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STEREOSELECTIVITY EFFECTED BY INTER-LIGAND, "HYDROPHOBIC" INTERACTION IN TRIS(1-ℓ-MENTHOXY-3-ACETYLACETONATO)COBALT(III) AND CHROMIUM(III)

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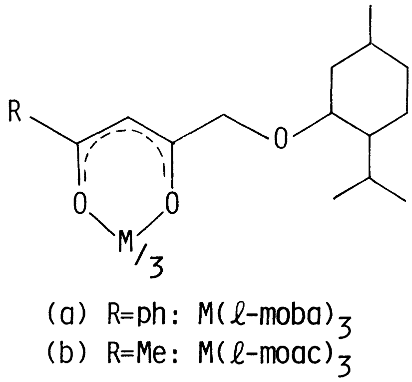
Cobalt(III) and chromium(III) complexes of 1-ℓ-menthoxy-3-acetylacetone (H(ℓ-moac)), Co(ℓ-moac)$_3$ and Cr(ℓ-moac)$_3$, have been synthesized and characterized. On the basis of NMR, electronic absorption and CD spectra, the complexes were demonstrated to have the cis-Λ-configuration. The stereoselectivity was attributed to the inter-ligand, "hydrophobic" interaction occuring between the ℓ-menthyl and the methyl groups.

Recently, it is known that inter-ligand, hydrophobic interactions effectively cause stereoselectivity in metal complexes$^{2-4)}$ and enhance stability of ternary complexes.$^{5)}$ Hydrophobic interactions are classified into three types based on the interacting groups, i.e., (1) "hydrophobic" interaction between alkyl or alicyclic groups, (2) hydrophobic stacking of aromatic rings,$^{5)}$ and (3) hydrophobic CH---π-interaction occuring between an aromatic ring and an alkyl (or alicyclic) group.$^{6)}$

Previously, we have shown that tris(1-ℓ-menthoxy-3-benzoylacetonato)M(III) complexes, M(ℓ-moba)$_3$ (Fig. 1a), prefer the cis-Δ-configuration.$^{2)}$ This stereoselectivity can be attributed to the inter-ligand, hydrophobic CH---π-interaction operating between the ℓ-menthyl and the phenyl groups. If the phenyl group in ℓ-moba$^-$ is replaced by an alkyl group, an inter-ligand, "hydrophobic" interaction (type (1) in the above classification) may occur between the alkyl and the ℓ-menthyl groups. This should also bring about a stereoselectivity. In this study, cobalt(III) and chromium(III) complexes of 1-ℓ-menthoxy-3-acetylacetone (abbreviated as H(ℓ-moac)), Co(ℓ-moac)$_3$ and Cr(ℓ-moac)$_3$ (Fig. 1b), have been prepared and the stereoselectivity was discussed in terms of the inter-ligand, "hydrophobic" interaction.



(a) R=ph: M(ℓ-moba)$_3$
(b) R=Me: M(ℓ-moac)$_3$

Fig. 1.

Syntheses of H(ℓ-moac), Co(ℓ-moac)$_3$ and Cr(ℓ-moac)$_3$ were carried out as follows.

H(ℓ-moac). To a stirred mixture of ethyl ℓ-menthoxyacetate (10 g) and NaH (1.6 g) in absolute ether (100 ml) was added dropwise acetone (2.5 g) at 45°C. Stirring was continued at this temperature for additional 30 min. Unreacted NaH was decomposed by adding ethanol (50 ml). Then, acetic acid (10 ml) was added and the mixture was stirred for 1 h to give a colorless mass. This was separated by filtration and washed with 50 ml portions of ether. The combined ether solution was shaken twice with a saturated sodium carbonate solution and twice with water. To this solution was added an ammoniacal solution (100 ml) of nickel(II) acetate tetrahydrate (6 g), and the mixture was vigorously shaken to give Ni(ℓ-moac)$_2$(H$_2$O)$_2$ as pale green mass. It was recrystallized from methanol as pale green crystals. Found: C, 59.99; H, 9.08%. Calcd for $C_{30}H_{54}O_8$: C, 59.98; H, 8.99%.

The nickel complex was dissolved in ether. To this was added 20% sulfuric acid and the mixture was vigorously shaken. The ether layer was separated, shaken twice with a saturated sodium carbonate solution and then twice with water, and dried over sodium sulfate. Evaporation of the solvent left H(ℓ-moac) as a pale yellow oil.

Co(ℓ-moac)$_3$. A mixture of basic cobalt(II) carbonate (0.15 g) and H(ℓ-moac) (1.0 g) was warmed at 90°C on a water bath, and to this was added dropwise hydrogen peroxide (30%, 10 ml) under stirring. The cobalt(III) complex was extracted with ether and passed through an alumina column (15×100 mm). Evaporation of ether gave Co(ℓ-moac)$_3$ as a deep green oily substance.

Cr(ℓ-moac)$_3$. A mixture of chromium(III) chloride tetrahydrate (0.23 g), H(ℓ-moac) (1 g), charcoal (0.1 g) and triethylamine (0.1 g) in ethanol (50 ml) was refluxed for 12 h. The charcoal was separated by filtration and the solvent was evaporated. The resulting oil was dissolved in benzene, and passed through an alumina column (15×100 mm). On evaporating the solvent, there remained a purple oily substance.

NMR spectrum of H(ℓ-moac) is given in Fig. 2. The spectrum clearly indicates

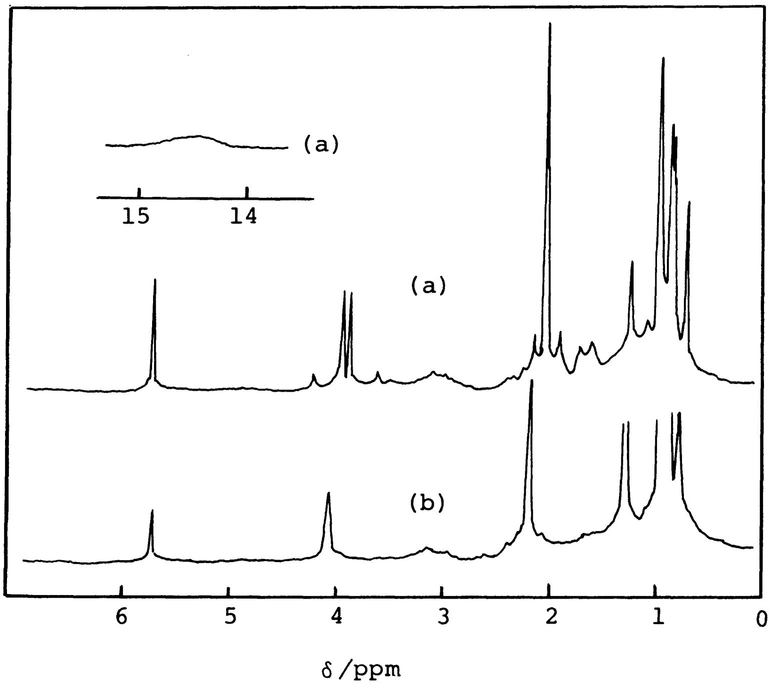


Fig. 2. NMR spectra of (a) H(ℓ-moac) and (b) Co(ℓ-moac)$_3$ measured in CCl_4

that H(ℓ-moac) exists as the keto-enol form; the signals at δ14.5(broad), 6.73 (singlet), 3.93(AB quartet) and 2.05 ppm(singlet) being assigned to the enol-OH, the methine group, the methylene group adjacent to the ℓ-menthoxy group, and the methyl group on the chelate ring, respectively. Other signals are ascribed to the ℓ-menthyl group.

Co(ℓ-moac)$_3$ was characterized on the basis of NMR and electronic absorption spectra. NMR spectrum of Co(ℓ-moac)$_3$ (Fig. 2b) is similar to that of H(ℓ-moac) and shows signals at 5.73, 4.10 and 2.21 ppm attributable to the methine, the methylene and the methyl protons on the chelate ring, respectively. Since the donating oxygens in H(ℓ-moac) are unequivalent, there are two possible geometrical isomers, cis and trans (or fac and mer), for M(ℓ-moac)$_3$. Because the methine, the methylene and the methyl signals are all singlet, cis-Co(ℓ-moac)$_3$ should be predominantly formed in solution. It is likely that the inter-ligand, "hydrophobic" interaction occuring between the ℓ-menthyl and the methyl groups much stabilizes the cis-isomer compared with the trans-isomer, as was observed for M(ℓ-moba)$_3$.[2)]

Electronic absorption and CD spectra of Co(ℓ-moac)$_3$ in CCl_4 are given in Fig. 3. The absorption spectrum bears a marked resemblance to those of other tris(1,3-diketonato)cobalt(III).[2,7-9)] The CD spectrum shows three bands in the ligand field region. Since the CD spectral pattern is the same as that of Λ-Co(acac)$_3$,[10)] we may conclude that Co(ℓ-moac)$_3$ is of the cis-Λ-configuration.

Electronic absorption and CD spectra of Cr(ℓ-moac)$_3$ in CCl_4 are given in Fig. 4. The absorption spectrum quite resembles those of tris(1,3-diketonato)-

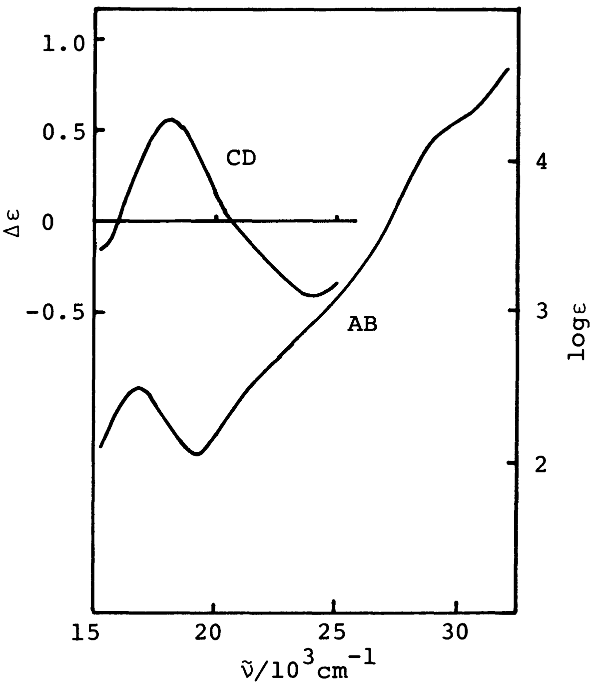


Fig. 3. Electronic absorption and CD spectra of Co(ℓ-moac)$_3$ in CCl_4

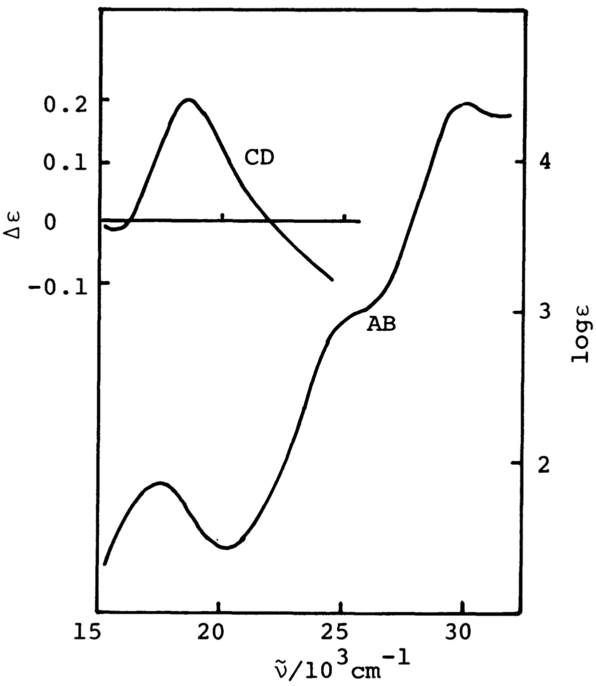


Fig. 4. Electronic absorption and CD spectra of Cr(ℓ-moac)$_3$ in CCl_4

chromium(III).[2,11] The CD spectrum exhibits three bands in the ligand field region, whose spectral pattern is quite reverse to that of Δ-Cr(acac)$_3$.[12] Hence, it is concluded that Cr(ℓ-moac)$_3$ also has a cis-Λ-configuration.

Because of lack of aromatic group in M(ℓ-moac)$_3$, the stereoselectivity appeared in these complexes can be attributed to the inter-ligand, "hydrophobic" interaction occuring between the ℓ-menthyl and the methyl groups. It is worth noting that the stereoselectivity effected by the inter-ligand, "hydrophobic" interaction in M(ℓ-moac)$_3$ quite differs from the stereoselectivity by the inter-ligand, hydrophobic CH···π-interaction in M(ℓ-moba)$_3$,[2] in which the cis-Δ-isomer is preferentially formed. Further, it is noticed that the CD intensities of Co(ℓ-moac)$_3$ and Cr(ℓ-moac)$_3$ are lower than those of Co(ℓ-moba)$_3$ and Cr(ℓ-moba)$_3$, respectively. This suggests that hydrophobic CH···π-interaction brings about a large stabilization compared with "hydrophobic" interaction.

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