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Ab Initio VCD Calculation of a Transition-Metal Containing Molecule and a New Intensity Enhancement Mechanism for VCD

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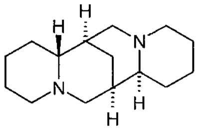
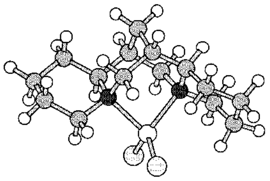
We report the first ab initio vibrational circular dichroism (VCD)[1] calculation for a molecule containing a transition metal, a closed-shell Zn(II) complex. We also report a new VCD enhancement mechanism in the corresponding open-shell Co(II) and Ni(II) complexes, which increases the VCD intensity by approximately an order of magnitude, with changes in sign for many transitions (differently for the two metals), but which leaves the unpolarized infrared (IR) absorption spectrum unchanged from that of the closed-shell system. Intensity-enhanced VCD shows promise as a sensitive new spectroscopic probe of stereochemistry and low-lying d−d transitions in molecules containing transition metals, including the active sites of metalloproteins.

Previously,[2] enhanced VCD intensity was reported in a narrow range of VCD bands in the CH stretching modes of (−)-sparteine complexes of Co(II) and Ni(II) compared to Zn(II). A Fano-type coupling mechanism,[3] arising from the presence of large underlying CD intensity from electronic open-shell d−d transitions, was invoked to explain the enhancement.[2] We report here the extension of these studies into the mid-IR range and demonstrate that the enhancement mechanism does not require underlying electronic CD intensity. We also show that the IR and VCD of the closed-shell Zn(II) complex can be accurately calculated by using existing theoretical methodology and explain why the open-shell cases with low-lying d−d transitions require calculations beyond this methodology.



6*R*,7*S*,9*S*,11*S*-(-)-Sparteine



Optimized geometry of $Zn(sp)Cl_2$

The complexes $M(sp)Cl_2$ (M = Co(II), Ni(II), Zn(II), sp = (−)-sparteine) were prepared with literature methods.[4] VCD spectra were recorded on a modified Chiral*ir* FT-VCD instrument[1] (Bomem/BioTools, Quebec, Canada) at 4 cm^{-1} resolution for samples 6 mg/100 μL of $CDCl_3$. Calculation of optimized geometries, vibrational frequencies, and IR and VCD intensities were carried out with Gaussian 98,[5] at the DFT level (B3LYP functional/LANL2DZ basis set[6,7]).

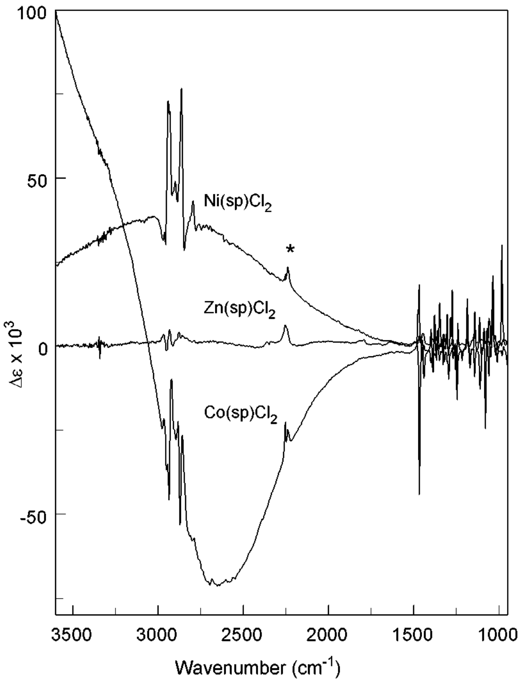


Figure 1. Observed VCD spectra of $Zn(sp)Cl_2$, $Co(sp)Cl_2$, and $Ni(sp)Cl_2$ in the 3600−950 cm^{-1} region, 0.1 mm path length cell, 5 h collection for sample and solvent, with the instrument optimized at 3000 cm^{-1}. The asterisk indicates an artifact arising from atmospheric CO_2.

The VCD spectra of the Co(II), Ni(II), and Zn(II) complexes are shown superimposed in Figure 1 for the 3600−930 cm^{-1} region. Detailed comparisons of the CH-stretching IR and VCD spectra are presented in Figure 2, and the 1500−930 cm^{-1} range is expanded in Figure 3. The CH-stretching modes for the Ni(II) and Co(II) complexes are superimposed on broad electronic CD bands for d−d transitions, which do not contribute to the absorption spectra (Figure 2), and these modes exhibit clear enhancement of the VCD intensity compared to the Zn(II) complex, as previously observed.[2] However, intense VCD signals for the open-shell complexes extend to below 1000 cm^{-1} without any diminishment in enhancement or distortion of band-shape (Figures 1 and 3), calling into question the earlier interpretation based on Fano-type interference,[2,3] which requires direct overlap with a broad underlying state. In addition, the mid-IR VCD enhancement occurs in the absence of any significant change in the IR absorption spectrum (Figure 3).

The calculation of VCD intensity incorporated into Gaussian 98 utilizes the magnetic field perturbation (MFP) method of

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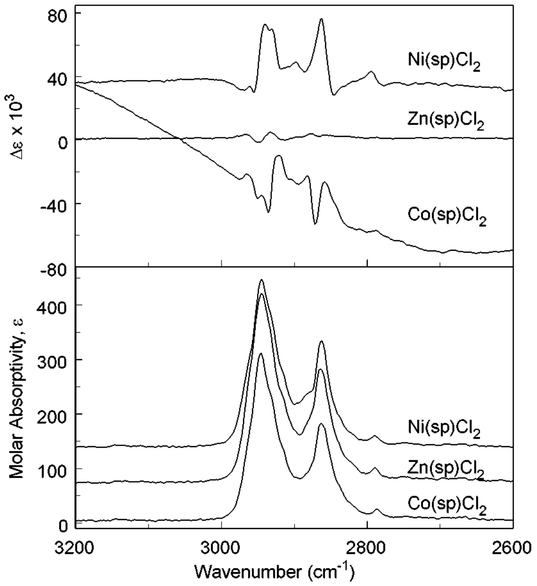

Figure 2. Observed VCD spectra of Zn(sp)Cl$_2$, Co(sp)Cl$_2$, and Ni(sp)Cl$_2$ in the CH-stretching region with conditions the same as in Figure 1. Offset for Co(sp)Cl$_2$ and Ni(sp)Cl$_2$ VCD arises from electronic CD of d−d transitions. IR spectra are offset for clarity.

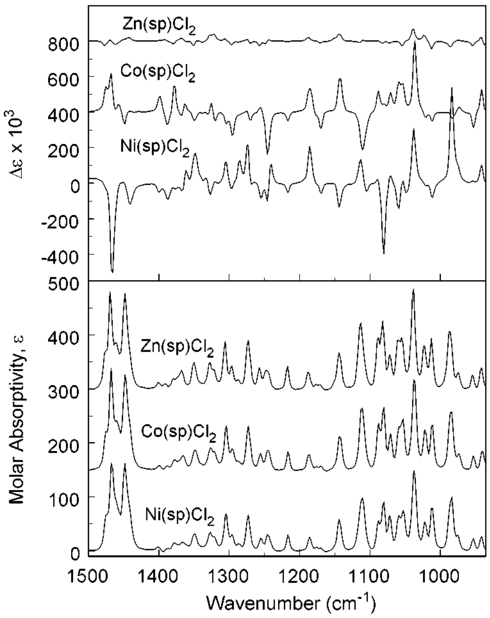

Figure 3. Observed VCD spectra of of Zn(sp)Cl$_2$, Co(sp)Cl$_2$, and Ni(sp)Cl$_2$ in the 1500−930 cm^{-1}, 0.2 mm path length cell, 1 h collection for sample and solvent, with the instrument optimized at 1400 cm^{-1}. IR and VCD spectra are offset for clarity.

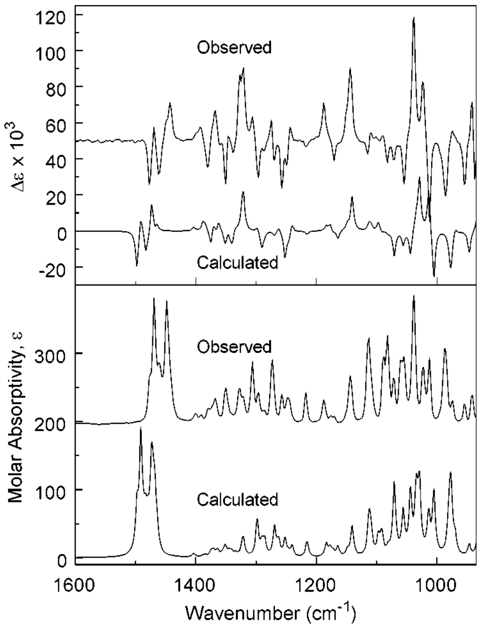

Figure 4. Comparison of observed and calculated IR and VCD spectra of Zn(sp)Cl$_2$. Observed spectra are offset for clarity.

Stephens,[8,9] which is formally equivalent to the sum-over-states vibronic coupling theory (VCT) of Nafie and Freedman.[10] The close agreement between observed and calculated IR and VCD spectra of Zn(sp)Cl$_2$ shown in Figure 4 demonstrates that the current implementation of VCD theory with the LANL2DZ basis set provides an adequate description of the electronic contributions to VCD for this closed-shell system.

For the open-shell Co(sp)Cl$_2$ and Ni(sp)Cl$_2$ complexes, the VCT expressions for the atomic axial tensor[1,10] show that low-lying magnetic-dipole allowed d−d transitions that are vibronically coupled to the ground state make large contributions to VCD intensity for all modes due to a small energy denominator. Accurate transition energies and wave functions for these states are required to reproduce the VCD intensities for such open-shell cases. In addition, the presence of small energy denominators negates the simplifying assumption of neglect of excited-state vibronic detail used in the VCT[10] and MFP[8] formulations of VCD intensity. Explicit consideration of contributions from such terms including vibronic corrections and investigation of additional basis sets for the metal ions are underway.

VCD is a probe of absolute configuration, optical purity, and solution conformation that has primarily been applied to organic systems, including increasing applications to pharmaceuticals and peptides. The utility of VCD relies heavily on the ability to calculate VCD intensities in close agreement with experiment. The results presented here demonstrate the potential of similar applications to closed-shell transition metal complexes, and now open the possibilities for more extensive VCD studies utilizing intensity enhancement to probe open-shell metal complexes, the active sites of metalloproteins,[11] and the details of low-lying electric dipole-forbidden electronic transitions.

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