Research Article

Molecular Structure of 1,2-Dibenzoyl-1',2',3',4',5'-pentamethylruthenocene Dioxime Hydrochloride

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The dioxime of 1,2-dibenzoylpentamethylruthenocene is synthesized from its parent diketone and hydroxylamine under standard basic conditions. The slightly air-sensitive product is crystallized in the form of its monohydrochloride. The solid-state structure is the first example of a dioxime monohydrochloride showing a typical metallocene core with peripheral intramolecular N–H–N and O–H–Cl hydrogen bonding.

1. Introduction

Simple vicinal dioximes represent the well-known chelating ligands with numerous applications in coordination chemistry [1, 2], catalysis [3, 4], and supramolecular chemistry [5–7]. Based on our earlier work [8, 9] with metallocene metalloligands, we address in this work a new organometallic hybrid dioxime composed of a redox-responsive ruthenocene core and conjugated dioxime functional groups. Synthetic and structural properties in solution and in the solid state are reported.

2. Materials and Methods

2.1. 1,2-Dibenzoyl-1',2',3',4',5'-pentamethylruthenocene Dioxime. In the first Schlenk vessel, a solution of 1,2-dibenzoyl-1',2',3',4',5'-pentamethylruthenocene [8, 9] (0.200 g, 0.40 mmol) in dry ethanol (5 mL) was prepared at room temperature. In the second Schlenk vessel, a solution of hydroxylamine hydrochloride (0.400 g, 5.76 mmol) in dry ethanol (5 mL) and freshly distilled, dry pyridine (4.96 mmol, 0.40 mL) was similarly prepared. Under protection from air, the two solutions were combined and heated to reflux for 45 minutes. Workup is as follows: pyridine and most volatile materials were removed on a vacuum line. Under protection

from air, the residue was repeatedly extracted with small portions (2 mL) of warm, dry ethanol. The ethanolic solutions were filtered through a syringe filter, and the combined extracts were cooled in an ice/water-bath for crystallization. Without protection from air, the crystallized product was filtered off, washed with two portions of cold water, and dried under vacuum, affording 0.125 g of orange-yellow 1,2-dibenzoyl-1',2',3',4',5'-pentamethylruthenocene dioxime in 57.9% yield. Note that this compound is air-stable in the solid state but slightly air-sensitive in solution. M.p.: 163°C (dec.).

¹H NMR (300 MHz, CD₂Cl₂): δ 1.78 (s, 15H, Cp*), 4.43 (d, 2H, Cp), 4.56 (t, 1H, Cp), 7.57 (br s, 10H, phenyl), 12.16 (s, 2H, N–OH). ¹³C NMR (75 MHz, CD₂Cl₂): δ 11.2 (Cp*), 78.1 (Cp), 79.8 (Cp), 81.2 (Cp*), 88.7 (Cp); 128.5, 129.2, 130.2, 131.0 (phenyl); 158.0 (C=N–OH). LSIMS: *m/z* 541.14 (M⁺ + H). Single crystals of the hydrochloride of 1,2-dibenzoyl-1',2',3',4',5'-pentamethylruthenocene dioxime were obtained at room temperature from a solution of dichloromethane/*n*-hexane (v/v = 1/1).

2.2. X-Ray Crystallography: Single-Crystal X-Ray Measurements and Structure Determination (Table 1). The data collection was performed on a Nonius Kappa CCD diffractometer equipped with graphite-monochromatized Mo-K_α-radiation

TABLE 1: Crystallographic data.

Empirical formula	$C_{29}H_{31}ClN_2O_2Ru$	
Formula weight	576.08	
Temperature	233(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$ (no. 14)	
Unit cell dimensions	$a = 16.6035(2)$ Å $b = 16.6935(4)$ Å $c = 20.0607(4)$ Å	$\alpha = 90^\circ$ $\beta = 105.432(2)^\circ$ $\gamma = 90^\circ$
Volume	$5359.77(18)$ Å ³	
Z	8	
Density (calculated)	1.428 g/cm ³	
Absorption coefficient	0.713 mm ⁻¹	
$F(000)$	2368	
Crystal size	$0.34 \times 0.15 \times 0.09$ mm ³	
Theta range for data collection	1.27 to 24.94°	
Index ranges	$-19 \leq h \leq 19, -19 \leq k \leq 19, -23 \leq l \leq 18$	
Reflections collected	30131	
Independent reflections	9334 [$R(\text{int}) = 0.0359$]	
Reflections [$I > 2\sigma(I)$]	7629	
Completeness to $\theta = 24.94^\circ$	99.6%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	9334/6/665	
Goodness-of-fit on F^2	1.037	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0379, wR_2 = 0.0880$	
R indices (all data)	$R_1 = 0.0518, wR_2 = 0.0935$	
Largest diff. peak and hole	0.428 and -0.784 e.Å ⁻³	

($\lambda = 0.71073$ Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK [10]. Several scans in the φ and ω directions were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces an empirical absorption correction. The structures were solved with direct methods (SHELXS-86) and refined against F^2 (SHELX-97) [11]. Hydrogen atoms at carbon atoms were added geometrically and refined using a riding model, whereas the hydrogen atoms at nitrogen and oxygen atoms were exactly localized and refined isotropically with bond restraints of 89 pm for N–H and 83 pm for O–H, respectively. The refinement of N–H distances without bond restraints leads to bond lengths of 99 and 103 pm for N2–H and N4–H. All nonhydrogen atoms were refined with anisotropic displacement parameters.

3. Results and Discussion

Synthetically, 1,2-dibenzoyl-1',2',3',4',5'-pentamethylruthenocene dioxime is obtained in 58% isolated yield from the diketone by reaction with hydroxylamine hydrochloride and pyridine. This dehydrative condensation is a standard procedure for dioxime formation; however, protection from

air is mandatory in this case due to the sensitivity of the product towards dehydration/dehydroxylation promoted by the strong electron-donating effect of the pentamethylruthenocene moiety. Structural properties in solution are in line with expectations, as shown by NMR spectroscopy. Interestingly, suitable single crystals for X-ray structure analysis were obtained only for the monohydrochloride of the product, but not for the neutral dioxime. In principle, oximes are acid-sensitive and give rise to the Beckmann rearrangement in the presence of electrophiles; therefore, this is quite unusual. There are many structural reports on dioximes, including studies focusing on their supramolecular chemistry based on N–H–O hydrogen-bonded architectures [12, 13], but to the best of our knowledge no protonated dioxime has been characterized in the solid state.

The compound crystallizes in the centrosymmetric space group $P2_1/c$ with a pair of planar chiral enantiomeric molecules in the asymmetric unit (Figure 1). The planar chirality is due to the resolved, localized protonation of the nitrogen atoms N2 and N4, thereby forming two chemically nonequivalent hydroxyliminoyl substituents in the 1,2-position of the lower cyclopentadienyl ring. Whereas a local pseudosymmetry of the monoprotonated 1,2-bis(hydroxyliminoyl)cyclopentadienide might seem evident, this symmetry is broken by the position of the five methyl groups

FIGURE 1: Two views of the enantiomeric pair of planar chiral molecules in the asymmetric unit, hydrogen atoms at carbon atoms are omitted for clarity and thermal ellipsoids are drawn on 20% probability level.

of the Cp* ligand of the ruthenocenedioxime molecule. Surprisingly, the N–H bonds are well ordered in the crystal lattice, and the influence of protonation leads to the increase of the N–O bond of around 1.6 pm and the decrease of the C=N double bond of around 0.5 pm for each molecule (Table 2). As a consequence of the strong intramolecular N–H–N bonds, the C=N double bonds are twisted to the conjugated cyclopentadienyl planes, shown by torsion angles of averaged $\pm 18^\circ$ (Table 3). The chloride anions are connected by two strong intramolecular O–H–Cl hydrogen

TABLE 2: Atomic coordinates ($\times 10^4$) and displacement parameters (in $\text{\AA}^2 \times 10^3$).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ru(1)	4452(1)	6377(1)	2455(1)	33(1)
Ru(2)	687(1)	3922(1)	2622(1)	36(1)
Cl(1)	6234(1)	3774(1)	4498(1)	71(1)
Cl(2)	−1164(1)	6607(1)	607(1)	58(1)
O(1)	6349(2)	4023(2)	3046(2)	67(1)
O(2)	6179(2)	5508(2)	4802(1)	66(1)
O(3)	−1146(2)	6361(1)	2103(1)	50(1)
O(4)	−1111(2)	4875(2)	327(1)	54(1)
N(1)	6059(2)	4801(2)	3071(2)	50(1)
N(2)	5986(2)	5679(2)	4108(1)	47(1)
N(3)	−875(2)	5575(2)	2077(1)	42(1)
N(4)	−859(2)	4695(2)	1020(1)	41(1)
C(1)	3673(2)	5572(2)	2869(2)	51(1)
C(2)	3357(2)	6349(2)	2854(2)	48(1)
C(3)	3119(2)	6629(2)	2170(2)	48(1)
C(4)	3293(2)	6015(3)	1736(2)	63(1)
C(5)	3633(2)	5346(2)	2182(2)	61(1)
C(6)	5686(2)	6577(2)	3154(2)	37(1)
C(7)	5355(2)	7338(2)	2874(2)	36(1)
C(8)	5227(2)	7322(2)	2150(2)	40(1)
C(9)	5476(2)	6560(2)	1967(2)	41(1)
C(10)	5761(2)	6083(2)	2574(2)	35(1)
C(11)	6059(2)	5251(2)	2552(2)	39(1)
C(12)	6346(2)	4987(2)	1945(2)	41(1)
C(13)	6933(2)	5443(2)	1736(2)	44(1)
C(14)	7227(2)	5203(3)	1183(2)	54(1)
C(15)	6942(3)	4519(3)	839(2)	67(1)
C(16)	6359(3)	4059(3)	1030(2)	72(1)
C(17)	6057(2)	4290(2)	1585(2)	63(1)
C(18)	5871(2)	6409(2)	3894(2)	38(1)
C(19)	5891(2)	7077(2)	4378(2)	44(1)
C(20)	5338(2)	7096(2)	4795(2)	51(1)
C(21)	5310(3)	7762(3)	5192(2)	68(1)
C(22)	5839(3)	8396(3)	5198(2)	79(1)
C(23)	6415(3)	8365(3)	4812(2)	78(1)
C(24)	6434(2)	7713(3)	4396(2)	62(1)
C(25)	1578(2)	4343(3)	2074(2)	58(1)
C(26)	1903(2)	3642(2)	2456(2)	55(1)
C(27)	2006(2)	3805(2)	3167(2)	49(1)
C(28)	1743(2)	4599(2)	3228(2)	50(1)
C(29)	1480(2)	4941(2)	2557(2)	56(1)
C(30)	−580(2)	3782(2)	1959(2)	35(1)
C(31)	−274(2)	3009(2)	2231(2)	40(1)
C(32)	−111(2)	3026(2)	2957(2)	43(1)
C(33)	−299(2)	3796(2)	3162(2)	41(1)

TABLE 2: Continued.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
C(34)	−593(2)	4286(2)	2558(2)	36(1)
C(35)	−852(2)	5122(2)	2600(2)	36(1)
C(36)	−1085(2)	5405(2)	3228(2)	43(1)
C(37)	−730(3)	6084(2)	3581(2)	69(1)
C(38)	−989(4)	6347(3)	4149(2)	99(2)
C(39)	−1589(4)	5934(4)	4363(2)	97(2)
C(40)	−1928(3)	5251(3)	4028(2)	76(1)
C(41)	−1682(2)	4985(2)	3458(2)	52(1)
C(42)	−803(2)	3957(2)	1218(2)	36(1)
C(43)	−972(2)	3289(2)	714(2)	41(1)
C(44)	−562(2)	3235(2)	195(2)	52(1)
C(45)	−735(3)	2602(3)	−264(2)	69(1)
C(46)	−1322(3)	2038(3)	−220(2)	71(1)
C(47)	−1738(2)	2094(2)	280(2)	66(1)
C(48)	−1558(2)	2715(2)	753(2)	52(1)
C(01)	3965(3)	5052(3)	3503(3)	90(2)
C(02)	3221(3)	6826(3)	3460(2)	87(2)
C(03)	2695(3)	7409(3)	1918(3)	100(2)
C(04)	3117(3)	6036(4)	964(2)	123(3)
C(05)	3879(3)	4537(3)	1961(4)	121(2)
C(06)	1396(3)	4466(4)	1309(2)	116(2)
C(07)	2153(3)	2874(3)	2163(3)	99(2)
C(08)	2390(2)	3242(3)	3749(2)	83(2)
C(09)	1782(3)	5026(3)	3898(2)	91(2)
C(010)	1180(2)	5783(3)	2383(3)	99(2)
H(10)	6370(30)	3880(20)	3437(12)	68(14)
H(20)	6210(30)	5018(12)	4790(20)	63(14)
H(30)	−1190(20)	6510(20)	1702(12)	69(14)
H(40)	−1140(30)	5365(12)	350(20)	73(15)
H(2N)	5990(20)	5298(18)	3791(15)	59(12)
H(4N)	−850(30)	5080(20)	1334(18)	92(16)

TABLE 3: Hydrogen bonds (Å and °) and selected bond lengths (Å) and torsion angles (°).

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
O1–H(10) ... Cl1	0.812(18)	2.21(2)	2.999(3)	165(4)
O2–H(20) ... Cl1	0.821(18)	2.16(2)	2.965(4)	167(4)
O3–H(30) ... Cl2	0.827(18)	2.21(2)	3.021(3)	165(4)
O4–H(40) ... Cl2	0.823(19)	2.14(2)	2.952(3)	170(4)
N2–H(2N) ... N1	0.902(18)	1.69(2)	2.574(4)	164(4)
N4–H(4N) ... N3	0.904(19)	1.71(2)	2.586(4)	163(4)

Selected bond lengths: O1–N1 1.390(4), O2–N2 1.374(4), O3–N3 1.392(3), O4–N4 1.374(3), N1–Cl1 1.283(4), N2–Cl1 1.289(4), N3–C35 1.286(4), N4–C42 1.290(4), C6–C18 1.461(4), C10–C11 1.478(4), C30–C42 1.464(4), C34–C35 1.469(4) and Cp-rings: C6–C10 1.458(4), C6–C7 1.437(4), C7–C8 1.412(4), C8–C9 1.416(5), C9–C10 1.427(4), C30–C34 1.472(4), C30–C31 1.439(4), C31–C32 1.409(4), C32–C33 1.410(5), and C33–C34 1.435(4).

Selected torsion angles: C6–C10–C11–N1 20.4(5), C10–C6–C18–N2 −14.3(5), C30–C34–C35–N3 −20.4(5), and C34–C30–C42–N4 17.2(5).

bonds with H–Cl distances between 214–221 pm, thereby preventing a supramolecular chemistry based on O–H–O hydrogen-bonds. Nevertheless, two weak intermolecular C–H–Cl hydrogen bonds at Cl1 with distances to phenyl hydrogen atoms of 285 and 286 pm lead to a distorted tetrahedral hydrogen coordination for Cl1 and build up a two-dimensional sheet along the crystallographic axes (010) and (101).

4. Conclusions

The crystal structure of the hydrochloride of 1,2-dibenzoyl-1',2',3',4',5'-pentamethylruthenocene dioxime is a unique example of a protonated oxime featuring intramolecular N–H–N and O–H–Cl hydrogen bonding as well as planar chirality.

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