Hydrogen-Bonded Oximate−Oxime Chelation and Variable Metal Valence. Syntheses and Structures of $RuCl_2(L)(HL)^z$ (HL = PhC(NOH)NNPh; z = 1−, 0)

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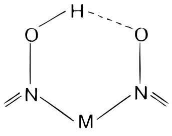
Introduction

A fascinating early find in structural coordination chemistry is the M(oximate)(oxime) motif **1**, first observed among dioxime chelates.[1] Complexes incorporating this motif have since been of persistent interest in several areas of inorganic research such as hydrogen bonding,[2,3] cobalamine modeling,[4] and metal−metal interaction.[5,6] The first M = Ru species were described some years ago,[7−9] and one ruthenium(II) family was recently structurally characterized.[3]



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In this work we scrutinize the little-known effect of variable metal valence on the dimensions and bonding in and around **1**. The II and III states of ruthenium have been chosen for the study because of their distinctive binding characteristics. The crucial prerequisite was to obtain geometrically similar complexes of these oxidation states having the same coordination number, stoichiometry, and environment. A pair of *trans*-RuN_4Cl_2 type complexes have been found to conform to these requirements, and their structures have been determined.

Results and Discussion

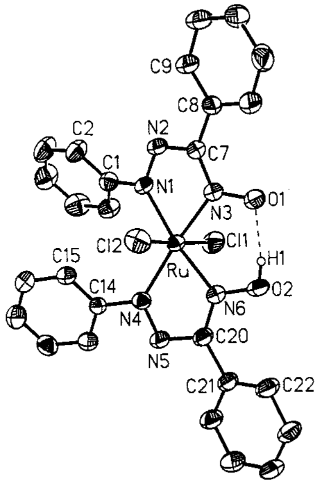


Figure 1. ORTEP plot and atom-labeling scheme for the $RuCl_2(L)(HL)^-$ anion of $Et_4N[RuCl_2(L)(HL)]\cdot{}^1/_2C_6H_6$. All non-hydrogen atoms are represented by their 30% probability ellipsoids.

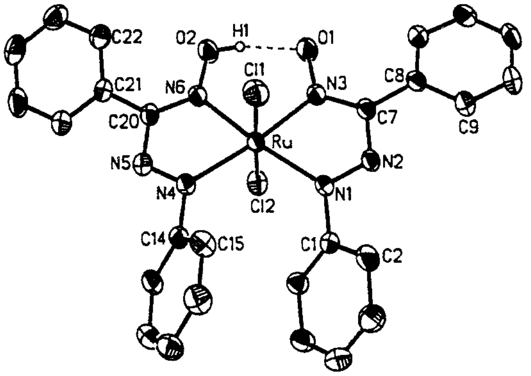
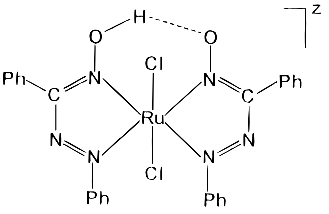


Figure 2. ORTEP plot and atom-labeling scheme for $RuCl_2(L)(HL)$. All non-hydrogen atoms are represented by their 30% probability ellipsoids.

Synthesis. The *trans*-RuN_4Cl_2 pair studied in this work has (phenylazo)benzaldoxime (HL) as the oxime ligand. The general formula for complexes is $RuCl_2(L)(HL)^z$ (**2**, **3**). The stoichiometric reaction of *trans*-$RuCl_2(Me_2SO)_4$ with HL afforded the green bivalent complex **2**, isolated as the Et_4N^+ salt.



2 z = -, Ru^{II}; Et_4N^+ salt
3 z = 0, Ru^{III}

Conversion to red **3** was conveniently achieved using *n*-butyl nitrite as the oxidant. Yields were good in both syntheses. Previously, **3** had been prepared in very poor yield from $RuCl_3\cdot 3H_2O$ and HL, and **2** was electrogenerated from **3** in solution but it could not be isolated.[8]

Geometry. The structures of both complexes have been determined. Perspective views are shown in Figures 1 and 2, and selected bond parameters are listed in Table 1. In what follows the coordinated oxime N and azo N atoms will be respectively identified as N^o and N^a. In the distorted octahedral complexes, the $RuCl_2$ fragment is approximately linear. The geometrical type of the coordinated atom pairs $Cl_2-N^o_2-N^a_2$ is trans-cis-cis corresponding to the cis chelation of the azo oxime ligands.

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Table 1. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations

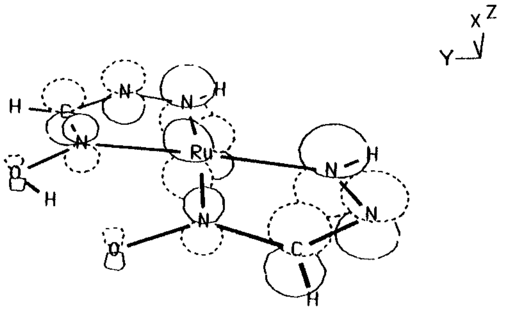
	$Et_4N[RuCl_2(L)(HL)]\cdot{}^1/_2C_6H_6$	$RuCl_2(L)(HL)$
	Distances	
Ru−Cl1	2.377(3)	2.314(1)
Ru−Cl2	2.378(3)	2.335(1)
Ru−N1	2.031(5)	2.053(3)
Ru−N4	2.048(6)	2.052(3)
Ru−N3	1.969(6)	1.992(3)
Ru−N6	1.966(6)	1.991(3)
N3−O1	1.344(9)	1.319(5)
N6−O2	1.333(9)	1.320(5)
N1−N2	1.289(8)	1.282(4)
N4−N5	1.280(8)	1.291(4)
N2−C7	1.398(10)	1.384(6)
N3−C7	1.304(8)	1.324(5)
N5−C20	1.389(10)	1.393(5)
N6−C20	1.310(9)	1.321(4)
O2−H1	0.92(3)	0.84(3)
O1···H1	1.63(4)	1.73(4)
O1···O2	2.517(7)	2.561(4)
	Angles	
Cl1−Ru−Cl2	177.0(1)	178.0(1)
Cl1−Ru−N1	89.2(2)	89.7(1)
Cl1−Ru−N4	88.8(2)	90.7(1)
Cl1−Ru−N3	85.3(2)	87.9(1)
Cl1−Ru−N6	93.3(2)	91.8(1)
Cl2−Ru−N1	90.8(2)	90.5(1)
Cl2−Ru−N4	94.0(2)	91.1(1)
Cl2−Ru−N3	91.8(2)	90.3(1)
Cl2−Ru−N6	86.3(2)	87.8(1)
N1−Ru−N4	113.1(2)	111.4(1)
N3−Ru−N6	97.3(3)	98.3(1)
Ru−N3−O1	121.6(4)	120.7(2)
Ru−N6−O2	121.7(4)	121.4(2)
O2−H1···O1	160(5)	170(5)

All the chelate rings in the two complexes are good planes (mean deviation 0.01−0.05 Å), and the nonmetallic bond parameters therein compare well with available data.[6,10] It is noteworthy that the N^o−Ru−N^o angle in the hydrogen-bonded six-membered chelate ring is 97.3(3)° in **2** and 98.3(1)° in **3** while the N^a−Ru−N^a angle lying opposite is 113.1(2)° in **2** and 111.4(1)° in **3**. This inequality represents a balance between two opposing factors: contraction due to OHO bridging and expansion due to cis repulsion between pendent N^a−Ph rings. The two rings make dihedral angle of 28.4° in **2** and 13.5° in **3**.

Hydrogen Bonding. Many of the hydrogen atoms including the crucial oxime hydrogen are directly observable in both the structures. The oxime hydrogen was refined isotropically, and approximate bond distances within the unsymmetrical hydrogen bridge are O2−H1 = 0.9 Å and H1···O1 = 1.7 Å. The esd's are large, and no meaningful differentiation between **2** and **3** is feasible (Table 1). The presence of a subtle difference is however reflected in the O2···O1 separation: 2.517(7) Å in **2** and 2.561(4) Å in **3**. This trend is consistent with the larger Ru−N^o length and N^o−Ru−N^o angle in **3** (Table 1). The difference electron density maps of **2** and **3** representing the oxime H atom were examined down the $RuCl_2$ axis. While the "eye" of the density in each case lay near O2 (the O2−H1 bond), it extended well in the direction of O1 (H1···O1). Consistent with such interaction of the oxime H atom with both oxime O atoms, the two N−O lengths in the complexes are virtually equal (Table 1). The present pair of complexes stand apart from cases where O···O separations are too large for effective hydrogen bonding resulting in very unequal N−O lengths. A case in hand is *trans*-$Ru(DPGH)_2(NO)Cl$: O···O = 2.743(4) Å, O−H = 0.76(6) Å, H···O = 1.99(6) Å, and N−O = 1.292(5), 1.377(5) Å (DPGH = diphenylglyoxime monoanion).[3]

Axial−Equatorial Contrast. The two complexes display opposite trends of axial (Ru−Cl) and equatorial (Ru−N) bond lengths. For Ru−Cl, the order is **2** > **3**, and for Ru−N^o and Ru−N^a, it is **2** < **3** (the inequality Ru−N^a > Ru−N^o in each complex (Table 1) arises from the strong trans influence[11] of N^o). In a primarily σ-bonded situation, the expected radius order is Ru(II) > Ru(III). The observed trend of Ru−Cl lengths in **2** and **3** is consistent with this. We note that the same trend applies to $Ru-OH_2$ and $Ru-NH_3$ lengths in aquo and ammine complexes.[12]

The equatorial inequality Ru(II)−N < Ru(III)−N implies that the bivalent state is subject to selective binding in addition to σ-binding. It is logical[13,14] to invoke dπ(Ru)−π*(azo oxime) back-bonding. Orbital mixing in **2** has been qualitatively scrutinized with the help of EHMO calculations on a model which was computer-generated from $RuCl_2(L)(HL)$ by replacing Ph by H and imposing C_s symmetry (exactly planar chelate rings and linear ClRuCl axis). The HOMO (a″ symmetry) of the model, depicted in **4** (Cl atoms not shown), has nearly equal metal and ligand characters. The primary metal orbitals are $4d_{xz}$ and $4d_{yz}$, and the ligand contribution arises from what were LUMOs of the free ligands. Such a ligand LUMO shown in **5** is 70% azo (NN) and 30% oxime (CNO) in character. In effect,



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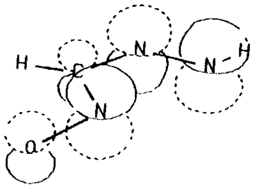

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[11] This effect also occurs in $[Pt(HL)(L)]_2$[6] and *mer*-NiL_3^- (Karmakar, S.; Choudhury, S. B.; Ganguly, S.; Chakravorty, A. Unpublished results.).

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the back-bonding in the model complex is primarily d_{xz},d_{yz}−π^*(azo) in nature.

Concluding Remarks. The first structurally characterized Ru(II), Ru(III) pair $RuCl_2(L)(HL)^z$ ($z = 1-, 0$) incorporating motif **1** has been realized using (phenylazo)benzaldoxime as the oxime ligand. In both cases the O−H···O hydrogen bonding is unsymmetrical but the bridging H atom interacts well with both the oxygen atoms (nearly equal N−O lengths). In the $RuCl_2N_4$ coordination sphere, the Ru−Cl bonds are primarily σ in character for both oxidation states but the Ru−N bonds involve very significant back-donation in the bivalent complex. The net effect is a contrast of axial and equatorial bond length trends: Ru(II)−Cl > Ru(III)−Cl but Ru(II)−N < Ru(III)−N. The latter trend makes the O···O separation significantly longer in the trivalent complex.

Experimental Section

Materials. Phenylazobenzaldoxime[15] and *trans*-$RuCl_2(Me_2SO)_4$[16] were prepared by reported methods.

Preparation of Compounds. Tetraethylammonium Dichloro((phenylazo)benzaldoximato)((phenylazo)benzaldoxime)ruthenium(II), $Et_4N[RuCl_2(L)(HL)]$. The complex *trans*-$RuCl_2(Me_2SO)_4$ (0.250 g, 0.52 mmol) was suspended in 35 mL of ethanol, and HL (0.235g, 1.04 mmol) was added. The red solution was heated to reflux for 10−12 min, during which the color became green. The solution was then cooled, and an aqueous solution of Et_4NCl (0.135 g, 1.04 mmol) was added. The solvent was evaporated in vacuo and the solid residue washed with water. The dried mass was dissolved in 15 mL of CH_2Cl_2 and the solution chromatographed on a silica gel (60−120 mesh) column. Benzene and then a 1:4 acetonitrile−benzene mixture were used as eluents to wash down impurities. The required complex was eluted as a green band using a 2:3 acetonitrile−benzene mixture. A crystalline solid was obtained after evaporation of the solvent in vacuo. Yield: 0.23 g (60%). Anal. Calcd for $C_{34}H_{41}N_7O_2Cl_2Ru$: C, 54.33; H, 5.46; N, 13.05. Found: C, 54.26; H, 5.42; N, 12.98. The electronic spectrum of the complex agrees with that reported for the electrogenerated anion.[8]

Dichloro((phenylazo)benzaldoximato)((phenylazo)benzaldoxime)ruthenium(III), $RuCl_2(L)(HL)$. To a hot and stirred methanolic solution (50 mL) of $Et_4N[RuCl_2(L)(HL)]$ (0.1 g, 0.133 mmol) was added dropwise *n*-butyl nitrite (0.07 g, 0.68 mmol) in methanol (12 mL). The color of the solution changed from green to red-violet. Stirring was continued for a few minutes, and the solution was then kept in a refrigerator for 3−4 h. The crystalline solid was collected by filtration, washed with methanol, and dried in vacuo. Yield: 0.08 g (92%). Anal. Calcd for $C_{26}H_{21}N_6O_2Cl_2Ru$: C, 50.24; H, 3.38; N, 13.53. Found: C, 50.22; H, 3.37; N, 13.50. The electronic spectrum and magnetic properties of the complex agree with those reported.[8]

Molecular Orbital Calculation. Extended Hückel calculations were performed on an IBM PC AT using the ICON software package originally developed by Hoffmann.[17] The atomic parameters and H_{ii} values for C, O, H, N, and Ru were taken from the literature.[18] The Cl−Ru−Cl axis was defined as the *z* axis, and the averaged experimental bond distances and angles were used in our calculations. The C−H distance was taken as 0.96 Å.

X-ray Structure Determination. Single crystals of $Et_4N[RuCl_2(L)(HL)]\cdot{}^1/_2C_6H_6$ (0.32 × 0.28 × 0.54 mm^3) were grown by slow diffusion of a hexane−benzene (9:1) mixture into a dichloromethane solution, and those of $RuCl_2(L)(HL)$ (0.24 × 0.52 × 0.60 mm^3) were grown by slow diffusion of hexane into an acetone solution, followed by slow evaporation. The unit cell parameters were determined by the least-squares fit of 30 machine centered reflections ($2\theta = 15-30°$). Data were collected by the ω-scan method in the 2θ range 3−52° on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Two check reflections measured after every 98 reflections showed no significant changes in intensity. Data were corrected for Lorentz−polarization effects and absorption (azimuthal scan[19]). Of the 7457 (Ru(II) complex) and 5108 (Ru(III) complex) unique reflections, 3827 and 3544, respectively, with $I > 3\sigma(I)$ were used for structure solution by direct (Ru(II)) and heavy-atom (Ru(III)) methods. All the non-hydrogen atoms were made anisotropic. The hydrogen atoms linked with O2, C5, C6, C15, C16, and C22 (Ru(II)) and with O2, C2, C3, C6, C9, C10, C11, C13, C17, C18, C19, C23, and C26 (Ru(III)) were directly located. The remainder of the hydrogen atoms were added at calculated positions with fixed *U* values (0.08 Å^2). The oxime hydrogen was refined isotropically. Least-squares refinements were performed by full-matrix procedures. All calculations were done on a MicroVax II computer with programs of SHELXTL-PLUS,[20] and crystal structure plots were drawn using ORTEP.[21] Significant crystal data are listed in Table 2. The methylene carbon of the Et_4N^+ cation in the ruthenium(II) complex displays 2-fold disorder, and the benzene of crystallization lies on the 2-fold axis.

Table 2. Crystallographic Data for $Et_4N[RuCl_2(L)(HL)]\cdot{}^1/_2C_6H_6$ and $RuCl_2(L)(HL)$

	$Et_4N[RuCl_2(L)(HL)]\cdot{}^1/_2C_6H_6$	$RuCl_2(L)(HL)$
empirical formula	$C_{37}H_{44}N_7O_2Cl_2Ru$	$C_{26}H_{21}N_6O_2Cl_2Ru$
fw	790.8	621.5
space group (No.)	*I*2/*a* (15)	$P2_1/c$ (14)
a, Å	25.663(14)	9.385(3)
b, Å	11.973(2)	29.436(11)
c, Å	25.647(9)	10.265(4)
β, deg	106.38(3)	114.45(3)
V, Å^3	7561(5)	2582(2)
Z	8	4
T, °C	22	22
λ, Å	0.710 73	0.710 73
ρ_{obsd}, g cm^{-3}	1.382	1.585
ρ_{calcd}, g cm^{-3}	1.395	1.599
μ, cm^{-1}	6.00	8.51
transm coeff[a]	0.78361/1	0.79225/1
R,[b] %	5.5	3.04
R_w,[c] %	6.6	3.96

[a] Maximum value normalized to 1. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.0002$ for $Et_4N[RuCl_2(L)(HL)]\cdot{}^1/_2C_6H_6$ and $g = 0.00068$ for $RuCl_2(L)(HL)$.

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Supporting Information Available: Crystal data (Table S1), atomic coordinates (Tables S2 and S7), bond distances (Tables S3 and S8) and angles (Tables S4 and S9), anisotropic thermal parameters (Tables S5 and S10), and hydrogen atom positional parameters (Tables S6 and S11) for $Et_4N[RuCl_2(L)(HL)]\cdot{}^1/_2C_6H_6$ and $RuCl_2(L)(HL)$ (12 pages). Ordering information is given on any current masthead page.

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