# A Diruthenum(III) Complex Possessing a Diazine and Two Chloride Bridges: Synthesis, Structure, and Properties

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#### Introduction

Diazine-bridged dinuclear transition metal complexes are known mainly with heterocyclic ligands such as pyrazole, pyridazine, phthalazine, and triazole.<sup>1</sup> In these complexes, the linkage between the two nitrogen atoms of the bridging N–N moiety is partially double bond in character. Recently some structurally characterized dinuclear complexes are reported with diazine ligands having an N–N single bond as the bridging unit. Most of the work published is on complexes of the first transition series metal ions with a neutral tetradentate N<sub>4</sub> donor Schiff base *N,N'*-bis(picolinylidene)hydrazine or its substituted derivatives.<sup>2</sup> In a complex of this type of ligand, the free rotation about the N–N single bond allows the ligand to adopt a trans, cis, or in between twisted structure depending upon the coligands bound to the metal ions and their preference for different



coordination geometry. Thus dinuclear complexes of this class are of interest not only with respect to their structures but also for the influence of the structure on the interaction between the two metal ions. Compared to the *N*,*N*'-bis(picolinylidene)hydrazine, structurally characterized complexes of a similar tetradentate N<sub>2</sub>O<sub>2</sub> donor Schiff base *N*,*N*'-bis(salicylidene)hydrazine (H<sub>2</sub>salhn (I), the two H's stand for the dissociable phenolic protons) are extremely rare. A few years ago we reported a neutral diiron(III) complex, [Fe<sub>2</sub>( $\mu$ -salhn)<sub>3</sub>], in which each metal ion is in a distorted octahedral N<sub>3</sub>O<sub>3</sub> coordination sphere and each of the three ligands is twisted along the N–N single bond.<sup>3</sup> Two more structurally characterized complexes containing this ligand are known. These are a dirhodium(I) complex, [Rh<sub>2</sub>(CO)<sub>4</sub>( $\mu$ -salhn)],<sup>4</sup> and a hexanuclear cobalt(II,III) complex, [{Co<sub>3</sub>L(CH<sub>3</sub>COO)(CH<sub>3</sub>O)<sub>3</sub>}<sub>2</sub>( $\mu$ -salhn)] (H<sub>3</sub>L is 2,6-bis(salicylideneamino-methyl)-4-methylphenol).<sup>5</sup> In both of these complexes, salhn<sup>2-</sup> is in the trans configuration. Herein we report the synthesis, structure, and physical properties of a salhn<sup>2-</sup>-bridged diruthenium(III) complex, [Ru<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>( $\mu$ -salhn)], in which salhn<sup>2-</sup> has a very close to cis configuration.

## **Experimental Section**

**Materials.** The Schiff base H<sub>2</sub>salhn was obtained in ~95% yield by reacting 2 mol of salicylaldehyde with 1 mol of hydrazine in methanol followed by recrystallization from the same solvent. [Ru-(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] was prepared by following a reported procedure.<sup>6</sup> All other chemicals and solvents used in this work were of analytical grade available commercially and were used without further purification.

Physical Measurements. Microanalytical (C, H, N) data were obtained with a Perkin-Elmer model 240C elemental analyzer. The electronic spectrum was recorded on a Shimadzu 3101-PC UV/vis/ NIR spectrophotometer. The infrared spectrum was collected by using a KBr pellet on a Jasco-5300 FT-IR spectrophotometer. The EPR spectrum was taken on a Varian E-109C spectrometer fitted with a quartz Dewar flask for liquid dinitrogen temperature (77 K) measurement. The spectrum was calibrated with the help of DPPH. The variabletemperature (20-300 K) magnetic susceptibility measurements were performed using the Faraday technique with a setup comprising a George Associates Lewis coil force magnetometer, a CAHN microbalance, and an Air Products cryostat. Hg[Co(NCS)<sub>4</sub>] was used as the standard. Diamagnetic corrections ( $-650 \times 10^{-6}$  cgsu for [Ru<sub>2</sub>Cl<sub>2</sub>- $(PPh_3)_2(\mu-Cl)_2(\mu-salhn)])$  calculated from Pascal's constants<sup>7</sup> were used to obtain the molar paramagnetic susceptibilities. Solution electrical conductivity was measured with a Digisun DI-909 conductivity meter. A Cypress model CS-1090/CS-1087 electroanalytical system was used for cyclic voltammetric experiment with a CH<sub>3</sub>CN solution of the complex containing tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The three-electrode measurement was carried out at 298 K under a dinitrogen atmosphere with a platinum working electrode, a platinum wire auxiliary electrode, and an Ag-AgCl reference electrode. The potentials reported in this work are uncorrected for junction contributions.

**Synthesis of [Ru<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(\mu-Cl)<sub>2</sub>(\mu-salhn)]. Solid [Ru(PPh<sub>3</sub>)<sub>3</sub>-Cl<sub>2</sub>] (364 mg, 0.38 mmol) was added to a light yellow solution of H<sub>2</sub>salhn (45 mg, 0.19 mmol) in 50 mL of CHCl<sub>3</sub>. The brown mixture was stirred in air at room temperature for 24 h. The resulting dark green solution was filtered to remove any unreacted solid starting materials followed by the addition of excess hexane with stirring. The green solid precipitated was collected by filtration. This solid was redissolved in CHCl<sub>3</sub> and precipitated by slow addition of hexane with stirring. The process of dissolution in CHCl<sub>3</sub> and precipitation by hexane was repeated two more times, and the solid obtained was dried in a vacuum. This procedure provided 130 mg (yield 62%) of the complex in high purity. Anal. Calcd for C<sub>50</sub>H<sub>40</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Ru<sub>2</sub>: C, 54.26; H, 3.64; N, 2.53. Found: C, 53.95; H, 3.70; N, 2.41. Selected IR bands (cm<sup>-1</sup>): 1595(s), 1533(m), 1481(w), 1433(s), 1279(m), 1188(m), 1092(s),** 

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**Table 1.** Crystallographic Data for [Ru<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(*µ*-Cl)<sub>2</sub>(*µ*-salhn)]•CHCl<sub>3</sub>

chem formula	$C_{51}H_{41}Cl_7N_2O_2P_2Ru_2$	Ζ	4
fw	1226.09	$\rho_{\rm calcd}$ , g cm <sup>-3</sup>	1.497
space group	monoclinic, $P2_1/n$	$\mu$ , mm <sup>-1</sup>	0.997
a, Å	17.857(3)	λ, Å	0.71073
b, Å	16.709(2)	$\mathbf{R}^{a}$	0.0762
<i>c</i> , Å	18.236(2)	$wR2^b$	0.1922
$\beta$ , deg	91.32(12)	$GOF^c$ on $F^2$	1.067
V, Å <sup>3</sup>	5439.5(13)		

 ${}^{a} \operatorname{R1} = \sum ||F_{o}| - |F_{c}|| \sum |F_{o}|. {}^{b} \operatorname{wR2} = \{\sum [(F_{o}^{2} - F_{c}^{2})^{2}] \sum [w(F_{o}^{2})^{2}] \}^{1/2}.$   ${}^{c} \operatorname{GOF} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / (n - p) \}^{1/2} \text{ where } n \text{ is the number of reflections and } p \text{ is the number of parameters refined; } w = 1 / [\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP] \text{ where } a = 0.1202 \text{ and } b = 0.$ 

978(m), 905(w), 745(s), 694(s), 525(s), 451(m). Electronic spectral data in CHCl<sub>3</sub> ( $\lambda$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)): 745 (2750), 243 (43 500).

X-ray Crystallography. Single crystals were grown by slow diffusion of a CHCl3 solution of the complex into an overlying layer of hexane. A crystal of dimensions  $0.38 \times 0.36 \times 0.25$  mm was selected, and the data were collected on an Enraf-Nonius Mach-3 singlecrystal diffractometer using graphite-monochromated Mo Ka radiation  $(\lambda = 0.71073 \text{ Å})$  by the  $\omega$ -scan method at 298 K. Unit cell parameters were determined by least-squares fitting of 25 reflections having  $\theta$ values in the range 9-11°. Intensities of three check reflections were measured after every 1.5 h during the data collection to monitor the crystal stability. No decay was observed in 99 h of exposure to X-ray. Data were corrected for Lorentz-polarization effects. The  $\psi$ -scans<sup>8</sup> of four reflections with  $2\theta$  in the range  $10-27^{\circ}$  and  $\chi$  within  $84-88^{\circ}$ were used for an empirical absorption correction with the help of the Datcor program.9 The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares procedures. The asymmetric unit contains a molecule of [Ru<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(µ-Cl)<sub>2</sub>(µ-salhn)] with a disordered CHCl3 molecule. The carbon of CHCl3 is found in two positions, and three chlorine atoms are found in six positions in between the carbon positions. These partial occupancy atoms are refined with geometrical restraints in such a way that a 6-fold axis is passing through the two carbon positions and six chlorine sites are around this 6-fold axis. All non-hydrogen atoms having full occupancies were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealized positions, but not refined. The calculations were performed using Xtal3.4 software<sup>10</sup> for data reduction, and SHELX-97 programs<sup>11</sup> for structure solution and refinement. The ORTEX6a package was used for molecular graphics.12 Significant crystal data are listed in Table 1.

#### **Results and Discussion**

**Synthesis and Some Properties.** The complex was synthesized in good yield by reacting 1 mol of H<sub>2</sub>salhn with 2 mol of  $[Ru(PPh_3)_3Cl_2]$  in CHCl<sub>3</sub> in air. The elemental analysis data are satisfactory with the molecular formula,  $[Ru_2Cl_4(PPh_3)_2(salhn)]$ . In solution, it is electrically nonconducting. The room-temperature magnetic moment (vide infra) suggests two unpaired electrons and hence the +3 oxidation state and low-spin nature of both metal ions. During the formation of the complex, aerial oxygen is the most likely oxidizing agent in the oxidation of the metal ions. The low reduction potentials observed (vide infra) for the complex are consistent with such an oxidation process.

**Description of the Structure.** The molecular structure of  $[Ru_2Cl_2(PPh_3)_2(\mu-Cl)_2(\mu-salhn)]$  is shown in Figure 1. Bond

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**Figure 1.** Structure of  $[Ru_2Cl_2(PPh_3)_2(\mu-Cl)_2(\mu-salhn)]$  with the atomlabeling scheme. All atoms are represented by their 20% probability thermal ellipsoids. Hydrogen atoms are omitted and selected carbon atoms are labeled for clarity.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for  $[Ru_2Cl_2(PPh_3)_2(\mu-Cl)_2(\mu-salhn)]\cdot CHCl_3$ 

L . 2 - 2( )/2( · · /2		- 5	
Ru(1)-O(1)	1.953(8)	Ru(2)-O(2)	1.969(7)
Ru(1)-N(1)	2.078(9)	Ru(2)-N(2)	2.078(10)
Ru(1)-Cl(3)	2.341(3)	Ru(2)-Cl(4)	2.320(3)
Ru(1)-Cl(2)	2.369(3)	Ru(2) - P(2)	2.385(4)
Ru(1) - P(1)	2.377(3)	Ru(2)-Cl(1)	2.403(3)
Ru(1)-Cl(1)	2.428(3)	Ru(2)-Cl(2)	2.410(3)
O(1) - Ru(1) - N(1)	89.2(4)	O(2) - Ru(2) - N(2)	89.4(3)
O(1) - Ru(1) - Cl(3)	92.6(3)	O(2) - Ru(2) - Cl(4)	92.5(3)
N(1) - Ru(1) - Cl(3)	90.5(3)	N(2) - Ru(2) - Cl(4)	90.2(3)
O(1) - Ru(1) - Cl(2)	94.8(3)	O(2) - Ru(2) - P(2)	87.0(3)
N(1) - Ru(1) - Cl(2)	82.8(3)	N(2) - Ru(2) - P(2)	176.4(2)
Cl(3)-Ru(1)-Cl(2)	169.97(11)	Cl(4) - Ru(2) - P(2)	90.29(12)
O(1) - Ru(1) - P(1)	85.3(3)	O(2) - Ru(2) - Cl(1)	94.8(3)
N(1) - Ru(1) - P(1)	173.2(3)	N(2) - Ru(2) - Cl(1)	81.3(3)
Cl(3) - Ru(1) - P(1)	93.63(14)	Cl(4)-Ru(2)-Cl(1)	168.79(12)
Cl(2) - Ru(1) - P(1)	93.73(15)	P(2) - Ru(2) - Cl(1)	98.60(11)
O(1) - Ru(1) - Cl(1)	176.0(3)	O(2) - Ru(2) - Cl(2)	175.9(2)
N(1) - Ru(1) - Cl(1)	89.1(3)	N(2) - Ru(2) - Cl(2)	89.8(2)
Cl(3) - Ru(1) - Cl(1)	91.01(12)	Cl(4) - Ru(2) - Cl(2)	91.56(12)
Cl(2) - Ru(1) - Cl(1)	81.42(11)	P(2) - Ru(2) - Cl(2)	93.73(11)
P(1) - Ru(1) - Cl(1)	96.18(13)	Cl(1) - Ru(2) - Cl(2)	81.11(12)
Ru(2) - Cl(1) - Ru(1)	87.62(10)	Ru(1) - Cl(2) - Ru(2)	88.82(11)
	( - )		- ( )

parameters associated with the metal ions are listed in Table 2. The metal ions are in distorted octahedral NOCl<sub>3</sub>P coordination spheres. The pair of salicylaldimine moieties in salhn<sup>2-</sup> bind the Ru centers through the phenolate-O and the imine-N atoms to form two six-membered chelate rings and provide the N-N bridge between them. In addition, the metal ions are bridged by two of the four chloride ligands. As expected the  $Ru_2(\mu$ -Cl)<sub>2</sub> unit is not planar due to the presence of the third diazine bridge. The angle between the planes containing Ru1, Cl1, Cl2 and Ru2, Cl1, Cl2 is 47.0(1)°. The Ru…Ru distance is 3.344(2) Å. The terminal chlorine atoms are trans to the bridging chlorine atoms, and the PPh3 molecules coordinate through P atoms at the trans sites of the imine-N atoms. The Ru-O(phenolate) and Ru-N(imine) distances (Table 2) are similar to those reported for Ru(III) complexes containing the same coordinating atoms.<sup>13,14</sup> The Ru(III)-P distances are unexceptional.<sup>14</sup> The Ru-Cl(bridging) distances, not surprisingly, are longer than the Ru-Cl(terminal) distances. These distances are comparable with the distances reported for other structurally characterized diruthenium(III) complexes containing bridging and terminal chlo-

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**Figure 2.** Inverse molar magnetic susceptibility ( $\bigcirc$ ) and effective magnetic moment ( $\square$ ) of [Ru<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>( $\mu$ -salhn)] as a function of temperature. The solid lines were generated from the best least-squares fit parameters given in the text.

rides.<sup>15</sup> Both salicylaldimine fragments are satisfactorily planar. The mean deviations are 0.05 and 0.08 Å for the first (O1, C1– C7, N1) and the second (N2, C8–C14, O2) fragments, respectively. The corresponding Ru centers, Ru1 and Ru2, are displaced from these planes by 0.45(1) and 0.57(1) Å, respectively. Thus the six-membered chelate rings are folded along the O, N line. The fold angles are 17.7(5)° and 22.1(5)° for the first and the second chelate ring, respectively. Similar folding has been also observed for  $[Fe_2(\mu-salhn)_3]$ .<sup>3</sup>

The solid-state structure of the uncomplexed H<sub>2</sub>salhn is known.<sup>16</sup> The compound is in the usual trans configuration ( $\mathbf{I}$ ). As mentioned before, there are three structurally characterized complexes containing bridging salhn<sup>2-</sup>. In two of them,  $[(CO)_2Rh(\mu-salhn)(CO)_2Rh]^4$  and  $[\{CO_3L(CH_3COO)(CH_3O)_3\}_2$ - $(\mu$ -salhn)],<sup>5</sup> only the diazine fragment of salhn<sup>2-</sup> is bridging two metal ions and the ligand is in the trans configuration. In the third complex,  $[Fe_2(\mu-\text{salhn})_3]^3$  the diazine fragments of three salhn<sup>2–</sup> bridge the two metal ions and all three ligands are twisted along the N-N bond. However, the extent of twisting is different for the three ligands. The maximum is 56.8°, and the minimum is 26.6°. In the present complex, the salhn<sup>2-</sup> is also in the twisted configuration but to a much lesser extent. The dihedral angle between the salicylaldimine moieties is 17.1-(4)°. The additional two chloride bridges and the trans arrangement of the terminal chlorides force the near cis configuration of salhn<sup>2–</sup> in this complex.

**Spectral Characteristics.** As expected the free Schiff base phenolic OH stretching<sup>17</sup> ( $\sim$ 3000 cm<sup>-1</sup>) is not observed in the infrared spectrum of the complex. The C=N stretching<sup>3,18</sup> is observed at 1595 cm<sup>-1</sup>, which is substantially lower than that displayed by H<sub>2</sub>salhn at 1622 cm<sup>-1</sup>. The electronic spectrum of the complex in CHCl<sub>3</sub> displays a strong band at 745 nm and an intense absorption at 243 nm. The origins of these absorptions are most probably ligand-to-metal charge transfer and intraligand transitions. The EPR spectrum of the complex in frozen (77 K)

CHCl<sub>3</sub>–C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (1:1) solution showed the typical axial pattern  $(g_{\perp} = 2.40, g_{||} = 1.74)$ , which is very common for low-spin Ru(III) complexes.<sup>19</sup> A very weak antiferromagnetic spin coupling is present between the two metal centers in [Ru<sub>2</sub>Cl<sub>2</sub>-(PPh<sub>3</sub>)<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>( $\mu$ -salhn)] (vide infra). The magnetic moment at 77 K is 2.28  $\mu_{\rm B}$  (Figure 2). This corresponds to 1.61  $\mu_{\rm B}$ /Ru center, which is slightly lower than the spin-only moment for one unpaired electron. Thus the axial spectrum observed is consistent for a dinuclear species containing two weakly coupled low-spin Ru(III) atoms.

**Redox Potentials.** The complex displays two quasi-reversible reduction responses in the cyclic voltammogram. These responses are observed at  $E_{1/2} = 0.05$  V ( $\Delta E_p = 80$  mV) and  $E_{1/2} = -0.18$  V ( $\Delta E_p = 90$  mV). The current heights observed for both responses are comparable with known one-electron redox processes under identical conditions.<sup>20</sup> Considering the dinuclear structure of the molecule, the weak antiferromagnetic spin coupling (vide infra), and the separation (230 mV) between the two reduction responses,<sup>21</sup> we assign the first reduction to the Ru<sup>III</sup>Ru<sup>III</sup>  $\rightarrow$  Ru<sup>III</sup>Ru<sup>II</sup> process and the second reduction to Ru<sup>III</sup>-Ru<sup>II</sup>  $\rightarrow$  Ru<sup>III</sup>Ru<sup>II</sup> process.

Magnetic Susceptibility. Magnetic susceptibility measurements with a powdered sample of [Ru<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(µ-Cl)<sub>2</sub>(µsalhn)] were conducted in the temperature range 20-296 K at a constant magnetic field of 5 kG. The effective magnetic moment (2.45  $\mu_{\rm B}$ ) at 296 K is essentially the spin-only moment for a dimer containing two metal ions having  $S = \frac{1}{2}$  spin states. The moment gradually decreases to 1.87  $\mu_B$  at 20 K (Figure 2) indicating an antiferromagnetic interaction between the two Ru-(III) centers. The data were fitted using an expression<sup>22</sup> for  $\chi_M$ vs T derived from the isotropic spin exchange Hamiltonian H=  $-2JS_1 \cdot S_2$ , where  $S_1 = S_2 = \frac{1}{2}$ . The best least-squares fit was obtained with J = -9.0(1) cm<sup>-1</sup>, g = 1.915(1), p = 1.33%, and TIP =  $2.31 \times 10^{-4}$  emu/mol, where J is the antiferromagnetic coupling constant, p is the mononuclear low-spin Ru(III) impurity, and TIP is the temperature independent paramagnetism.<sup>23</sup> Dicopper(II) complexes containing the =N-N= bridge are known to exhibit very weak to strong intramolecular antiferromagnetic spin coupling.<sup>2b-d,f</sup> In these complexes, the extent of interaction is determined mainly by the twist along the N-N single bond.<sup>2c,d,f</sup> Dinuclear complexes of other 3d metal ions having the same linkage between the metal centers<sup>2e,3,24</sup> display no coupling or very weak intramolecular spin coupling as observed in the present complex. In addition to the diazine bridge there are two chloride bridges between the Ru(III) centers in the present complex. The folding of the  $Ru_2(\mu-Cl)_2$  core<sup>25</sup> along the Cl, Cl line (vide supra) and the nearly orthogonal Ru-Cl-Ru bridge angles<sup>26</sup> (87.62(10)° and 88.82(11)°) are most likely not conducive to an effective antiferromagnetic superexchange interaction via the chloride bridges; thus a small J value  $(-9.0(1) \text{ cm}^{-1})$  is observed.

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Concluding Remarks. Structurally characterized dinuclear complexes containing an N-N single bond as the bridge between the metal ions are known mainly with copper(II)<sup>2b-d,f</sup> and a few other 3d transition metal ions.<sup>2a,e,3</sup> Except one dirhodium(I) complex,<sup>4</sup> no such complex of a 4d transition metal ion is known. In this work, a diruthenium(III) complex, in which the metal ions are bridged by the =N-N= moiety provided by salhn<sup>2-</sup> as well as by two chloride ligands, is reported. The molecular structure has been determined by single-crystal X-ray diffractometry. The spectroscopic and redox properties are consistent with the dinuclear structure in solution. Both the metal ions in the complex are in the low-spin state, and a very weak antiferromagnetic spin coupling is operative between them. We are currently involved in synthesizing and exploring the chemistry of other dinuclear ruthenium complexes bridged by salhn<sup>2-</sup> or its substituted derivatives and containing different coligands.

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**Supporting Information Available:** X-ray crystallographic data for  $[Ru_2Cl_2(PPh_3)_2(\mu-Cl)_2(\mu-salhn)]$ ·CHCl<sub>3</sub> in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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