Circular Dichroism of the Square Planar Nickel(II) Complexes of $[Ni(N)_4]$ Type with L-Amino Acid Amides

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In spite of its fundamental importance, the electronic spectral study has not been made enough on the ligand field bands of square planar nickel(II) complexes of $[Ni(N)_4]$ type. This communication is concerned with the confirmation of the spectral correspondence between the bis(L-α-amino-acid-amidato)-nickel(II) and -palladium(II) complexes on the basis of solvent effect on the complexes. The latter has been spectroscopically determined to be the *trans* form.[1]

Bis(L-leucinemethylamidato)nickel(II) and *trans*-bis(L-leucinemethylamidato)palladium(II) were newly isolated as $[Ni(L\text{-leuma})_2]\cdot H_2O$[2] (Found: C, 46.58; H, 8.72; N, 15.45%. Calcd for $C_{14}H_{32}N_4O_3Ni$: C, 46.30; H, 8.88; N, 15.43%.) and $[Pd(L\text{-leuma})_2]$ (Found: C, 42.53; H, 7.78; N, 14.08%. Calcd for $C_{14}H_{30}N_4O_2Pd$: C, 42.81; H, 7.70; N, 14.26%). As is seen in Figs. 1 and 2, the negative CD bands at *ca.* 19000 cm^{-1} for then ickel-(II) and at 27100—28100 cm^{-1} for the palladium-(II) complexes change their sign to positive as the solvent changes from water or ethanol to *N,N*-dimethylformamide (DMF). The same spectral behavior was also observed for the nickel(II) and *trans* palladium(II) complexes with L-valinamidate or L- phenylalaninamidate. Furthermore, the higher wave number CD bands of the nickel(II) complexes (*ca.* 24000 cm^{-1})were affected parallel with those of the palladium(II) complexes (*ca.* 36000 cm^{-1}) by the solvents employed.

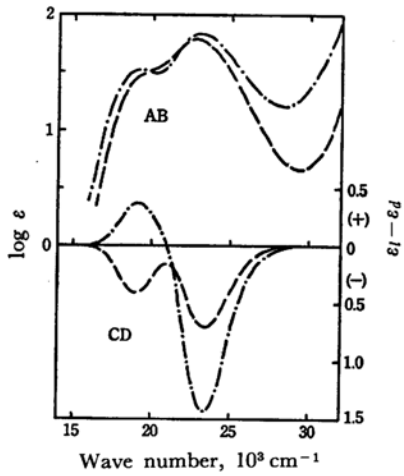

Fig. 1. Absorption (AB) and circular dichroism (CD) spectra of *trans*-$[Ni(L\text{-leuma})_2]$.
--- in ethanol, -·-· in DMF

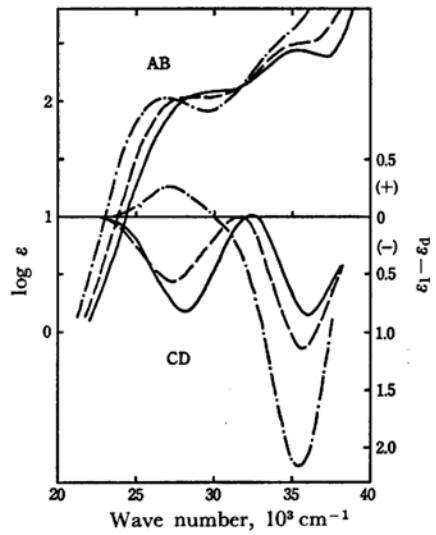

Fig. 2. AB and CD spectra of *trans*-$[Ni(L\text{-leuma}_2]$.
—— in water, --- in ethanol, -·-· in DMF

The effect of the solvents on the CD of the *cis* palladium(II) complexes is distinctly different from that in the case of the *trans* complexes, especially in the higher wave number CD band (*ca.* 36000 cm^{-1}): the negative intensity of this band is lowered in the *cis* complex with L-leucinamidate or L-valinamidate as the solvent changes from water or ethanol to DMF.

These facts point out that the three nickel(II) complexes cited have the *trans* form in the solutions, and that their CD (or absorption) bands at *ca.* 19000 and *ca.* 24000 cm^{-1} correspond in electronic nature to the bands at *ca.* 28000 and *ca.* 36000 cm^{-1}, respectively, in the corresponding palladium(II) complexes.

1) T. Komorita, J. Hidaka and Y. Shimura, This Bulletin, **41**, 854 (1968).

2) Abbreviation: leuma^{-1}=leucinemethylamidate anion.