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Preparation, Crystal Structure and Chiroptical Properties of $Rh_2[camphanate]_4 (MeOH)_2$

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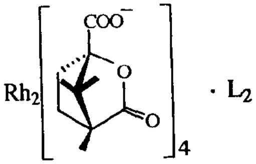
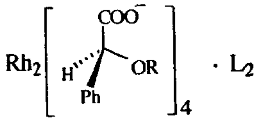
Key Words: Dirhodium tetracamphanate, X-ray structure determination, CD spectra.

Abstract: Chiral Rh (II) complex of camhanic acid, versatile chiral agent, is prepared, and its structure discussed on the basis of X-ray, UV/VIS and CD data.

Chiral dirhodium tetracarboxylate complexes have recently attracted considerable interest due to their specific structural[1,2] and catalytic [2-7] properties. Their preparation was first described by Shchelkov et al.,[8] and subsequently various other methods were developed.[1,7,9] Using chiral Rh(II) carboxylates, $Rh_2(OOCR^*)_4 L_2$, where R* represents chiral organic subunit, and L represents a Lewis base, enantioselective hydrogenation[2] and cyclopropanation of prochiral olefins,[4] as well as various intra-[3,5-7] and intermolecular[7] C-H bond insertions were achieved. Whereas the former catalytic transformation proceeded with low optical yields (ref. 2., e.e.'s ≤15%), the latter two afforded cyclopropane derivatives with moderate optical yields (ref. 4-7., e.e.'s ≤45%)

Camphanic acid, as a strong α-oxy acid (pKa ca. 2.5), was repeatedly used as chiral agent for separation of racemic alcohols,[10-12] amines,[13] and aminoacids.[14] It was also converted into chiral monophosphine ligand, and its Rh(I) complex was tested as catalyst in asymmetric hydrogenation.[15] Here we report on preparation, structure, and chiroptical properties of dimeric Rh(II) complex of camphanic acid (**1**), envisaged as chiral catalyst in some enantioselective transformations.





	L	R
1	MeOH	
2	Py	
3	EtOH	H
4	THF	CH_3

Using a method of Callot and Metz,[9] Rh(II) complex **1** was prepared in 90%yield.[16] Other attempted method[4] resulted with considerably lower yields of **1**. Crude complex, pale-green crystalls, was purified on silica gel column using.dichloromethane-ethanol 93:7 as eluant. Good quality single crystals, for X-ray structure determination were obtained from methanol.

The molecule of compound **1** has local D_{4h} symmetry at the $Rh_2(Oeq)_8\,(Oax)_2$ chromophore, which is reduced to D_{2h} if the anisotropy of the axial ligand (MeOH) is considered, and the entire molecule posses C_1 symmetry because of the pair-wise matching of the two chiral carboxylates, Fig. 1[17]. The distorted octahedral coordination of Rh(II) is of five oxygen atoms from four camphanate ligands and methanol, and on more Rh atom. The camphanate ligands with equatorially disposed oxygen atoms act as the bidentate bridging with Rh-O distances ranging from 2.031(8) to 2.070(10)Å. Two methanol molecules are axially coordinated in the binuclear unit at *trans* position to the Rh-Rh bond with Rh-O bond of 2.239(12)Å.

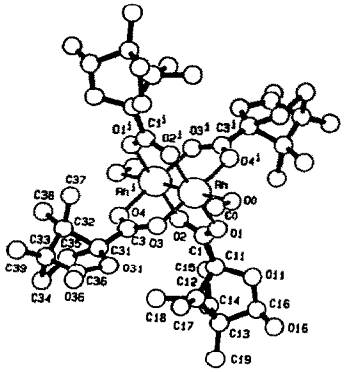


Figure 1. The centrosymmetric dimer molecule of **1** with octahedral coordination of Rh(II). The atomic numbering is given including the centrosymetryc coordinated oxygen atoms marked by i (-x, -y+1, -z).

UV/VIS and CD spectra of compound **1**, and its Rh_2[camphanato]$_4$ (pyridine)$_2$ (**2**) congener are presented in the Figs. 2. and 3., *resp*, and are notably different from those reported[1] for Rh_2[(S)-mandelate]$_4$ (EtOH)$_2$ (**3**) and for its O-methylether (THF)$_2$(**4**).

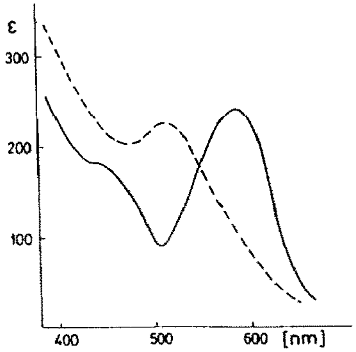


Figure. 2. UV/VIS Spectra of **1** (—) and **2** (- - -) in MeOH; conc. of **1** 1.3x10^{-3} M, conc. of pyridine 1.2x10^{-2} M.

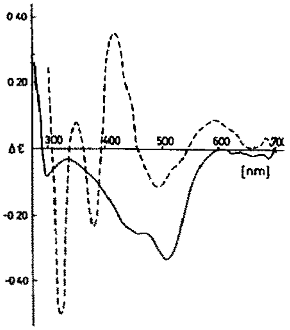


Figure. 3. CD Specra of **1** (—) and **2** (- - -) in MeOH.

UV/VIS Spectrum of **1** exhibits a long-wavelength maximum at 584 nm ($\varepsilon = 240$), and a second one as a shoulder at 445 nm ($\varepsilon = 180$). A distinct short-wavelength band at 445 nm, observed in the Rh(II) mandelate complexes **3** and **4**, is missing. Compound **2**, prepared *in situ*, exhibited only one band at 515 nm ($\varepsilon = 225$). This change in the spectrum on going from **1** to **2** is in accordance with the known hypsochromic shift of the "band I" at 580-600 nm to *ca.* > 50 nm shorter wavelength when more basic amine is apically bound.[19]

It is interesting to note that the CD of **1** exhibited strong negative band at 508 nm, and another negative band appears at 458 nm as the shoulder on the first band at the shorter-wavelength side. There is no distinct band at 580-600 nm. Again, this is notably different feature as compared to the spectra of **3** and **4**.[1] Both mentioned compounds exhibited two "outer" CD bands, at *ca.* 450 nm and at 590 nm, corresponding to the observed electronic transitions in the visible region, along with the "inner" one, **of the opposite sign**, at *ca.* 500 nm. Besides, the strongest band at *ca.* 500 nm is of the opposite sign for **1** and **3**. The third band was assigned to an overlap of two magnetically allowed transitions at *ca.* 590 nm and 450 nm, which are active in the CD by the reverse-mixing process. Since the 500 nm band does not appear in the electronic spectrum of **1**, it is magnetically allowed transition.

As announced by Cotton et al.,[1] magnetically allowed δ (Rh-Rh) $\longrightarrow \sigma^*$ (Rh-O) transition is also active in dirhodium tetracarboxylates, and therefore could effect relative intensities of the three CD peaks. This seems to be the case with the CD of **1**; the first and third band are much less intensive than the "mixed" one at 500 nm. This also confirmes the CD spectrum of the complex **2**, Fig. 3. Axially bound pyridine enhances the intensity of the two "outer" bands, to $\Delta\varepsilon$ +0.11 at 602 nm, and to $\Delta\varepsilon$ +0.36 at 423 nm, as compared to the "inner" one at 495 nm ($\Delta\varepsilon$ -0.14). Besides, the sign of the "outer" bands are now opposite to that of the "inner" one, as observed for the CD of two chiral complexes studied previously[1].

Different chiroptical properties of dimeric complexes **1** and **3**, which posses similar crystal structure and the same (S) absolute configuration at the chiral centre next to the carboxy group in the ligand, can be explained by diverse structure and polarity (anisotropy) of the two groups, beside carboxy group and O-atom, connected to the chiral centre in the two homochiral ligands.

Camphanic acid subunit in **1** is characterized by the fixed conformation and large difference in the steric requirements of the three groups on the chiral centre. In view of this property, and the above discussed difference in chiroptical properties between **1** and **3**, it seems a worthwile goal to compare their catalytic efficacy and direction of enantioselectivity in some enantoselective transformations. This is object of our ongoing investigation.

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16. Mp. >300°C. IR (KBr): 3590, 3480, 2970, 1785, 1605, 1440, 1330, 1290, 1185, 1170, 1115, 1065, 1015, 930, 815 cm^{-1}. ^{1}H-NMR (CDCl$_3$), δ: 0.72 (s, 3H), 0.88 (s, 3H), 1.04 (s, 3H), 1.6 (m, 1H), 1.6-1.8 (m, 2H), 2.25 (m, 1H). ^{13}C-NMR (CDCl$_3$), δ, 9,67, 16.75, 16.85, 18.27, 28.77, 30.81, 53.66, 54.54, 58.90, (2x CH$_3$OH), 91.35, 178.14, 186.45.
17. A least-square fit on 25 reflections ($8<\theta<17$) ended with a triclinic unit cell (Z=2), a=10.815(14), b=10.892(16), c=13.088(18)Å, α=111.43(7), β=104.85(7), γ=106.32(7)°. Data collection was performed using Enraf-Nonius CAD4F diffractometer with MoK α radiation (λ=0.71073Å) at 103K in ω-scan mode ($\Delta\omega=1+0.35\ \mathrm{tg}\theta$). 17375 reflections in the range $3<\theta<32°$ were collected. Data reduction was performed by Enraf-Nonius SDP/VAX package. A considerable decay of 12.5% was detected. The intensities were corrected for crystal deterioration, Lorentz, and polarization effects. The experimental absorption correction based on a ψ-scan of 9 reflections was used. Structure determination based on direct methods integrated in the SHELX86 package of computer programs confirmed the space group $P\bar{1}$. The structure was refined on the base of 8208 reflections ($F_o>5\,\sigma F_o$) by full-matrix least-squares procedure to the residual factor R=0.137 and wR=0.140. The hydrogen atoms were introduced on the base of stereochemical grounds and refined under the constrain of the pivot carbon atoms. The refinement was carried out by the SHELX77 package of computer programs. The atomic coordinates for **1** have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK. Please give complete literature citation when ordering.
    Absolute configuration of camphanic moiety is known.[18]
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