Metal-Promoted Nucleophilic Addition of Water to Coordinated 2,3-Bis(2-pyridyl)benzoquinoxaline in Rhenium(V) Complexes. Crystal Structure of the Hydration Product $ReOCl_2(C_{22}H_{15}N_4O)$

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Introduction

The expected mode of coordination of diimines such as 2,3-bis(2-pyridyl)benzoquinoxaline (BBQ; Figure 1) to metal ions is assumed to be a five-membered ring involving chelation through a pyrazine nitrogen and a pyridine nitrogen atom, and crystal structure determinations of ruthenium(II)[1] and cobalt(II)[2] complexes of diimines have shown this to be the case. However, in previous work with copper(II)[3] and nickel(II)[4] as central ions and BBQ as ligand, it was shown that coordination to the metals occurs in a bidentate manner through the nitrogen atoms of the two pyridine rings placed in a *cis* conformation to form a seven-membered chelate ring (coordination mode *A* in Figure 1).

We have studied the reaction of BBQ with $ReOCl_4^-$ and have found that the diimine coordinates to rhenium(V) through the two nitrogens of the two pyridine rings to form a seven-membered metallocycle. In addition, we discovered that BBQ has the ability to undergo metal-promoted nucleophilic addition of water at the imino carbon of the benzoquinoxaline to produce the corresponding condensation product "BBQ-hydrate" (Figure 1). A consequence of this hydration is that the hydroxyl group attached to the sp^3 hybridized carbon atom will necessarily occupy a position close to one of the octahedral coordination sites at right angles to the ReN_2 plane, and would probably lead to steric interaction with any ligand in that position, or alternatively, it may coordinate to the metal ion, with the ligand now behaving as a terdentate.

This communication deals with the crystal structure of $ReOCl_2(BBQ{\cdot}OH)$, in which BBQ·OH behaves as a uninegative terdentate ligand, with coordination through the two pyridyl nitrogen atoms and the deprotonated hydroxyl oxygen of "$BBQ{\cdot}H_2O$".

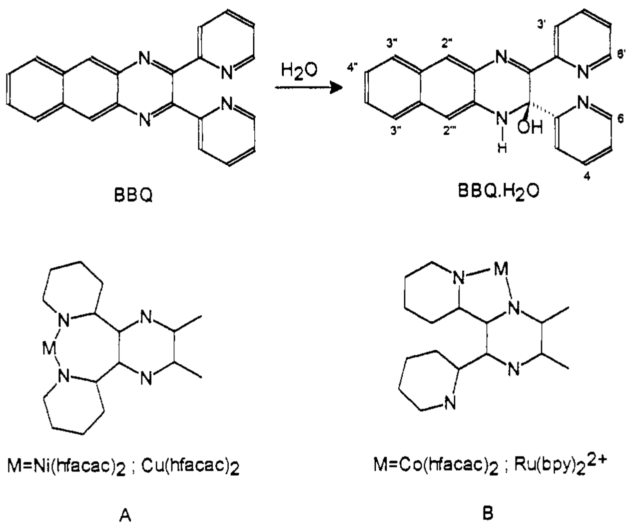

Figure 1. 2,3-Bis(2-pyridyl)benzoquinoxaline (BBQ) and "BBQ-hydrate" ($BBQ{\cdot}H_2O$), with possible coordination modes for BBQ.

Table 1. Crystallographic Data for $ReOCl_2(BBQ{\cdot}OH)$

chem formula: $C_{22}H_{15}Cl_2N_4O_2Re$	$T = 21$ °C
fw = 624.5	$\lambda = 0.710\ 73$ Å
$a = 13.535(4)$ Å	$\rho_{obsd} = 1.97$ g cm^{-3}
$b = 14.606(4)$ Å	$\rho_{calcd} = 1.97$ g cm^{-3}
$c = 21.266(6)$ Å	$\mu = 61.0$ cm^{-1}
cryst syst: orthorhombic	$\mu R \simeq 1.2$ (R = av cryst radius)
space group: *Pbca*	transm coeff = 0.68–0.92
$V = 4204(2)$ Å^3	$R^a = 0.047$
$Z = 8$	$R_w{}^a = 0.057$

[a] $R = \sum \Delta F / \sum |F_o|$. $R_w = \sum w \Delta F / \sum w |F_o|$.

Experimental Section

Synthesis of $ReOCl_2(BBQ{\cdot}OH)$. To 100 mg (170 μmol) of $(n\text{-}Bu_4N)[ReOCl_4]$ in 10 cm^3 of ethanol (containing 0.2% water) was added a solution of 28 mg (84 μmol) of BBQ in 25 cm^3 of acetone (containing 0.2% water). The color of the solution immediately turned green, and stirring was continued for 30 min at room temperature under aerobic conditions, with the continuous precipitation of a dark blue crystalline powder. The precipitate was collected by filtration, washed with ethanol, and dried *in vacuo* (yield: 81% with respect to BBQ). Recrystallization from acetonitrile gave blue crystals that were suitable for crystallographic analysis. Anal. Calcd for $C_{22}H_{15}Cl_2N_4O_2Re$: C, 42.31; H, 2.42; N, 8.97; Cl, 11.35. Found: C, 42.07; H, 2.28; N, 8.96; Cl, 11.00. IR(KBr): ν(Re=O) 932, ν(C=N) 1570, 1607, ν(C=C) 1636, ν(C—O) 1219, ν(Re—N) 438, ν(N—H) 3295, ν(Re—Cl) 318 cm^{-1}. ^{1}H NMR[$(CD_3)_2SO$]: δ(NH) 7.14 (1H, s); $\delta(H_5)$ 7.28 (1H, t); $\delta(H_5')$ 7.42 (1H, t); $\delta(H_4)$ 7.72 (1H, t); $\delta(H_4')$ 7.77 (1H, t); $\delta(H_3, H_3', H_2'', H_2''', H_3'', H_4'')$ 7.85–8.07 (8H, m); $\delta(H_6)$ 8.78 (1H,d); $\delta(H_6')$ 8.82 ppm (1H,d). Conductivity (10^{-3}M, DMF): 48.4 Ω^{-1} cm^2 mol^{-1}. Electronic spectrum (DMF, nm (ϵ M^{-1}cm^{-1})): 377 (7700), 292 (42 500). Mp: 259 °C.

The formation of the product is independent of the molar ratio of reactants, but we found that the best yield was obtained at the above-mentioned 2:1 ratio of $ReOCl_4^-$ to BBQ. In the absence of water under a strictly dry nitrogen atmosphere, the green compound $ReOCl_3(BBQ)$ was isolated.[5] Recrystallization of $ReOCl_3(BBQ)$ from acetonitrile under aerobic conditions gave $ReOCl_2(BBQ{\cdot}OH)$.

Crystallography. Data were collected at room temperature on a Nicolet Siemens R3m/V diffractometer with graphite-filtered Mo Kα radiation ($\lambda = 0.710\ 73$ Å), using the ω–2θ scan technique to a maximum 2θ value of 45° for a suitable crystal of dimensions *ca.* 0.1 × 0.1 × 0.2 mm, mounted on a glass fiber. Details of crystal data, measurement of intensities, and data processing are summarized in Table 1. The intensities of two representative reflections were measured after every 100 reflections to monitor crystal and electronic stability. Data were corrected for Lorentz and polarization effects but not for absorption. In fact, a series of Ψ-scans for three reflections at $\chi \simeq 90°$ showed negligible absorption effects. The structure was solved by standard heavy-atom methods and refined by full-matrix least-squares methods, using the 1341 observed ($|F_o| > 3\sigma(F_o)$) reflections (of a total of 2736) and minimizing the function $\sum w(|F_o| - |F_c|)^2$ ($w^{-1} = \sigma^2(F) + 0.0087F^2$), with anisotropic thermal parameters only for the heteroatoms. The refinement converged to agreement factors $R = 0.047$ and $R_w = 0.057$ (GOF, 0.53; variables, 170). All calculations were performed using the SHELXTL-PLUS package (release 4.2, 1990).[6] Selected bond distances and angles are reported in Table 2.

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(5) Anal. Calcd. for $C_{22}H_{14}Cl_3N_4ORe$: C, 41.10; H, 2.19; N, 8.71; Cl, 16.54. Found: C, 41.29; H, 2.21; N, 8.84; Cl, 16.82. IR (KBr): ν(Re=O) 968, ν(C=N) 1605, 1636; ν(Re—Cl) 298, 321 cm^{-1}. ^{1}H NMR[$(CD_3)_2SO$]: δ 7.66–9.12 ppm (14H, m). Conductivity (10^{-3}M, DMF): 26 Ω^{-1} cm^2 mol^{-1}. Electronic spectrum (DMF, nm (ϵ M^{-1}cm^{-1})): 380 (7400), 289 (52 800). Color: green. Mp: 215 °C.

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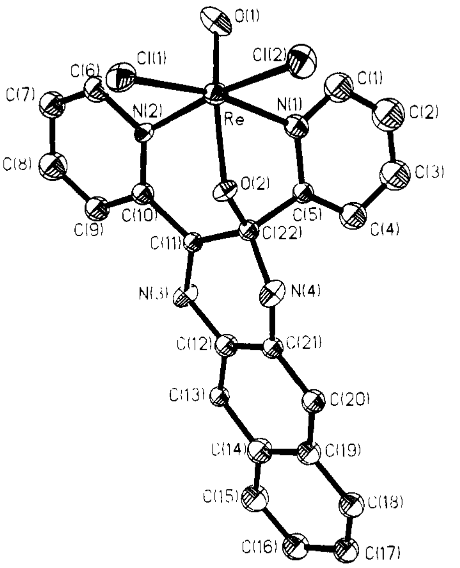

Figure 2. ORTEP drawing of the complex. The atom-numbering scheme and the thermal ellipsoids at the 50% probability level are shown.

Table 2. Relevant Bond Lengths (Å) and Angles (deg)

Re–Cl(1)	2.365 (6)	Re–O(1)	1.69 (1)
Re–Cl(2)	2.367 (5)	Re–O(2)	1.95 (1)
Re–N(1)	2.13 (2)	O(2)–C(22)	1.39 (2)
Re–N(2)	2.15 (1)	C(11)–C(22)	1.54 (3)
N(3)–C(11)	1.32 (2)	N(4)–C(21)	1.44 (2)
N(3)–C(12)	1.39 (2)	N(4)–C(22)	1.45 (2)
O(1)–Re–O(2)	160.1 (6)	Cl(1)–Re–Cl(2)	91.6 (2)
Cl(1)–Re–N(1)	168.1 (5)	Cl(1)–Re–O(1)	104.1 (5)
Cl(2)–Re–N(2)	172.8 (4)	Cl(2)–Re–O(1)	98.7 (5)
N(1)–Re–N(2)	93.7 (6)	Cl(2)–Re–O(2)	91.4 (4)
N(1)–C(5)–C(22)	110 (1)	Re–O(2)–C(22)	118 (1)
Re–N(1)–C(5)	116 (1)	N(2)–C(10)–C(11)	121 (2)
C(11)–N(3)–C(12)	118 (1)	Re–N(2)–C(10)	126 (1)
O(2)–C(22)–C(11)	109 (1)	C(21)–N(4)–C(22)	118 (1)
N(4)–C(22)–C(11)	110 (1)	O(2)–C(22)–N(4)	108 (1)
C(5)–C(22)–C(11)	110 (1)	O(2)–C(22)–C(5)	108 (1)
N(4)–C(22)–C(5)	112 (1)		

Results and Discussion

The structure of $ReOCl_2(BBQ{\cdot}OH)$ contains discrete, monomeric, neutral monooxorhenium(V) complex units (Figure 2), and the crystal packing is governed by van der Waals contacts. Neither intermolecular nor intramolecular hydrogen bonds are observed. The donor atoms surrounding the rhenium are at the apices of a distorted octahedron, in which the equatorial plane is occupied by the two *cis* chlorides and by the two terminal pyridyl nitrogen atoms of the bidentate ligand, with the O(1) oxo ligand *trans* to the O(2) alcoholate atom. Severe distortions from the ideal Re-centered octahedral configuration are as follows: (i) the Re atom lies out of the equatorial mean plane by 0.19 Å, toward the oxo ligand; (ii) the nonlinear O(1)–Re–O(2) axis of 160.1(6)° is accomplished by Cl(1)–Re–N(1) and Cl(2)–Re–N(2) angles of 168.1(5) and 172.8(4)°, respectively; (iii) the edge distances are observed in a rather large range (from 2.51 Å for N(1)---O(2) to 3.39 Å for Cl(1)---Cl(2)) and the interligand angles in the equatorial plane depart from the ideal 90° (from 86.1 to 93.7°); (iv) in the $Cl_2N_2O_2$ coordination polyhedron the Re atom is +1.00 Å away from the Cl(2)Cl(1)O(1) plane and −1.23 Å from the N(1)N(2)O(2) one, the angle between the two triangles being 13.1°. These structural properties are a common feature for the numerous six-coordinate octahedral monooxo complexes of Re(V),[7] and in particular, the present complex closely resembles $ReOCl_2[(C_5H_4N)_2C(O)(OH)]$.[8] For instance, the two pyridine rings make a dihedral angle of 69.2° to be compared with the value of 65.9° in the above-mentioned complex, and in addition, the Re-O(2)–C(22) plane is virtually normal (dihedral angle of 90.6°) to the equatorial mean plane, as found in the first complex (91.5°). On the other hand, the most significant feature of the structure is that it unambiguously establishes the tetrahedral environment around the C(22) atom (Figure 3), as confirmed by the bond angle pattern. The C(11)N(3)C(12)C(21) portion is planar within ±0.02 Å, while N(4) and C(22) are out of the plane by 0.23 Å in the opposite direction.

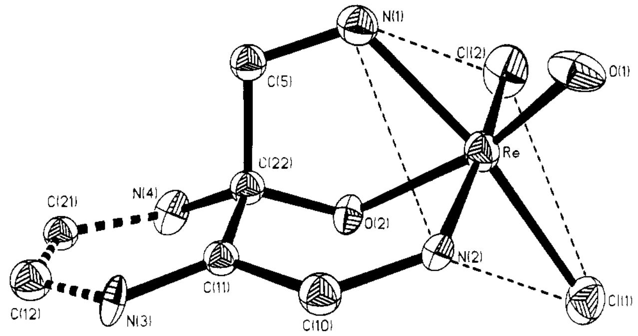

Figure 3. Tetrahedral environment around the C(22) atom.

We interpret the driving force for the nucleophilic addition of water to the imino carbon C(22) after coordination of BBQ to rhenium(V) as being the result of angular strain that is caused in BBQ by the formation of the seven-membered metallocycle. The formation of a planar seven-membered ring between rhenium and BBQ will be difficult, and the formation of a chelate in the boat form, with the metal and C(22) above the plane of the two nitrogens (N(1) and N(2)) and two 2-carbon atoms of the pyridine rings will be more easily achieved to relieve this strain. In the latter case the coplanarity of the ligand and the conjugation over the 1,4-diazine group will be destroyed, and as a result the nucleophilic attack on the imino carbon will be facilitated. An additional driving force may be the coordination of the deprotonated alcoholate oxygen O(2) of $BBQ{\cdot}OH^-$ to the metal, as can be expected for metal ions (such as rhenium(V)) with a propensity to form octahedral complexes.[7]

Nucleophilic attack to BBQ or related diimines has not been observed previously, and the results reported in this study may present interesting possibilities in the rapidly expanding field of reactions of coordinated ligands.

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Supplementary Material Available: A summary of the structure determination (Table A), final atomic coordinates and equivalent isotropic displacement coefficients (Table B), a full listing of bond lengths (Table C) and angles (Table D), and the anisotropic displacement coefficients (Table E) (5 pages). Ordering information is given on any masthead page.

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