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Vibrational Circular Dichroism of Metal Complexes Containing trans-1,2-Diaminocyclohexane

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The vibrational circular dichroism of (1R,2R)-diaminocyclohexane complexes of Pd(II), Cu(II), Ni(II), and Co(III) in CD_3CN are characterized by positive and negative bands for the antisymmetric and symmetric NH_2 stretching vibrations, respectively. This feature is attributable to the λ conformation of the chelate ring.

Vibrational circular dichroism (VCD) which has been developed over the past decade as a new spectroscopy, has recently been applied to conformational and configurational studies of optically active metal complexes by Nafie et al.1-2) In one of such studies, Young et al. examined the VCD of NH and CH stretching vibrations of optically active $[Co(en)_3]X_3$ ($X=Cl^-$, Br^-, I^-) in solutions, and related it to chiral conformation of the ethylenediamine chelate ring.2) However, their interpretion of the VCD data was based on the assessment of a somewhat delicate difference in the abundance of δ and λ conformers of the chelate rings. Therefore, it is highly desirable to obtain VCD data with compounds which assume a fixed conformation of either δ or λ. In this letter, the VCD are presented for some metal complexes containing (1R,2R)-diaminocyclohexane (RR-chxn), which is known to assume exclusively the λ conformation on complexation.

The complexes studied are $[Pd(RR\text{-}chxn)_2](ClO_4)_2$, $[Cu(RR\text{-}chxn)_2](ClO_4)_2$, $[PdCl_2(RR\text{-}chxn)]$, $[Ni(RR\text{-}chxn)_3](ClO_4)_2$, $[Ni(RR\text{-}chxn)_3](BF_4)_2$, and lel_3 and ob_3 forms of $[Co(RR\text{-}chxn)_3](BF_4)_3$, prepared according to the procedures described in the literature,3-6) and confirmed by electronic absorption and CD spectra and elementary analyses. trans-1,2-Diaminocyclohexane was resolved according to Galsbøl's method.7) The IR and VCD spectra were obtained with a JASCO A-302 infrared spectrometer and a JASCO J-200E infrared spectropolarimeter,8) respectively.

Fig. 1 shows the IR and VCD spectra in the NH stretching region of RR-chxn complexes of Pd and Cu in CD_3CN. The observed frequencies and intensities are given in Table 1. The IR spectrum in each case shows three absorption bands assignable, from the high frequency side, to the antisymmetric and symmetric NH_2 stretching vibrations, and the overtone of the NH_2 scissors enhanced by Fermi resonance interaction with the symmetric stretching mode. The corresponding VCD spectrum of $[Pd(RR\text{-}chxn)_2](ClO_4)_2$ appears quite simple, consisting of positive, negative, and negative bands associated with the antisymmetric and symmetric stretching modes, and the Fermi-enhanced overtone, respectively. The VCD spectrum of $[Cu(RR\text{-}chxn)_2](ClO_4)_2$ is a little more complex: the positive band for the NH_2 antisymmetric stretching mode is accompanied with a weak negative band on the low frequency side and the negative band for the NH_2 symmetric stretching mode accompanied with a weak positive band on the high frequency side. As far as the main components of the VCD bands are concerned, the VCD feature of the Cu complex is similar to that of the Pd complex: positive and negative for the NH_2 antisymmetric and symmetric stretching modes and negative for the overtone, respectively. The oppositely signed weak components for each vibration might be due to a dipole coupling interaction between amino groups on adjacent chxn rings.

In Fig. 2 are shown the IR and VCD spectra of $[Pd(RR\text{-}chxn)_2](ClO_4)_2$ and non-ionic $[PdCl_2(chxn)]$ in $(CD_3)_2SO$ (DMSO-d_6). Both spectra show IR absorption peaks due to NH_2 antisymmetric and symmetric stretching vibrations but in this case the peak corresponding to Fermi resonance is not clearly observable. However, the situation that the antisymmetric and symmetric stretching modes are associated with positive and negative VCD bands, respectively, is unaltered even in this solvent. Very similar VCD features of the two compounds in DMSO-d_6 seems to prove that the ion-pair formation which is considered to occur⁹⁾ in the former complex does not produce any sizable effect on its VCD.

The IR and VCD spectra of $[Ni(RR\text{-}chxn)_3](ClO_4)_2$ and $[Ni(RR\text{-}chxn)_3](BF_4)_2$ and the lel_3 and ob_3 forms of $[Co(RR\text{-}chxn)_3](BF_4)_3$ in CD_3CN are shown in Fig. 3. The main features in the IR spectra are similar to the above cases of Pd(II) and Cu(II) complexes in the same solvent with three peaks corresponding to antisymmetric and symmetric stretching modes, and the Fermi-enhanced overtone in the order of decreasing frequency. The VCD spectrum of the tris Ni(II) complex is comparatively similar to those of the bis complexes of Pd and Cu described above, with the (+−−) pattern corresponding to the above three modes. However, an additional weak negative band was observed at the high frequency side of the IR band of NH_2 anti-

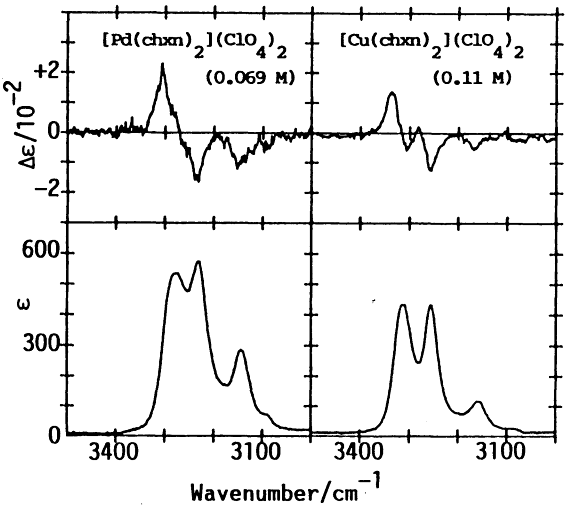

Fig. 1. IR and VCD spectra of RR-chxn complexes of Pd(II) and Cu(II) in CD_3CN.

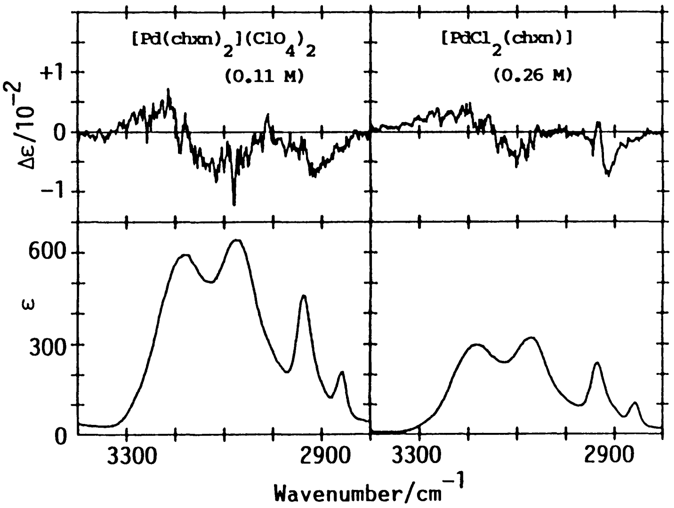

Fig. 2. IR and VCD spectra of RR-chxn complexes of Pd(II) in DMSO-d_6.

symmetric stretching mode. It should be noted that this complex has not only conformational chirality but also configurational chirality; the complex is considered to be predominantly Δ(λλλ)-lel_3 which is thermodynamically more stable for the λ conformation.[5] A weak negative VCD band observed at the high frequency side may be characteristic of the Δ(λλλ)-lel_3 structure (vide infra).

Table 1. Frequencies, Intensities, and Assignments of IR Absorption and VCD Spectra in the NH Stretching Region of RR-chxn Complexes in CD_3CN and DMSO-d_6 Solutions

Absorption		VCD		Absorption		VCD		
Freq.	Intens.	Freq.	Intens.	Freq.	Intens.	Freq.	Intens.	Assignment
ν/cm^{-1}	ε	ν/cm^{-1}	Δε/10^{-2}	ν/cm^{-1}	ε	ν/cm^{-1}	Δε/10^{-2}	
$[Pd(RR\text{-}chxn)_2](ClO_4)_2/CD_3CN$				$[Cu(RR\text{-}chxn)_2](ClO_4)_2/CD_3CN$				
						3335	+1.3	
3274	540	3305	+2.2	3313	440	3305	-0.5	NH_2 antisym. str.
						3282	+0.2	
3233	580	3235	-1.6	3256	430	3257	-1.2	NH_2 sym. str.
3145	280	3148	-1.1	3158	120	3168	-0.5	overtone of NH_2 scis.
$[Pd(RR\text{-}chxn)_2](ClO_4)_2$/DMSO-$d_6$				$[PdCl_2(RR\text{-}chxn)]$/DMSO-d_6				
3175	590	3220	+0.4	3182	295	3200	+0.3	NH_2 antisym. str.
3080	640	3110	-0.6	3070	315	3100	-0.5	NH_2 sym. str.
$[Ni(RR\text{-}chxn)_3](BF_4)_2/CD_3CN$				$[Ni(RR\text{-}chxn)_3](ClO_4)_2/CD_3CN$				
		3360	-0.5			3350	-1.0	
3339	720	3335	+4.0	3335	890	3336	+5.1	NH_2 antisym. str.
3282	400	3293	-5.1	3275	550	3290	-5.6	NH_2 sym. str.
3185	60	3180	-0.3	3180	80	3180	-0.5	overtone of NH_2 scis.
lel_3-$[Co(RR\text{-}chxn)_3](BF_4)_3/CD_3CN$				ob_3-$[Co(RR\text{-}chxn)_3](BF_4)_3/CD_3CN$				
		3295	-4.4					
3279	1030	3280	+1.4	3274	700	3300	+0.6	NH_2 antisym. str.
3244	760	3255	-5.1	3240	780	3250	-2.2	NH_2 sym. str.
		3225	-0.5					
3158	360	3150	-1.2	3154	460	3155	-3.1	overtone of NH_2 scis.

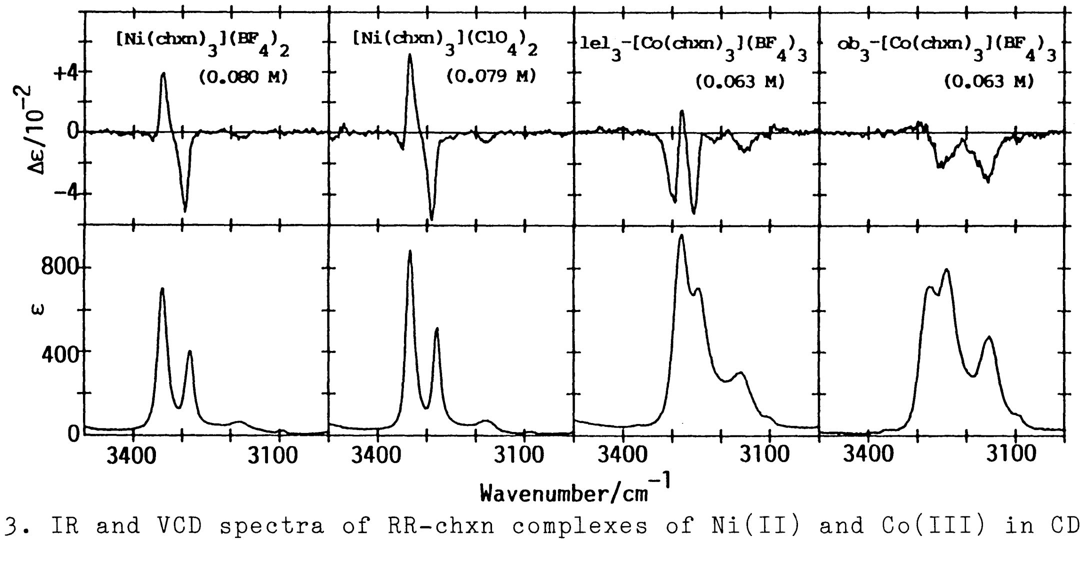

Fig. 3. IR and VCD spectra of RR-chxn complexes of Ni(II) and Co(III) in CD_3CN.

The VCD spectrum of lel$_3$-[Co(RR-chxn)$_3$](BF$_4$)$_3$ appears somewhat differently from those discussed above, assuming a (-+--) pattern. If we look at the signs of VCD exactly at the positions of IR absorption peaks, however, we find that it still retains the previous pattern of (+--) corresponding to antisymmetric and symmetric stretching NH$_2$ vibrations, and the overtone, respectively. Thus an appearance of an additional negative peak on the high frequency side might be the characteristic of this complex, which could possibly be related to the $\Delta(\lambda\lambda\lambda)$-lel$_3$ structure, when we recall that the nickel complex also had this sort of negative peak, although weak. The VCD of the less stable isomer, $\Lambda(\lambda\lambda\lambda)$-ob$_3$-[Co(RR-chxn)$_3$](BF$_4$)$_3$ restored the "normal" pattern, (+--) without an additional VCD peak.

All of the metal complexes of (1R,2R)-diaminocyclohexane studied in this research including non-electrolytic [PdCl$_2$(RR-chxn)] thus exhibited positive and negative VCD bands at the IR peak positions of antisymmetric and symmetric NH$_2$ stretching vibrations. Since the (1R,2R)-diaminocyclohexane chelate ring takes λ conformation, it seems possible to conclude that this VCD pattern is inherent to the λ conformation of the chelate ring. In the recent VCD study of [Co(en)$_3$]$^{3+}$, Young et al.$^{2)}$ examined the effect of solvents and couter-ions. Their VCD in DMSO-d$_6$ with excess chloride is conformable to our conclusion. They ascribed the origin of the appearance of this sort of spectrum to ion-pairing with chrolide although our VCD pattern of the chxn complexes are all similar irrespective of ion-pair formation. In their case of [Co(en)$_3$]$^{3+}$ in D$_2$O-D$_2$SO$_4$ or DMSO-d$_6$ with little or no ion-pair formation with the chrolide ion, the VCD bands much reduced in intensity and in some cases reversed in sign.

It is not attempted in this paper to give a theoretical interpretation of the above emprical relationship. As the factors responsible for the discrepancy between en and chxn comlexes might be counted the fixed ring conformation of diaminocyclohexane chelates, effect of ring substituent, difference of solvent, etc., but the exact situation is not clear at this moment. Much seems to be done before any satisfactory explanation to be made on the above findings, with the aid of other information such as NMR and electronic CD.$^{10)}$ We are currently performing additional experiments to obtain more detailed information.

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