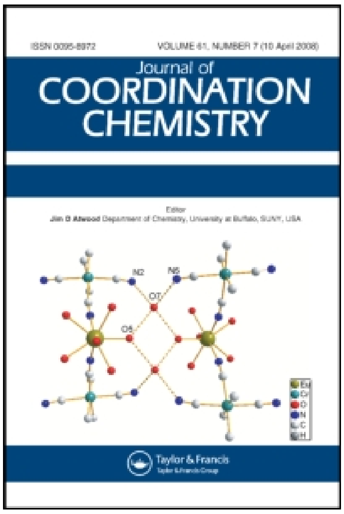

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SOLID STATE STRUCTURE OF A RHENIUM BIBENZIMIDAZOLE COMPLEX

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$Re(CO)_5Br$ readily forms a complex with 2,2′-bibenzimidazole ($bbimH_2$) of the general composition $(bbimH_2)Re(CO)_3Br$, **1**. The complex was characterized by NMR, IR, electronic and emission spectroscopy. The orange-brown compound is sparingly soluble in apolar solvents but could be crystallized from a DMF/toluene mixture. An X-ray structural investigation shows that the rhenium ion has a distorted octahedral geometry. Nitrogen atoms of the bibenzimidazole are *trans* to two carbonyl ligands. The secondary amine protons of the bibenzimidazole ligand form a hydrogen bond to the amide oxygen of a DMF molecule; N3–O4 2.725(7) Å, N4–O4 2.761(7) Å. The bending angle of the two benzimidazole units is 168°; the greatest deviation from planarity within the ligand is 0.14 Å. Crystal data: monoclinic, space group $P2_1/n$, $a = 10.9743(2)$, $b = 12.9182(2)$, $c = 15.1864(3)$ Å, $\beta = 91.647(1)^\circ$, $V = 2152.06(7)$ Å^3, $T = -90^\circ$C, $Z = 4$, $R_1 = 0.025$, $wR_2 = 0.062$ for 4296 reflections with $F_o > 4\sigma(F_o)$ out of 4886 independent reflections.

Keywords: Rhenium; N-ligands; Hydrogen bonds; Solid-state structure

INTRODUCTION

Rhenium biimidazole and bibenzimidazole complexes are important precursors for the construction of luminescent molecular [1] and supramolecular assemblies [2]. The significance of hydrogen bonding for the assembly of multicomponent systems capable of performing efficient energy transfer has recently been demonstrated by our group [3]. It is of paramount importance for the successful application of this principle to obtain information on the influence of different metal centres on structural properties of the ligand (such as bending and torsion angles), as the ligand geometry determines its hydrogen bond donor properties. A very convincing example of the influence of the respective position of secondary amine protons in various related ligands on hydrogen bond association can be found in the comparison of bibenzimidazole and tetratolyloxalamidine (H_2TTOA) ligands in ruthenium complexes and their interaction with

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trifluoroacetic acid (TFA). The secondary amine protons of the more flexible H_2TTOA ligand form a double hydrogen bond to the carbonyl oxygen of TFA, whereas each of the secondary amine protons of the more rigid bibenzimidazole ligand forms a chelating hydrogen bond to the carboxylate oxygens of a TFA molecule [4]. We present here the structural characterization of a rhenium tricarbonyl bibenzimidazole complex.

EXPERIMENTAL

The ligand 2,2′-bibenzimidazole (bbimH$_2$) was synthesized according to the method of Lane [5]. Re(CO)$_5$Br was obtained from Aldrich. All manipulations were carried out under argon using conventional Schlenk apparatus. All solvents were dried and distilled prior to use.

(bbimH$_2$)Re(CO)$_3$Br (1) bbimH$_2$ (60 mg; 0.256 mmol) was dissolved with heating in 3 cm^3 of DMF; 30 cm^3 of toluene was added and the resulting mixture heated to reflux. Re(CO)$_5$Br (100 mg; 0.246 mmol) was dissolved in 2 cm^3 of DMF and added to the solution, which was kept at reflux for 5 h. The solution was filtered and the solvent removed after the solution was allowed to cool. The resulting orange brown solid was washed with CHCl$_3$. Yellow crystals, suitable for X-ray structure determination, were grown from a saturated toluene/DMF mixture. ^{1}H NMR (d_6-DMSO, δ ppm): 7.87 (m 2H), 7.52 (m 2H); ^{13}C NMR (d_6-DMSO, δ ppm): 197.76, 188.66, 144.74, 140.82, 133.83, 125.83, 125.02, 117.71, 114.19; IR (KBr) ν (cm^{-1}): 3060 (NH), 2038, 1912, 1892 (CO stretch), 1595 (ligand); MS: FAB 584 (7%) [M + H], 556 (2%) [M–CO + H], 528 (7%) [M–2 CO + H], 505 (20%) [M–Br + H]; DEI 504 (0.1%) [M–Br–H], 476 (0.09%) [M–Br–CO–H], 448 (0.04%) [M–Br–2CO–H], 420 (0.2%) [M–Br–3CO–H], 234 (11%) [M–Re–Br–3CO–H].

Crystal Structure Determination

Intensity data for the compound were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz, polarization and absorption effects [6,7]. The structure was solved by direct methods (SHELXS [8]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97 [9]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [9]. The program XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations [10].

Crystal data for **1**: $C_{17}H_{10}BrN_4O_3Re \cdot C_3H_7NO$, $Mr = 657.50$, yellow prisms, size $0.10 \times 0.10 \times 0.09$ mm, monoclinic, space group $P2_1/n$, $a = 10.9743(2)$, $b = 12.9182(2)$, $c = 15.1864(3)$ Å, $\beta = 91.647(1)°$, $V = 2152.06(7)$ Å^3, $T = -90$°C, $Z = 4$, $\rho_{calc.} = 2.029$ g cm^{-3}, μ(Mo Kα) = 75.4 cm^{-1}, transmin: 0.789, transmax: 0.653, $F(000) = 1256$, 24 006 reflections in $h(-14/13)$, $k(-14/16)$, $l(-19/19)$, measured in the range $3.66° \leq \Theta \leq 27.47°$, completeness $\Theta_{max} = 99.1\%$, 4886 independent reflections, $R_{int} = 0.046$, 4296 reflections with $F_o > 4\sigma(F_o)$, 281 parameters, 0 restraints, $R_1 = 0.025$, $wR_2 = 0.062$, $R_1 = 0.032$, $wR_2 = 0.066$ (all reflections), goodness-of-fit = 1.052, largest difference peak and hole: 0.964 and -1.182 e Å^{-3}.

RESULTS AND DISCUSSION

The low solubility of bibenzimidazole requires highly polar solvents for an efficient synthesis. The synthesis was therefore carried out in a mixture of DMF and toluene. The bright yellow compound obtained after removal of the solvent could be characterized by ^{1}H NMR and mass spectroscopy. It showed the expected signals in the NMR, and the corresponding molecular ion could be detected in the MS. Electronic and emission spectroscopic data for (bbimH_2)Re$(CO)_3$Br are virtually identical to the values reported for the analogous chloro-complex [11].

Crystals of **1** could be obtained by careful crystallization from toluene/DMF. One molecule of DMF is incorporated in the crystalline product as apparent from the X-ray structural investigation. The molecular structure of **1** is depicted in Fig. 1. Relevant distances and bond angles are listed in Table I.

The carbonyl ligands assume *facial* coordination at the rhenium centre as expected from the IR spectrum. Bond distances for Re–N_{bim} (2.19 Å) are considerably longer than that (2.152 Å) in the comparable structure of a Re(I)tricarbonyl bromide complex of 2,6-bis(1′,5′,6′-trimethylbenzimidazol-2-yl)pyridine [12]. The measured Re–N bond length for **1** is also considerably longer than values obtained for Re(I)tricarbonyl halogenide complexes with bipyridine ligands (*ca* 2.170–2.180 Å) [13,14].

The bibenzimidazole ligand is bent around the rhenium center with an angle of 168° [15]. The two ligand-based secondary amine protons are directed outwards and form a relatively strong hydrogen bond with one carbonyl oxygen of the DMF molecule.

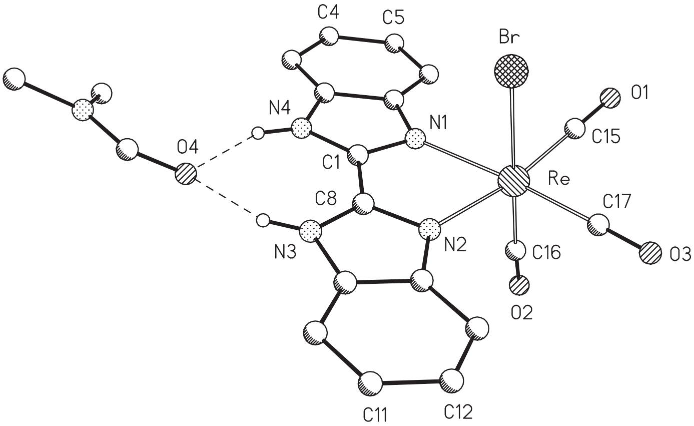

FIGURE 1 Molecular structure of (bbimH_2)Re$(CO)_3$Br, **1**; hydrogen atoms except for NH are omitted for clarity.

TABLE I Selected bond distances (Å) and angles (°) for **1**

Re–C(15)	1.907(4)	N(1)–Re–N(2)	74.27(11)
Re–C(16)	1.934(5)	C(15)–Re–C(17)	88.19(19)
Re–C(17)	1.932(4)	C(15)–Re–C(16)	88.22(15)
Re–N(1)	2.194(3)	C(16)–Re–C(17)	89.30(17)
Re–N(2)	2.190(3)	C(15)–Re–N(1)	99.29(14)
Re–Br	2.6320(4)	C(17)–Re–N(2)	98.02(15)
O(4)–N(3)	2.725(7)	C(16)–Re–Br	176.91(10)
O(4)–N(4)	2.761(6)		

From this knowledge it will be possible to construct more elaborate molecular architectures based on supramolecular building concepts.

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