

Synthesis and CD Spectra of Chiral Molybdenum-fullerenyl Complexes with Pineno-bipyridine Ligands

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Abstract: The synthesis and characterization of two chiral fullerene complexes $(+)\text{-}_{430}^{\text{CD}}\text{-}[\text{Mo}(\eta^2\text{-C}_{60})(\text{CO})_3(\text{L}^{\text{RR}})]$ **1** and $(-)\text{-}_{430}^{\text{CD}}\text{-}[\text{Mo}(\eta^2\text{-C}_{60})(\text{CO})_3(\text{L}^{\text{SS}})]$ **2** were described. The CD spectra of **1** and **2** in the visible range show weak Cotton effects, which are approximately of mirror image, indicating that the appended pineno-groups with opposite chirality in bipyridines can perturb the fullerene chromophores through the molybdenum centers and lead to induced CD effects.

Keywords: Mo complexes, chirality, bipyridine, fullerenes, CD spectra.

Recently, researches on the synthesis, structural characterization and properties of novel metal complexes with chiral organic ligands have been of much concern because of their remarkable applications to various fields such as enantioselective catalysis and molecular recognition. On the other hand, optically active organometallic fullerene derivatives have drawn more and more attention¹ due to their potential as the precursors for asymmetric catalysis², as materials for non-linear optics or as candidates for biological activity. Three main chiral transition metal-fullerene binding types have been described³: (a) direct attachment of the metal complex, whose chirality is mostly in the other ligands or at the metal center, to a fullerene (C_{60} or C_{70})⁴; (b) coordination of the metal center to chiral ligating groups of appendants previously attached to a fullerene core²; (c) dissymmetric addition of two or more metal centers with achiral ligands to a single fullerene core⁵. The C_{60} chromophore in both type (a) and (b) is still symmetric but could be asymmetrically perturbed by the chiral substituents⁵, while it is by virtue of the addition pattern on the icosahedral carbon cluster in the type (c) that the C_{60} chromophore itself is chiral, which could lead to very large Cotton effects^{5,6}.

Chiral organometallic fullerene derivatives of type (a) so far have been limited to the η^2 -fullerene complexes of the VIIB or VIII group metals (Mo, W, Pd or Pt) with a chiral diphosphine ligand (+)- or (-)-DIOP [2,3-*O,O'*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphinobutane)]⁴. The first optically active fullerene complexes by X-ray structural characterization were $[\text{Pd}(\eta^2\text{-C}_{60})\{(+)\text{-DIOP}\}]$ and $[\text{Pt}(\eta^2\text{-C}_{60})\{(+)\text{-DIOP}\}]$ ^{4a,4b}. The present paper reports the synthesis and characterization of two chiral molybdenum-

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fullerenyl complexes $[\text{Mo}(\eta^2\text{-C}_{60})(\text{CO})_3(\text{L}^{RR})]$ **1** ($\text{L}^{RR} = (8R, 10R)\text{-}(-)\text{-}[4,5]\text{-pineno-2,2'}$ -bipyridine) and $[\text{Mo}(\eta^2\text{-C}_{60})(\text{CO})_3(\text{L}^{SS})]$ **2** ($\text{L}^{SS} = (8S, 10S)\text{-}(+)\text{-}[4,5]\text{-pineno-2,2'}$ -bipyridine) by means of elemental analysis, UV-Vis, IR, XPS and CD spectra. To the best of our knowledge, **1** and **2** are first examples of chiral fullerene complexes bearing chiral bipyridine ligands.

Unless otherwise stated, all chemicals were obtained commercially and used without further purification. All reactions were carried out under highly purified nitrogen using standard Schlenk or vacuum-line techniques. Standard literature procedures were used to dry and distill solvents. The chiral ligands (L^{RR} and L^{SS})⁷ and the chiral precursors ($[\text{Mo}(\text{CO})_4(\text{L}^{RR})]$ and $[\text{Mo}(\text{CO})_4(\text{L}^{SS})]$)⁸ were prepared by literature procedures previously reported. Infrared spectra (KBr pellets) were recorded on a Nicolet 370 FT-IR spectrometer. Electronic spectra were performed on a Perkin-Elmer Lambda 35 spectrometer. Elemental analysis was obtained from a Carlo Erba-1110 elemental analyzer. CD and XPS spectra were measured with a JASCO J-810 spectrophotometer and a Quantum 2000 Scanning Esca Microprobe. Melting points were determined with a XT-4 micro melting point apparatus and the thermometer was uncorrected.

In a typical experiment as shown in **Scheme 1**, $[\text{Mo}(\text{CO})_4(\text{L}^{RR})]$ (0.137 g, 0.3 mmol) and C_{60} (0.126 g, 0.3 mmol) were dissolved in 100 mL of dried toluene. After stirring for 6 h under reflux, a black precipitate was filtrated off and washed with toluene and acetone respectively. The filter residue was extracted several times with carbon disulfide and the resulting dark green extract was concentrated *in vacuo*. The residue was purified by column chromatography using light petroleum ether, carbon disulfide/light petroleum ether (3:1, v/v), carbon disulfide/acetone (3:1, v/v) in turn as the eluents. Three bands were separated and the dark green band afforded 0.146 g (42 %) black powder of **1**. The complex **2** was obtained in the similar way as described for **1**, except using $[\text{Mo}(\text{CO})_4(\text{L}^{SS})]$ instead of $[\text{Mo}(\text{CO})_4(\text{L}^{RR})]$. Yield: 0.200 g (58 %).

Scheme 1

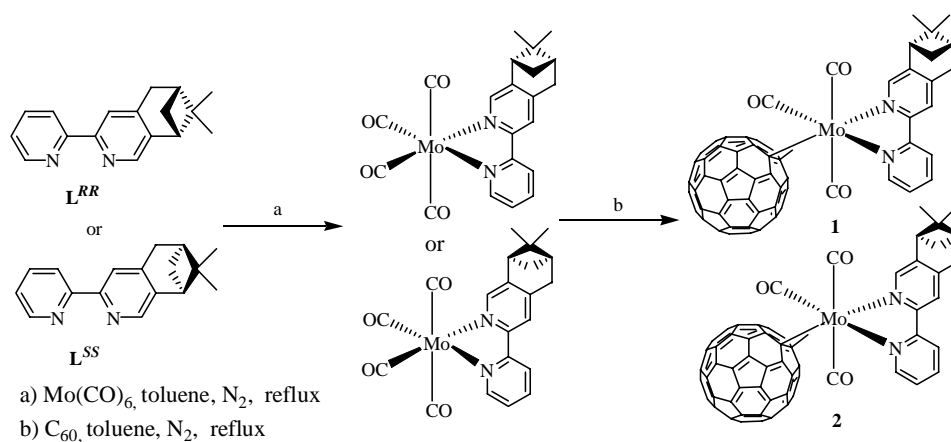
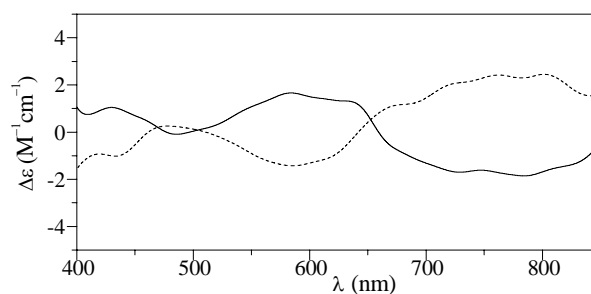


Table 1 Physical, XPS spectra and element analysis data of complexes **1** and **2**

Complex	mp (°C)	binding energy of Mo 3d _{2/5} (eV)	element analysis (calcd.)		
			C	H	N
1	> 310	227.2	83.82 (83.48)	1.79 (1.58)	2.08 (2.43)
2	> 310	227.3	83.86 (83.48)	1.88 (1.58)	2.05 (2.43)

Table 2 IR and UV-Vis spectra data of complexes **1** and **2**

Complex	IR (cm ⁻¹)	UV-Vis in CHCl ₃ λ/nm (log ε)
1	1998w, 1954s, 1894vs ν(C≡O)	647 (4.06), 611sh (4.03), 440 (4.29), 316 (4.85), 258 (5.08)
	1602w ν(C=N)	
	1385vw δ(>C(Me) ₂)	
	1421m, 1183m, 577m, 525s ν(C ₆₀)	
	427m ν[Mo(η ² -C=C)]	
2	1993w, 1955s, 1895vs ν(C≡O)	647 (4.00), 611sh (3.96), 440 (4.23), 316 (4.63), 258 (5.01)
	1602w ν(C=N)	
	1384w δ(>C(Me) ₂)	
	1421m, 1184m, 574m, 527s ν(C ₆₀)	
	426m ν[Mo(η ² -C=C)]	

Figure 1 The CD spectra of the chiral fullerene complexes **1** (—) and **2** (-----) in CS₂ (1 cm cell)

Small deviations of CD curves are due to different enantiomeric purities of the chiral ligands.

Complexes **1** and **2** are air and moisture-stable in both solution and solid state. They are insoluble in common organic solvents except for the slight solubility in carbon disulfide and chloroform, which prevented them from NMR measurements.

As shown in **Table 1**, the photoelectron spectra of the both complexes reveal a Mo 3d_{2/5} peak at 227.2 eV for **1** and 227.3 eV for **2** respectively. These data are between that of Mo(0) (228.0 eV) and [Mo(CO)₄(bipy)] (226.3 eV), but analogous with that of [Mo(CO)₃(C₅H₅)] (227.4 eV)⁹. The binding energy of the 3d_{2/5} electron of Mo suggests that the electrons of related ligands flowed to the Mo center. As a result, there is a negative valency metal in the complex, implying that the chiral bipyridines are on the borderline between hard and soft Lewis bases.

The absorption spectra of **1** and **2** exhibit five intense absorption bands in the range 250-650 nm. The band at 440 nm (shifted from 408 nm in free C₆₀) in each complex serves as a fingerprint for mono-adducted fullerenes at a 6-6 double bond, suggesting the Mo center coordinates in an η^2 -fashion to the C₆₀ cage. The CD spectra of the related pair of isomers (**1** and **2**) in the visible range show weak Cotton effects, which are approximately of mirror image, indicating that the appended pineno-groups with opposite chirality in bipyridines can perturb the fullerene chromophores through the molybdenum centers and lead to induced CD effects. Similar to UV/Vis spectra, the rather weak but identical CD bands of **1** and **2** near 430 nm provide further evidences that they are η^2 -type of complexes^{6,10}. **Figure 1** illustrates the CD spectra of **1** and **2** in CS₂ solution and their UV-Vis and IR data are summarized in **Table 2**.

The IR bands of **1** and **2** between 1421 and 525 cm⁻¹ indicated the presence of C₆₀ ligands. Three absorption bands in the region 1998-1894 cm⁻¹ could be assigned to the terminal carbonyl groups and account for the assumed *mer*-isomers shown in **Scheme 1**^{4c}. But further structural characterization would be carried out to verify the geometrical isomers as proposed above.

In conclusion, the results indicated that the chiral pineno-bipyridines are analogous to the chiral diphosphine ligand DIOP, which could be introduced to prepare very stable molybdenum-fullerenyl complexes. Detailed studies including the application of the resulting chiral complexes in some enantioselective catalysis are being underway.

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