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Crystal Structure Analysis and Chiral Recognition Study of Δ-[Ru(bpy)$_2$(py)$_2$][(+)-*O,O′*-dibenzoyl-D-tartrate]·12H$_2$O and Λ-[Ru(bpy)$_2$(py)$_2$][(−)-*O,O′*-dibenzoyl-L-tartrate]·12H$_2$O

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The molecular structure and crystal-packing mode of the enantiopure chiral building blocks Δ-[Ru(bpy)$_2$(py)$_2$]-[(+)-*O,O′*-dibenzoyl-D-tartrate]·12H$_2$O (**I**) and Λ-[Ru(bpy)$_2$(py)$_2$][(−)-*O,O′*-dibenzoyl-L-tartrate]·12H$_2$O (**II**) have been determined by single-crystal X-ray diffraction data. This study proposes a model of how the L- and D-dibenzoyltartrate anions recognize the chirality of the hydrophobic [Ru(bpy)$_2$(py)$_2$]$^{2+}$ complex. The monoclinic unit cell contains four complex cations, four tartrate anions, and 48 water molecules. Since there are no possibilities to form hydrogen bonds between the cations and anions, chiral recognition is due to crystal packing. Two benzoyl rings of two different tartrate anions are gripping the two bpy-planes of the Ru-complex. Further a third benzoyl ring from a tartrate anion is packed between the two pyridine rings, favoring one enantiomeric form to crystallize from aqueous solution. Crystal structure data for **I** at 153 K: $a = 15.342(3)$ Å, $b = 19.200(4)$ Å, $c = 18.872(4)$ Å, $\beta = 104.841(3)°$, monoclinic space group C_2, $R_1 = 0.0239$ ($I > 2\sigma(I)$), $R_2 = 0.0606$, Flack parameter $= 0.0115$ (with esd 0.0166). For **II** at 293 K: $a = 15.376(4)$ Å, $b = 19.388(11)$ Å, $c = 19.085(7)$ Å, $\beta = 105.11(2)°$, monoclinic space group $C121$, $R_1 = 0.0686$ ($I > 2\sigma(I)$), $R_2 = 0.1819$, Flack parameter $= -0.0100$ (with esd 0.0521).

Introduction

The resolution of *rac*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ (bpy = 2,2′-bipyridine, py = pyridine) with dibenzoyltartrate was developed in our laboratory and has recently been described by X. Hua.[1,2] This resolution method yields excellent chiral building blocks since the two pyridine ligands in Δ- or Λ-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ can easily be substituted under complete retention of configuration. These building blocks are now already used in several applications. For instance, Hua describes in his article the replacement of the two pyridine ligands with a chelating one and further the syntheses of dinuclear Ru-complexes, with defined stereochemistry at the metal centers.

Tor et al.[3] describe the substitution of the pyridine ligands with bromo-1,10-phenanthroline and utilization of these enantiopure chiral tris-chelated Ru-complexes as building blocks for diastereomerically pure di- and trinuclear complexes.[4]

We present here the crystal structure analysis of Δ-[Ru(bpy)$_2$(py)$_2$][(+)-*O,O′*-dibenzoyl-D-tartrate]·12H$_2$O (**I**) and Λ-[Ru(bpy)$_2$(py)$_2$][(−)-*O,O′*-dibenzoyl-L-tartrate]·12H$_2$O (**II**), which shows interesting features explaining the mechanism of chiral recognition between the dibenzoyl tartrate ion and the Ru-complex.

Experimental Section

Syntheses, resolution, and crystallization followed the procedures described by X. Hua.[1]

X-ray Structure Determination of I and II. The data collection for the structure determination was performed on a Hilger&Watts diffractometer at 153 K for **I** and on a Syntex P21 at 293 K for **II** using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Twenty-two high-angle reflections were used to determine the unit cell and orientation matrix for data collection. The crystallographic data for **I** and **II** are summarized in Table 1. The structure was solved by heavy pattern method with SHELXS[5] and refined by full matrix least squares on F^2 with SHELXL.[6] All non-hydrogen atoms were refined anisotropically (SHELXL). The aromatic hydrogen atom positions were calculated, and their displacement parameters (thermal motion ellipsoids) were calculated with the respective carbon atom multiplied

Table 1. Crystallographic Data for Δ-[Ru(bpy)$_2$(py)$_2$][(+)-*O,O′*-dibenzoyl-D-tartrate]·12H$_2$O (**I**) and Λ-[Ru(bpy)$_2$(py)$_2$][(−)-*O,O′*-dibenzoyl-L-tartrate]·12H$_2$O (**II**)

	I	II
empirical formula	$C_{48}H_{62}N_6O_{20}Ru$	$C_{48}H_{62}N_6O_{20}Ru$
fw	1144.11	1144.11
temperature	153(2) K	293(2) K
wavelength	0.71073 Å	0.71073 Å
space group	C_2 (No. 5)	C_2 (No. 5)
unit cell dimens	$a = 15.342(3)$ Å	$a = 15.376(4)$ Å
	$b = 19.200(4)$ Å	$b = 19.388(11)$ Å
	$c = 18.872(4)$ Å	$c = 19.085(7)$ Å
	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 104.84(3)°$	$\beta = 105.11(2)°$
	$\gamma = 90°$	$\gamma = 90°$
volume	5374(2) Å^3	5493(4) Å^3
Z	4	4
density (calcd)	1.414 g/cm^3	1.384 g/cm^3
abs coeff	0.372 mm^{-1}	0.364 mm^{-1}
R^a	0.0239	0.0686
$R_w{}^b$	0.0606	0.1819

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \{\sum[w(|F_o| - |F_c|)]^2]/\sum[w|F_o|^2]\}^{1/2}$.

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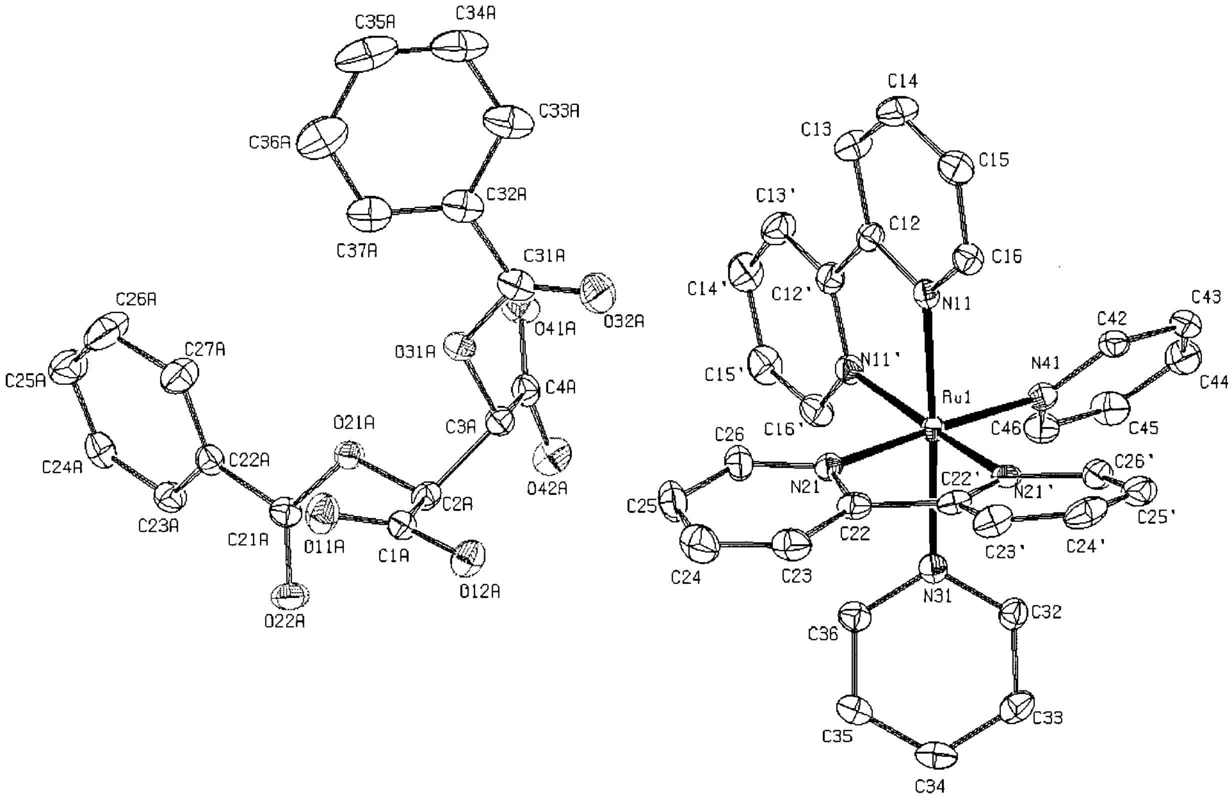

Figure 1. Labeling system and molecular structure (thermal vibrational (30%) ellipsoids) of Δ-[Ru(bpy)$_2$(py)$_2$][(+)-*O*,*O*′-dibenzoyl-D-tartrate] (**I**) (hydrogen atoms and solvent molecules are left out for clarity).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **I** and **II**

	I	**II**
Ru(1)−N(11)	2.075(2)	2.053(7)
Ru(1)−N(11′)	2.079(2)	2.065(7)
Ru(1)−N(21)	2.059(3)	2.061(6)
Ru(1)−N(21′)	2.085(3)	2.071(6)
Ru(1)−N(41)	2.112(3)	2.116(7)
Ru(1)−N(31)	2.126(2)	2.118(7)
N(21)−Ru(1)−N(11)	90.55(9)	91.0(3)
N(21)−Ru(1)−N(11′)	95.88(10)	94.8(3)
N(11)−Ru(1)−N(11′)	78.78(9)	79.0(3)
N(21)−Ru(1)−N(21′)	79.05(11)	78.2(3)
N(11)−Ru(1)−N(21′)	94.13(9)	95.8(3)
N(11′)−Ru(1)−N(21′)	171.32(10)	171.3(3)
N(21)−Ru(1)−N(41)	177.38(10)	177.2(2)
N(11)−Ru(1)−N(41)	91.46(9)	86.7(2)
N(11′)−Ru(1)−N(41)	86.17(10)	86.3(3)
N(21′)−Ru(1)−N(41)	99.13(10)	100.5(3)
N(21)−Ru(1)−N(31)	87.43(9)	90.3(2)
N(11)−Ru(1)−N(31)	177.47(9)	177.8(3)
N(11′)−Ru(1)−N(31)	99.90(9)	99.1(3)
N(21′)−Ru(1)−N(31)	86.99(9)	86.3(3)
N(41)−Ru(1)−N(31)	90.60(9)	92.1(2)

by 1.2. For structure **I** (low-temperature data set) the hydrogen atom positions of the water molecules were found in the Fourier-difference electron density map and refined by SHELXL. For structure **II** they could not be localized.

Since the two resolved complexes are enantiomers, the two structures are almost identical. The proof for the opposite chirality is also given from the Flack parameter,[7] which is 0.0115 for **I** and −0.0100 for **II**.

Results and Discussion

Compounds **I** and **II** crystallize in the monoclinic space group C_2. The unit cell contains four complex cations, four tartrate anions, and 48 water molecules.

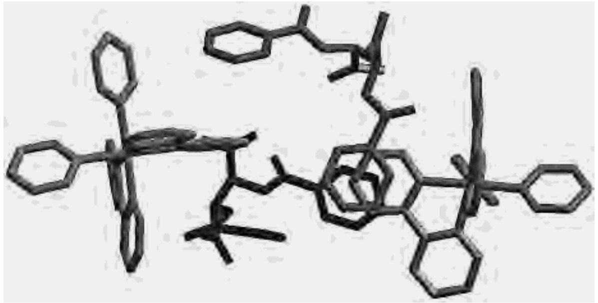

Figure 2. Cerius^{2} [10] drawing of **I**.

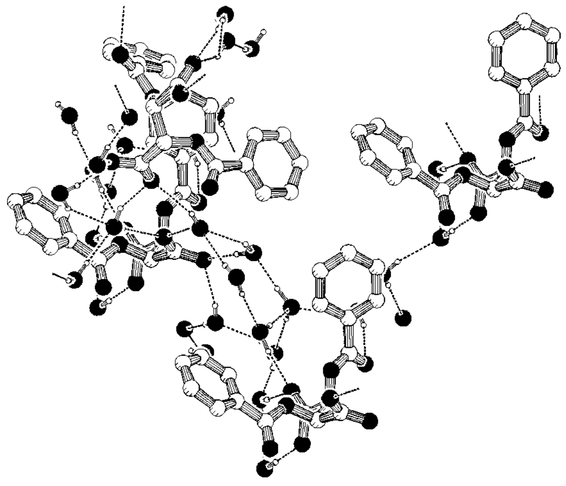

Figure 3. Drawing[8] of the anions and water molecules (with hydrogen bonds) packed in the unit cell without the cation of structure **I**.

The R_1 value after final refinement for **I** is 0.0239 and for **II** 0.0686. The residual electron density of compound **II** is found to be around the metal center. Table 2 gives selected bond

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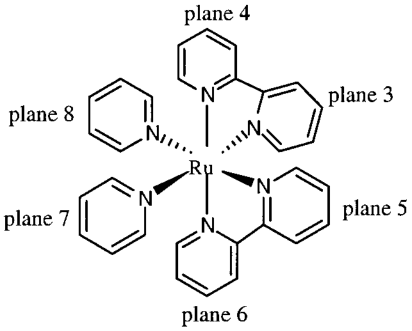
Table 3. Angles between Pyridine and Bipyiridine Planes of Structure **I**



planes	angle (deg)
3−4	6.39 (18)
3−5	85.89 (19)
3−6	84.92 (18)
3−7	50.85 (18)
3−8	87.02 (18)
4−5	84.94 (19)
4−6	87.09 (19)
4−7	56.70 (19)
4−8	87.49 (18)
5−6	14.19 (19)
5−7	75.03 (19)
5−8	50.79 (19)
6−7	89.22 (19)
6−8	39.46 (18)
7−8	61.98 (18)

lengths and angles. Some angles between selected planes, for example, between pyridine and bipyridine units, are listed in Table 3. From Table 2 one can see that the Ru−N bond lengths to the bipyridine ligands are significantly shorter (ca. 0.05 Å) than those to the pyridine ligands. This difference is most likely caused by stronger π-back-bonding between Ru^{II} and bipyridine, as compared to pyridine, due to stronger delocalization of π^* orbitals in the former. Another contribution of the shortening is the bite angle of the chelate.

As structures **I** and **II** are essentially the same, we will discuss only the results of compound **I**, whose data were measured at low temperature and therefore gave the more accurate structure. The ORTEP[8] drawing in Figure 1 shows the structure and the labeling system for the cation and the anion of **I** (hydrogen atoms are omitted for clarity).

Since there are no possibilities to form hydrogen bonds between the cations and anions, chiral recognition is due to crystal packing. The presentation in Figure 2 shows that two benzoyl rings of two different tartrate anions are gripping the two planes of the bipyridine ligands of the Ru-complex, thus yielding an optimal packing in the solid. The distances between the bipyridine plane and the benzoyl rings were found to be in a range of 3.48−3.92 Å. The 12 water molecules build a network of hydrogen bonds between themselves and the oxygen atoms of the benzoyltartrate anions (Figure 3), where there is just enough space left for the chiral cations.

It is interesting to note that the two similar complexes $[Ru(bpy)_2(py)_2]^{2+}$ and $[Ru(phen)_2(py)_2]^{2+}$ (phen = *o*-phenanthroline), respectively, can be resolved; however the resolving agents are mutually exclusive. The former needs benzoyltartrate and the latter arsenyltartrate.[9] Apparently the two additional aromatic −CH groups increase the cation volume to such a degree that crystal packing is no longer favorable. All attempts to obtain crystals of Δ-$[Ru(phen)_2(py)_2][(+)$-*O*,*O′*-dibenzoyl-D-tartrate] failed, showing again the importance of chiral recognition resulting in completely different packing modes.

Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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