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Circular dichroism of configurationally chiral dimolybdenum complexes with chiral diamine ligands ☆

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Abstract

The electronic absorption spectrum and the CD spectrum of the chiral molecule [$Mo_2Cl_4(R,R\text{-dach})_2$] (dach = (−)-*trans*-1,2-diaminocyclohexane) have been investigated and correlated with the CD rules for the corresponding chiral diphosphine complexes. The sign of the two bands at 546 and 461 nm for the transitions $\delta_{xy} \rightarrow \delta^*_{xy}$ and $\delta_{xy} \rightarrow \delta_{x^2-y^2}$, respectively, are consistent with the helicity rule for this kind of inherently chiral dimolybdenum complexes.

Keywords: Circular dichroism; Molybdenum complexes; Diamine complexes; Dinuclear complexes; Chirality

1. Introduction

Dinuclear transition metal complexes are a very useful tool for the determination of chirality of optically active compounds. Chiral ligands can induce Cotton effects within the absorption bands of the electronic transitions of dimetallic chromophores. Applications are reviewed in several papers [1–4].

Configurationally chiral dimolybdenum complexes are well-known and CD rules for this kind of compounds with bridging, bidentate diphosphine ligands first were developed by Cotton and co-workers [5,6].

Chiral dimolybdenum complexes with diamine ligands and their CD spectra were reported by Peacock and co-workers [7,8]. They have prepared [$Mo_2(R\text{-pn})_4$]$^{4+}$ and [$Mo_2(S,S\text{-bn})_4$]$^{4+}$ (pn = 1,2-diaminopropane; bn = 2,3-diaminobutane), the CD spectra of which were enantiomeric to each other as expected. The negative sign at 477 nm and the positive sign at 360 nm for [$Mo_2(R\text{-pn})_4$]$^{4+}$ were opposite to those of [$Mo_2(R\text{-dppp})_4$]$^{4+}$ (dppp = 1,2-bis(diphenylphosphino)propane) with configurationally identical ligands. In analogy to the CD rules of diphosphine complexes they conclude that the twist angle between the two Mo–N bonds of the N–Mo–Mo–N unit must have a value between 45 and 90°. *R*-pn and *S,S*-bn can adopt these angles with a change of their conformation by rotation around C–C single bonds. The purpose of this work was to prepare a chiral complex with restriction on conformational changes in the ligand in order to validate proposed CD rules. The dach ligand promised to be a good choice, because its cyclohexane structure with *trans* arrangement of the two amino groups restrains the possibilities of complexation to the one in which the twist angle between the N–Mo–Mo–N bonds can only be smaller than 45°. Synthesis including elemental analysis of the Mo_2 complex has already been described by Gibson [9].

2. Experimental

$K_4Mo_2Cl_8$ was prepared by a literature method [10]. (*R,R*)-(−)-1,2-diaminocyclohexane was obtained commercially from FLUKA. The electronic absorption spectrum (EAS) was recorded using a Cary 17-D spectrophotometer, the CD spectrum was measured with a dichrograph JASCO J-600. The IR spectrum was recorded on an IBM FT-IR/40 instrument. Mass spectrometry was done with a Varian MAT CH-5 machine.

2.1. *Tetrachloro-bis[(R,R)-trans-1,2-diaminocyclohexane]dimolybdenum(II),* [$Mo_2Cl_4(R,R\text{-dach})_2$]

A red suspension of 90 mg (0.14 mmol) $K_4Mo_2Cl_8$, 32 mg (0.27 mmol) *R,R*-dach and 5 ml MeOH was refluxed under argon for 1 h to give a light pink

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☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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microcrystalline precipitate, which was filtered and washed with MeOH, water and THF. After drying in vacuo 70 mg (89%) of a pink powder were obtained. All spectroscopic measurements were carried out with Nujol mulls, because of the insolubility of the powder in all common solvents, including water and DMSO.

UV–Vis (nm): 315, 380, 555.

CD (nm): 308 pos., 398 pos., 461 neg., 547 pos.

IR (cm^{-1}): 3415 νNH_{assoc}; 3299, 3273, 3251, 3213, 3191, 3155, 3116 $\nu_{s,as}NH$; 2954, 2916 νCH_2; 2853 νCH; 1577, 1543 δNH; 1447, 1367 δCH_2 and CH; 1172, 1128, 1107, 1047, 1034 νCN; 680 $\gamma_{rock}CH_2$ and CH, γNH.

MS (*m/z*): 281(0.3, $M^{\cdot +}/2$), 256 (0.25), 207 (1.8, $M^{\cdot +}/2-HCl$), 188 (1.5), 147 (2), 114 (3, dach$^+$), 97 (17), 69 (25), 36 (100).

Reaction of excess of dach with $(NH_4)_5Mo_2Cl_9$ as starting material resulted in the same product, proved by identical IR and UV–Vis spectra. [Mo_2Cl_4(*R*,*R*-dach)$_2$] shows no reaction with 5 M aqueous HCl or aqueous NaOH. Under air it is stable for several days, but after one week it becomes brown. The brown product is only soluble in 5 M aqueous HCl and shows no electronic absorptions in low energy range.

Many attempts to get single crystals failed because of the insolubility of the product.

3. Results and discussion

The complexation of the diamine to the dimolybdenum core affects the N–H vibrations νNH as well as δNH. The IR spectrum of neat diamine in Nujol has a very broad absorption band in the range 3700–3100 cm^{-1} with only a very slight structure indicating strong inter- and intramolecular interactions. Strong bondings of the amino groups to the molybdenum cluster reduce these interactions dramatically. Several very sharp peaks are observable from 3300 to 3100 cm^{-1} in the IR spectrum of [Mo_2Cl_4(*R*,*R*-dach)$_2$] (Fig. 1), but weak intermolecular interactions still occur shown by a broad band at 3415 cm^{-1} with lower intensity. The formation of a metal–nitrogen bond shifts the electron density from the lone pair of the nitrogen into the metal-localized orbitals leaving a partial positive charge on the nitrogen atom. This causes a decrease of the NH deformation frequency, which is then substantially lower than in free diamine. The diamine shows its δNH vibrations as a broad band at 1610 cm^{-1} whereas for the complex two sharp peaks appear at 1577 and 1543 cm^{-1}. These positions are typical for δNH vibrations in spectra of secondary ammonium ions [11,12].

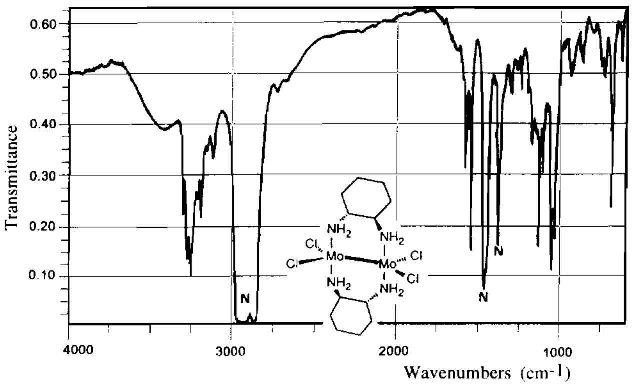

Fig. 1. IR spectrum of [Mo_2Cl_4(*R*,*R*-dach)$_2$] as Nujol mull (N = Nujol bands, dach = *R*,*R*-*trans*-1,2-diaminocyclohexane).

Additionally, the gain in intensity of the γNH rocking vibration also reflects the positive charge on the nitrogen atom. The IR spectrum does not define the coordination mode (α- or β-form) of the dach ligand.

Since the spectroscopic measurements were carried out with Nujol mulls, due to the insolubility of the diamine complex, the interpretation of the electronic absorption spectrum (EAS) and of the CD spectrum is restricted to a qualitative nature.

The EAS and CD spectra of [Mo_2Cl_4(*R*,*R*-dach)$_2$] are shown in Fig. 2. One can observe two significant bands, one at 547 nm with positive sign and one at 461 nm with negative sign. The two positive bands at 308 and 398 nm correspond to the absorption bands in the EAS. Table 1 gives a list of the energies of the low energy absorptions for some selected compound classes with bidentate ligands and $[Mo_2Cl_8]^{4-}$.

For the interpretation of the CD spectrum one can assume a bridging ligation of the diamine molecules (β-form). This seemed to be very straightforward, because α-dimolybdenum with chelating diphosphines shows no measurable CD under either the band for the $\delta_{xy} \rightarrow \delta^*_{xy}$ or $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ transition. A second argument

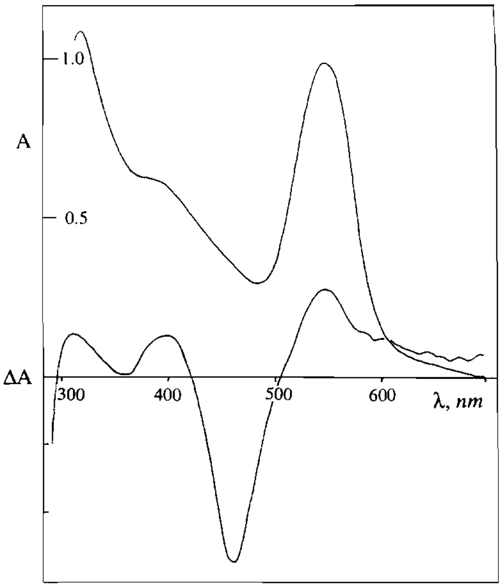

Fig. 2. Electronic absorption spectrum (upper curve) and CD spectrum (lower curve) of [Mo_2Cl_4(*R*,*R*-dach)$_2$]. The CD is shown as the differential absorbance $\Delta A = A_L - A_R$.

Table 1
Positions of the low energy bands in the EAS of dimolybdenum complexes for the $\delta_{xy} \rightarrow \delta^*_{xy}$ and $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ transitions (P–P and N–N represent bridging, bidentate phosphine or amine ligands, respectively)

Complex	$\delta_{xy} \rightarrow \delta^*_{xy}$ λ (nm)	$\delta_{xy} \rightarrow \delta_{x^2-y^2}$ λ (nm)	Reference
$[Mo_2Cl_4(P\text{–}P)_2]$	740	470	[5]
$[Mo_2Cl_4(N\text{–}N)_2]$	555	450	this work
$[Mo_2Cl_8]^{4-}$	530	420	[13]
$[Mo_2(OAc)_2(P\text{–}P)_2]^{2+}$	505		[14]
$[Mo_2(OAc)_2Cl_4]^{2-}$	495		[15]
$[Mo_2(N\text{–}N)_4]^{4+}$	480	360	[7]

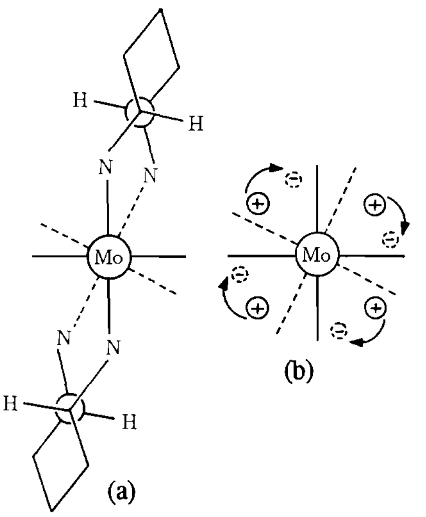

Fig. 3. (a) Fixed conformation of the diamine complex with a positive torsional angle of each N–Mo–Mo–N moiety. (b) Figure of the transition multipole of the $\delta_{xy} \rightarrow \delta^*_{xy}$ transition. Electron charge is transported along a right-handed screw resulting in a positive Cotton effect.

is that $[Mo_2Cl_4(R,R\text{-dach})_2]$ was prepared by refluxing in methanolic solution for 1 hour. These reaction conditions should give the thermodynamically more stable β-isomer as observed for diphosphine complexes [16–18]. Additionally, a crystallographic study of a dimolybdenum complex with bridging ethylenediamine was reported by Eichhorn et al. [19].

Thus, the signs for the low energy bands are consistent with both the absolute configuration of the diamine ligand and the twist angle smaller than 45°, by applying the helicity rule developed for the corresponding diphosphine complexes. Fig. 3 shows the absolute configuration of the chiral complex viewed along the Mo–Mo bond. Using the procedure reported elsewhere [5–8] Fig. 3(b) shows that the electron charge is rotated on a right-handed screw during the excitation for the $\delta_{xy} \rightarrow \delta^*_{xy}$ transition. The electric dipole moment μ_z and the magnetic moment m_z have a mutual parallel arrangement and thus the CD should be positive. For the $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ transition the opposite helicity rule is valid and the CD band at 461 nm should be negative. Both predictions are confirmed by this experiment.

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