized by the reaction of *l*-menthyloxyacetyl chloride[7] and benzyl alcohol, in a similar way to that for ethyl *l*-menthyloxyacetate.

1-Ethoxy-3-benzoylacetone (Heoba). This was prepared from ethyl ethoxyacetate and acetophenone by a method similar to that for H(*l*-moba). It was isolated and purified as nickel(II) complex Ni(eoba)$_2$(CH$_3$OH)$_2$.

Found: C, 58.55; H, 6.47%. Calcd for C$_{26}$H$_{34}$O$_8$Ni: C, 58.56; H, 6.43%.

The free ligand was obtained as follows. The nickel complex (2 g) was dissolved in ether (100 cm^3). To this was added 20% sulfuric acid (100 cm^3) and the mixture was vigorously shaken. The ether layer was separated, shaken twice with saturated sodium hydrogencarbonate solution and then twice with water, and dried over sodium sulfate. Evaporation of the solvent left Heoba as a colorless liquid.

*Pd(*l*-moba)$_2$.* Palladium chloride (0.2 g, 1.12 mmol) and ammonium chloride (0.12 g, 2.24 mmol) were added to methanol (30 cm^3), and the mixture was vigorously stirred for 2 h to give a brown solution. To this was added dropwise a methanol solution of H(*l*-moba) (0.71 g, 2.24 mmol) and KOH (0.13 g, 2.24 mmol). A cream yellow precipitate thus obtained was collected and recrystallized from methanol.

Found: C, 64.92; H, 7.35%. Calcd for C$_{40}$H$_{54}$O$_6$Pd: C, 65.17; H, 7.38%.

*Cu(bpy)(*l*-moba)ClO$_4$·2H$_2$O.* A solution of Cu(bpy)$_2$(ClO$_4$)$_2$ (0.08 g, 0.14 mmol) and Cu(*l*-moba)$_2$ (0.1 g, 0.14 mmol) in methanol (100 cm^3) was heated for an hour. The reaction mixture was concentrated to 20 cm^3 and water was added drop by drop to this mixture to give a green precipitate. It was collected and recrystallized from methanol–water as green crystals. The product appeared to be pure crystals under a microscope observation.

Found: C, 53.17; H, 5.90; N, 4.02%. Calcd for C$_{30}$H$_{39}$N$_2$O$_9$ClCu: C, 53.72; H, 5.86; N, 4.18%.

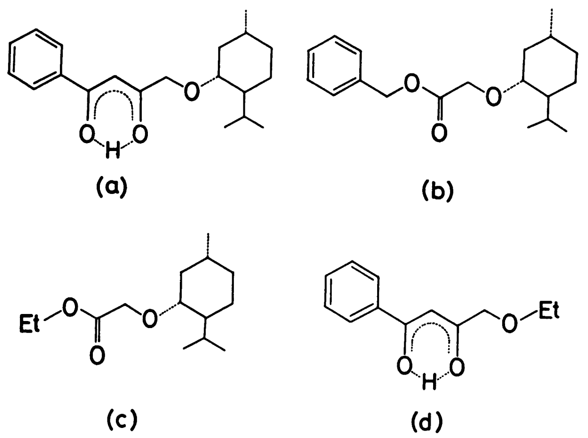
*Pd(bpy)(*l*-moba)ClO$_4$.* To a suspension of Pd(bpy)$_2$Cl$_2$[8] (0.3 g, 1.7 mmol) in methanol (30 cm^3) was added a solution of H(*l*-moba) (0.29 g, 0.9 mmol) and KOH (0.05 g, 0.9 mmol) in methanol (10 cm^3), and the mixture was stirred for 1 h. To this reaction mixture was added a solution of AgClO$_4$ (0.38 g) in methanol to yield a precipitate of AgCl, which was separated by filtration. The filtrate was further stirred for additional 2 h and was filtered. The filtrate was concentrated to 10 cm^3. When water was added drop by drop to the solution, a yellow precipitate was separated. It was collected and dried *in vacuo* over diphosphorus pentaoxide.

Found: C, 52.36; H, 5.13; N, 4.03%. Calcd for $C_{30}H_{35}N_2O_8ClPd$: C, 52.00; H, 5.09; N, 4.04%.

Measurements. NMR spectra were measured on a Hitachi NMR Spectrometer Model R-20-B in carbon tetrachloride and JEOL Fourier Transform NMR Spectrometer FX90Q in $CDCl_3$, tetramethylsilane being used as an internal standard. Circular dichroism spectra were measured on a JASCO ORD/CD optical dispersion recorder. Electronic absorption spectra were measured on a Shimadzu Multipurpose Spectrophotometer Model MSP-5000. The elemental analyses were carried out at the Service Center of Elemental Analysis, Kyushu University.

Results and Discussion

The proton NMR spectra of H(*l*-moba), Pd(*l*-moba)$_2$, and pd(bpy)(*l*-moba)ClO_4 are given in Fig. 2. The most characteristic feature in these spectra is the AB quartet around 4 ppm attributable to the methylene protons adjacent to the *l*-menthyloxy group. One of the possible origins of the AB quartet of the methylene protons is the effect of the chirality of the neighbouring *l*-menthyl group. In order to examine this, we measured the NMR spectra of benzyl *l*-methyloxyacetate and ethyl *l*-menthyloxyacetate (Fig. 1(b) and (c)) and found that the methylene protons adjacent to the *l*-menthyloxy group of these esters appeared as singlet. Therefore, the AB quartet of the methylene protons of H(*l*-moba), Pd(*l*-moba)$_2$, and Pd(bpy)(*l*-moba)ClO_4 should be attributed to a particular configuration of *l*-moba$^-$. We showed in the previous paper[2] that the ligand assumes the enol form in the metal-free state as well as in the metal complexes. However, benzyl *l*-menthyloxyacetate and ethyl *l*-menthyloxyacetate can not form such an intramolecular hydrogen bonding. Therefore, we assume that an intramolecular interaction is operating between the *l*-menthyl group and the metal chelate ring of the *l*-moba complexes or the hydrogen-bonded ring of H(*l*-moba). This interaction would hinder the free rotation around the methylene group and hence bring about the inequivalence of the methylene protons. In the NMR spectrum of 1-ethoxy-3-benzoylacetone (Fig. 1(d)), the methylene protons appeared as singlet at 4.0 ppm. The Dreiding model consideration has indicated that the ethyl group can not approach so close to the hydrogen-bonded ring as to cause an appreciable interaction with the benzene ring.



(a) (b)

(c) (d)

Fig. 1. Chemical structure of (a) 1-*l*-menthyloxy-3-benzoylacetone (H(*l*-moba)), (b) benzyl *l*-menthyloxyacetate, (c) ethyl *l*-menthyloxyacetate, and (d) 1-ethoxy-3-benzoylacetone (Heoba).

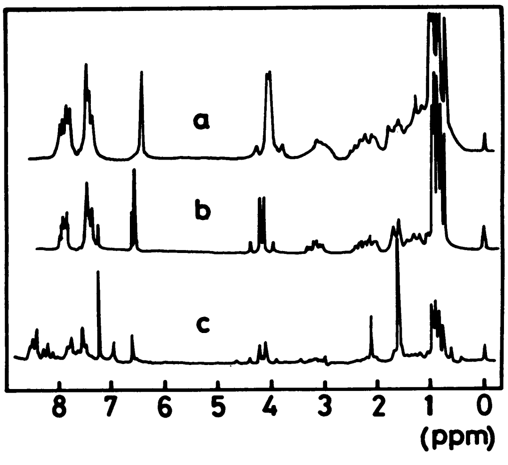


Fig. 2. NMR spectra of (a) H(*l*-moba), (b) Pd(*l*-moba)$_2$, and (c) Pd(bpy)(*l*-moba)ClO_4.

The NMR spectra have revealed that the coupling constants of the methylene protons of Pd(*l*-moba)$_2$ and Pd(bpy)(*l*-moba)ClO_4 are larger than that of H(*l*-moba). This implies that the interaction between the *l*-menthyl group and the ring is enhanced when H(*l*-moba) coordinates to palladium(II) ion. There is little difference between Pd(*l*-moba)$_2$ and Pd(bpy)(*l*-moba)ClO_4 in chemical shift and the coupling constant of the methylene protons. This suggests that in Pd(bpy)(*l*-moba)ClO_4 the *l*-menthyl group does not interact with the π-system of bpy but with the chelate ring of *l*-moba$^-$. This interaction differs from the intramolecular CH/π-interaction observed for the ternary complexes composed of 2,2′-bipyridyl (or 1,10-phenanthroline) and a carboxylic acid,[5] 2,2′-bipyridyl and a sulfonic acid,[5] and 2,2′-bipyridyl and an amino acid.[6] Based on the Dreiding model consideration, no interaction seems to operate between the *l*-menthyl group and the bpy molecule, so long as bpy and *l*-moba$^-$ are planarly coordinated to palladium(II) ion.

Another characteristics in the NMR spectrum of Pd(*l*-moba)$_2$ is two singlets at 6.60 and 6.62 ppm which can be assigned to the methine proton on the chelate ring. This may be reasonably explained by assuming that the sample of Pd(*l*-moba)$_2$ is the mixture of the *cis*- and *trans*-isomers.

In order to investigate further an interaction operating between the *l*-menthyl group and the chelate ring of *l*-moba$^-$, we examined the CD spectra of Cu(*l*-moba)$_2$, Cu(bpy)(*l*-moba)ClO_4, and Ni(*l*-moba)$_2$(H_2O)$_2$. The absorption and CD spectra of Cu(*l*-moba)$_2$ and Cu(bpy)(*l*-moba)ClO_4 in chloroform are shown in Figs. 3 and 4, respectively. The absorption spectrum of Cu(*l*-moba)$_2$ showed three d-d bands at 15200, 17700, and 18900 cm^{-1}; this spectrum resembles that of Cu-

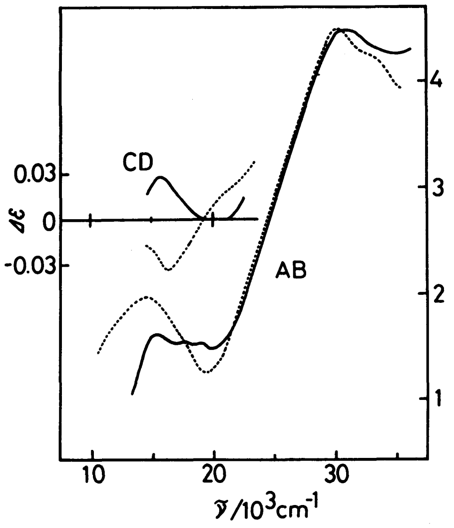


Fig. 3. Absorption and CD spectra of Cu(l-moba)$_2$ in $CHCl_3$ (——) and in pyridine (------).

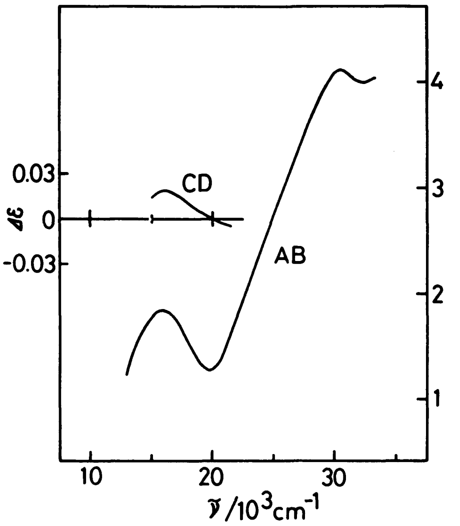


Fig. 4. Absorption and CD spectra of Cu(bpy) (l-moba)-ClO_4 in $CHCl_3$.

(acac)$_2$.[9,10] The chloroform solution of Cu(l-moba)$_2$ showed a weak, positive CD around 15500 cm^{-1}. On adding excess pyridine or t-butylamine to this solution, the CD spectral pattern changed dramatically and a weak, negative CD appeared around 17000 cm^{-1}. In the presence of excess pyridine or t-butylamine, Cu(l-moba)$_2$ will take a square-pyramidal configuration with the base(B) at the axial site. Because the sixth coordination site is still vacant, one of the l-menthyl groups can approach the vacant site of the coordination plane to cause the menthyl/chelate-interaction. The chloroform solution of Cu(bpy)(l-moba)ClO_4 showed a d-d band at 16000 cm^{-1} and a weak, positive CD at 16200 cm^{-1}. The marked resemblance in CD spectra between Cu(l-moba)$_2$ and Cu(bpy)(l-moba)ClO_4 indicates that the l-menthyl group of the latter complex does not interact with the π-system of 2,2′-bipyridyl but with the chelate ring of l-moba$^-$, similarly to the case of the Pd analogue.

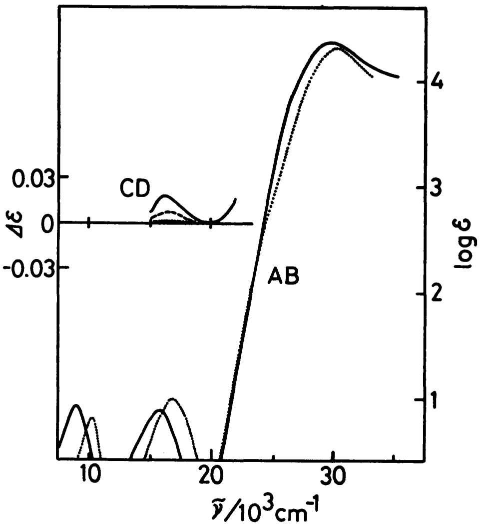


Fig. 5. Absorption and CD spectra of Ni(l-moba)$_2$-$(H_2O)_2$ in $CHCl_3$ in the absence and in the presence of propylamine: [propylamine]/[Ni(l-moba)$_2$$(H_2O)_2$]$=0$ (——), 1.5 (------), and 15 (······).

The absorption spectrum of Ni(l-moba)$_2$$(H_2O)_2$ in chloroform showed d-d bands at 8800 and 15600 cm^{-1} (Fig. 5), indicating a nearly octahedral symmetry around the metal ion.[11,12] This solution showed a positive CD band near 16000 cm^{-1}. It is likely that the water molecules coordinated at the apical positions do not sterically hinder the interaction between the l-menthyl group and the chelate ring. Then, we have examined the CD spectra of Ni(l-moba)$_2$$(H_2O)_2$ in the presence of an amine or an alcohol. The CD spectral change for Ni(l-moba)$_2$$(H_2O)_2$ on adding propylamine is shown in Fig. 5 as an example. The positive CD at 16000 cm^{-1} gradually decreased its intensity on increasing the amine ratio and finally disappeared. The absorption spectrum of Ni(l-moba)$_2$$(H_2O)_2$ in the presence of a large excess of propylamine showed d-d bands at 10000 and 16700 cm^{-1}, implying that the species in the solution is Ni(l-moba)$_2$(n-prNH_2)$_2$. Thus, the CD spectral change mentioned above can be rationalized by assuming that propylamine coordinated at the apical position sterically hinders the intramolecular interaction between the l-menthyl group and the chelate ring of the l-moba$^-$ molecule. Similar CD spectral behaviors were also observed when other amines (pyridine, piperidine, t-butylamine, and dipropylamine), alcohols (methanol, ethanol, 1-propanol, 1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol), DMF and DMSO were added. In all cases, the interaction between the l-menthyl group and the chelate ring must be inhibited due to the steric effect of the molecules coordinated at the apical positions. When triethylamine was added to the chloroform solution of Ni(l-moba)$_2$$(H_2O)_2$, no absorption and CD spectral change occured. It is likely that triethylamine can not coordinate to the nickel(II) ion because of the F-strain of the amine.

In the case of addition of excess pyridine, piperidine, t-butylamine, 2-methyl-1-propanol, or 2-butanol to the chloroform solution of Ni(l-moba)$_2$$(H_2O)_2$, a weak, negative CD peak appeared around 16500 cm^{-1} ($\Delta\varepsilon \approx -0.005$). The origin of this CD is unclear at present, but some intra- or inter-ligand interactions other than

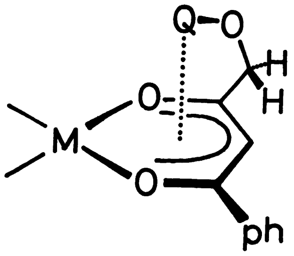


Fig. 6. Schematic representation of the intramolecular menthyl/chelate-interaction.

the *l*-menthyl/chelate-interaction, such as the interaction between the *l*-menthyl group and the hydrophobic moiety of an amine or an alcohol, might contribute to the weak CD induction.

Based on these facts we conclude that in the *l*-moba metal complexes an intramolecular interaction occurs between the *l*-menthyl group and the chelate ring, and this interaction causes an chirality around the metal ion. It is most likely that the *l*-menthyl group bondingly interacts with the π-system of the chelate ring (Fig. 6). Such a new-type interaction resembles the inter-ligand π/π-interaction suggested for mixed-chelate cobalt(III) complexes containing acetylacetonate ion and (2-aminoethyl)methylphenylphosphine.[13]

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