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cis-Dihalobis(arylazo oxime)ruthenium(II): Synthesis, Structure, and Reactions

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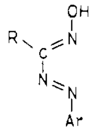
The reaction of RuX_3 (X = Cl, Br) with arylazo oximes (ArN=NC(=NOH)R, HL) in boiling ethanol under a dinitrogen atmosphere affords dark crystals of composition $RuX_2(HL)_2$. In all, a group of five complexes differing in R, Ar, and/or X are reported along with one iodo (X = I) complex. These are uniformly diamagnetic and display a $t_2(Ru) \rightarrow \pi^*(HL)$ charge-transfer transition near 500 nm. The complex dichlorobis(α-(phenylazo)benzaldoxime)ruthenium(II) has been X-ray crystallographically characterized. The crystals belong to the orthorhombic space group $Pc2_1n$, and unit cell dimensions are $a = 11.879$ (3) Å, $b = 12.155$ (3) Å, $c = 18.418$ (3) Å, $V = 2659$ (3) Å^3, and $Z = 4$. The $RuCl_2N_4$ coordination shell has approximate C_2 symmetry. The two chlorine atoms are cis to each other, and two oxime nitrogen atoms are trans to each other. Each oxime group is involved in an N-O-H···Cl type hydrogen bond with a cis chlorine atom. The backbone of each ligand along with the chlorine atom hydrogen bonded to it is meridionally disposed and is essentially planar. The average Ru-N distance is 1.986 [2] Å, indicating that π-bonding is strong. Infrared (doublet ν_{RuX_2}) and ^1H NMR spectra indicate that the other complexes have cognate structures. A general reaction of $RuX_2(HL)_2$ is their facile dehydrohalogenation in the presence of bases. The complexes display a cyclic voltammetric one-electron metal oxidation peak in MeCN near 1.2 V vs. SCE. The high value of the potential is a result of the strong Ru-N π-bonding.

Introduction

The transition-metal complexes of arylazo oximes (HL, **1**)—particularly those of the 4d and 5d series—are being currently examined in these laboratories. The studies made so far[2-8] indicate that this area abounds in interesting chemistry. Palladium(II) arylazo oximates undergo highly selective bond cleavage reactions and equilibria.[3-5] Bis chelates of platinum(II) occur in cis and trans forms; the structure of *cis*-Pt$(L^1)_2$ is known accurately.[2] The cis isomer alone undergoes an unusual but facile one-electron oxidation to PtL_2^+. Isomerism is also displayed[6] by the tris chelates of rhodium(III); again the cis (facial) and trans (meridional) isomers differ dramatically in their electron-transfer properties.[7] We note that reports on systematic studies of such variations in the properties of cis and trans isomers in heavier transition-element chemistry are sparse.



R	Ar	
Me	Ph	HL^1
Ph	Ph	HL^2
Ph	*p*-Tolyl	HL^3

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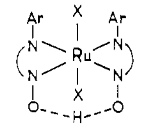
The present work stems from our interest in isomeric arylazo oximates of ruthenium. In an earlier paper[8] red-violet complexes of the type $Ru^{III}X_2(HL)(L)$ (X = Cl, Br) were shown to be formed by the reaction of RuX_3 with HL in methanol. Though X-ray confirmation is lacking, the available information[8] shows that the structure of $Ru^{III}X_2(HL)(L)$ is almost certainly **2**. Here *trans*-RuX_2 is held in the matrix of hydrogen-bonded L···H-L spanning the perpendicular plane. In solution, **2** is reversibly reduced[8] to the corresponding ruthenium(II) complex, $Ru^{II}X_2(HL)(L)^-$ (2^-), which is believed to have the same gross structure as **2**. Our search for the cis isomers[9] of **2** has not met with success. However, a protonated form of a cis isomer of 2^- has been discovered. This new group of complexes, which forms the subject matter of the present study, is of composition $Ru^{II}X_2(HL)_2$ and is furnished as dark colored crystals by the reaction of RuX_3 with HL in boiling ethanol under inert atmosphere. Characterization data and selected reactions of the new complexes are reported. The three-dimensional X-ray crystallographic examination of one of the complexes, viz. $RuCl_2(HL^2)_2$, has led to an exact definition of the coordination geometry and dimensions. A relatively uncommon type of hydrogen bonding among ligands and strong metal-ligand π interactions are shown to be present.



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We note that until recently[8,10-12] authentic ruthenium oximates of any sort were few in number. Accurate structural results are so far available only for a tris(violurato) complex.[13]

Results and Discussion

Synthesis. The reaction between RuX_3 and HL proceeds smoothly in boiling ethanol under nitrogen atmosphere (eq 1).

$$RuX_3 + HL \xrightarrow{EtOH} RuX_2(HL)_2 \qquad (1)$$

On cooling, dark colored crystals of composition $RuX_2(HL)_2$ deposit. In this synthesis ethanol presumably acts both as a solvent and as a reducing agent. While chloro and bromo complexes have been prepared generally, the iodo complex is

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[2] Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.*, in press. Mascharak, P. K.; Chakravorty, A. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 179

[3] Mascharak, P. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1980**, 1698. Bandyopadhyay, P.; Mascharak, P. K.; Chakravorty, A. *Inorg. Chim. Acta* **1980**, *45*, L219.

[4] Bandyopadhyay, P.; Mascharak, P. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1981**, 623.

[5] Bandyopadhyay, P.; Mascharak, P. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1982**, 675.

[6] Kalia, K. C.; Chakravorty, A. *Inorg. Chem.* **1969**, *8*, 2586.

[7] Ghosh, P.; Chakravorty, A., unpublished results.

[8] Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 3138. Chakravarty, A. R.; Chakravorty, A. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 307.

[9] Three such isomers are possible in principle. Intramolecular hydrogen bonding of the type present in **2** cannot occur in the cis isomers.

[10] Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 275. Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1982**, 615, 1765.

[11] Middleton, A. R.; Thornback, J. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 174. Kuek, H. T.; West, B. O.; Yandell, J. K. *Inorg. Chim. Acta* **1981**, *52*, 1.

[12] Bremard, C.; Nowogrocki, G.; Sueur, S. *Inorg. Chem.* **1979**, *18*, 1549. Mukaida, M.; Yoneda, M.; Nomura, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3053.

[13] Abraham, F.; Nowogrocki, G.; Sueur, S.; Bremard, C. *Acta Crystallogr., Sect. B* **1980**, *B36*, 799.

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Table I. Infrared and UV-Visible Spectral Data of $RuX_2(HL)_2$

	IR data,[a,b] cm^{-1}				UV-vis data[c]	
complex	ν_{OH}	ν_{CN}	ν_{NO}	ν_{RuX}	solvent	λ, nm (ε, M^{-1} cm^{-1})
$RuCl_2(HL^1)_2$	3175	1585	1270	366, 325	MeCN	490 (8000), 360 (15 800)
$RuCl_2(HL^2)_2$	3065	1590	1270	363, 331	MeCN	503 (7800), 370 sh (8900), 293 (28 500), 270 (29 000)
$RuBr_2(HL^2)_2$	3140	1595	1270	*d*	MeCN	502 (9880), 340 sh (14 260), 280 sh (22 800)
$RuI_2(HL^2)_2$	3160	1580	1265	*d*	CH_2Cl_2	515 (7060), 340 sh (19 100)
$RuCl_2(HL^3)_2$	3060	1600	1260	370, 326	MeCN	510 (7200), 373 (11 500), 258 (27 400)
$RuBr_2(HL^3)_2$	3000	1595	1258	288, 258	CH_2Cl_2	518 (8250), 358 sh, 348 (16 100)

[a] In KBr disk. [b] Characteristics: ν_{OH}, medium and broad; ν_{CN}, medium and sharp; ν_{NO}, strong and broad; ν_{RuX}, weak and broad. [c] sh = shoulder. [d] Not studied.

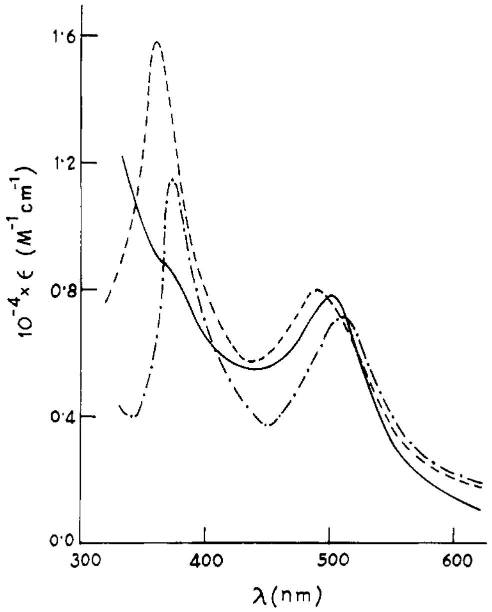


Figure 1. Electronic spectra of $RuCl_2(HL^1)_2$ (---), $RuCl_2(HL^2)_2$ (—) and $RuCl_2(HL^3)_2$ (-·-) in MeCN.

also reported in the case of the HL^2 ligand (Table I). All complexes are diamagnetic and soluble in common organic solvents, giving nonelectrolytic reddish pink solutions. The stability of such solutions usually increases as I < Br < Cl. Solution molecular weights where determined correspond to the $RuX_2(HL)_2$ formulation.

Spectra. Both $RuCl_2(HL^1)_2$ and $RuX_2(HL^3)_2$ (X = Cl, Br) display a single sharp ^1H NMR methyl signal: δ_{Me} values are respectively 3.00 and 2.33. The presence of a single signal demonstrates that in each complex the two HL ligands are in equivalent environments.

Selected infrared frequencies are in Table I. Significant observations are (i) doublet RuX_2 frequencies expected of a cis geometry, (ii) a strong ν_{NO} characterizing[3-8,10] the formation of the five-membered arylazo oximate chelate ring, and (iii) weak and broad ν_{OH} at relatively low frequencies suggesting the presence of some kind of hydrogen bonding.

In UV-visible spectra a characteristic feature of $RuX_2(HL)_2$ is an allowed band near 500 nm (Figure 1, Table I). This is assigned to the metal-to-ligand charge-transfer (MLCT) transition $t_2(Ru) \rightarrow \pi^*(HL)$ within the framework of pseudooctahedral ruthenium(II) stereochemistry. The $\pi^*(HL)$ orbital is believed to belong to the azoimine (N=C—N=N) group, which is isoelectronic with the diimine function (N=C—C=N) that is present in, e.g., 2,2′-bipyridine (bpy). In *cis*-$RuCl_2(bpy)_2$ an MLCT band occurs[14] at 550 nm. In *cis*-$RuCl_2(pap)_2$ (pap = 2-(phenylazo)pyridine), which also has the azoimine function, the MLCT band is at 580 nm.[15]

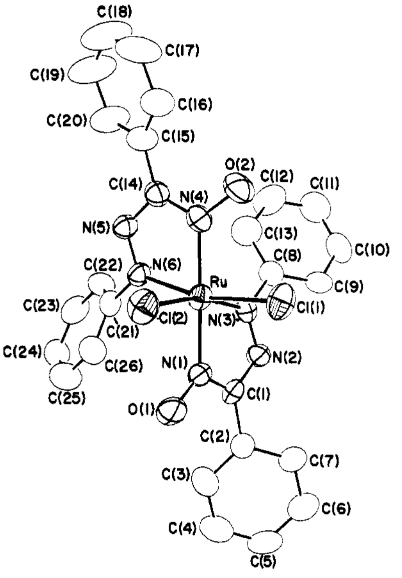


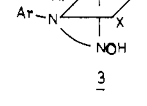
Figure 2. Molecular structure, atom-labeling scheme, and 50% probability ellipsoids for *cis*-$RuCl_2$ $(HL)_2$. The view direction is along the pseudo-twofold axis of the molecule.

Table II. Important Bond Distances (Å) and Their Estimated Standard Deviations for *cis*-$RuCl_2(HL^2)_2$[a]

Ru-Cl(1)	2.408 (3)	N(2)-N(3)	1.299 (10)
-Cl(2)	2.394 (3)	-C(1)	1.368 (12)
-N(1)	1.986 (7)	N(3)-C(8)	1.431 (12)
-N(3)	1.989 (7)	N(4)-C(14)	1.321 (11)
-N(4)	1.989 (7)	N(5)-N(6)	1.292 (9)
-N(6)	1.979 (7)	-C(14)	1.375 (11)
O(1)-N(1)	1.369 (11)	N(6)-C(21)	1.425 (11)
O(2)-N(4)	1.372 (9)	C(1)-C(2)	1.487 (13)
N(1)-C(1)	1.306 (14)	C(14)-C(15)	1.448 (12)

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits.

Structural Studies. The ^1H NMR and IR spectra of $RuX_2(HL)_2$ suggested the presence of the *cis*-RuX_2N_4 coordination sphere having a twofold axis of symmetry. Probable structures are therefore **3** and **4**. In structure **5** (C_1 symmetry) the two chelate rings are in different environments.



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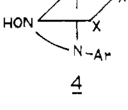

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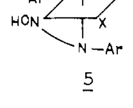

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In order to sort out the structural problem and to examine the details of bonding, crystals of $RuCl_2(HL^2)_2$ were subjected to three-dimensional X-ray diffraction. It has been found that the structure is qualitatively of type 3 but includes O–H···Cl

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(14) Johnson, E. C.; Sullivan, B. P.; Salmon, D. J.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 2211.

(15) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 2737. Krause, R. A.; Krause, K. *Inorg. Chem.* **1980**, *19*, 2600.

Table III. Important Bond Angles (deg) for *cis*-$RuCl_2(HL^2)_2$[a]

Cl(1)–Ru–Cl(2)	89.9 (1)	N(3)–N(2)–C(1)	112.7 (8)
–N(1)	90.9 (2)	Ru–N(3)–N(2)	118.3 (6)
–N(3)	86.1 (2)	–C(8)	128.7 (7)
–N(4)	90.0 (2)	N(2)–N(3)–C(8)	112.6 (8)
–N(6)	165.5 (2)	Ru–N(4)–O(2)	123.8 (6)
Cl(2)–Ru–N(1)	89.6 (4)	–C(14)	117.6 (6)
–N(3)	164.7 (3)	O(2)–N(4)–C(14)	118.4 (7)
–N(4)	90.5 (3)	N(6)–N(5)–C(14)	114.9 (7)
–N(6)	90.1 (2)	Ru–N(6)–N(5)	118.2 (6)
N(1)–Ru–N(3)	75.7 (4)	–C(12)	129.0 (6)
–N(4)	179.0 (4)	N(5)–N(6)–C(21)	112.7 (7)
–N(6)	103.6 (3)	N(1)–C(1)–N(2)	115.9 (8)
N(3)–Ru–N(4)	104.2 (4)	–C(2)	127.1 (9)
–N(6)	97.4 (3)	N(2)–C(1)–C(2)	116.9 (9)
N(4)–Ru–N(6)	75.5 (3)	N(4)–C(14)–N(5)	112.7 (8)
Ru–N(1)–O(1)	125.0 (8)	–C(15)	129 (1)
–C(1)	116.3 (7)	N(5)–C(14)–C(15)	117.9 (8)
O(1)–N(1)–C(1)	118.1 (7)		

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits.

intramolecular hydrogen bonding. The molecule is shown in Figure 2, and important bond distances and angles (following the labeling scheme of Figure 2) are listed in Tables II and III.

The ruthenium atom is coordinated by four nitrogen atoms and two chlorine atoms arranged in an irregular octahedron. The two chlorine ligands are cis to each other, and the two oxime nitrogen atoms from the chelating arylazooxime ligands are trans to each other. This gives the immediate coordination shell approximate C_2 symmetry, with the twofold axis bisecting the Cl(1)–Ru–Cl(2) bond. However, the entire molecule constitutes the asymmetric unit and no rigorous crystallographic symmetry is imposed.

The four Ru–N distances are equal to each other within experimental error, with an average value[16] of 1.986 [2] Å. The Ru–Cl(1) (2.408 (3) Å) and Ru–Cl(2) (2.394 (3) Å) bond distances are almost identical, statistically speaking, differing by only 0.016 (4) Å. Nor are the chelate bite angles, N(1)–Ru–N(3) (75.7 (4)°) and N(4)–Ru–N(6) (75.5 (3)°), significantly different from each other; they are comparable to the average value of 76.5 [3]° found in the planar, four-coordinate species *cis*-$Pt(L^1)_2$.[2] The Cl(1)–Ru–Cl(2) angle is 89.9 (1)°. Given these angles, it is necessary that a number of other angles between cis ligand atoms be greater than 90° and this is the case for all three of the *cis*-N–Ru–N bond angles: N(1)–Ru–N(6), 103.6 (3)°; N(3)–Ru–N(4), 104.2 (4)°; N(3)–Ru–N(6), 97.4 (3)°. While this geometrical effect may be simply an accommodation of the chelate bite angle, it is also consistent with the steric interaction among the ligand phenyl groups, since, from Figure 2, there does not appear to be any crowding among the phenyl groups.

There are two intramolecular hydrogen bonds within the complex, O(1)···Cl(2), 3.036 (8) Å, and O(2)···Cl(1), 3.038 (8) Å; the sum of the O and Cl van der Waals radii is 3.20 Å. When these interactions are taken into consideration, the complex can be regarded as consisting of two equivalent meridionally arranged sets of ligands. The backbones of the HL^2 bidentate ligands are almost rigorously planar and the chlorine atom hydrogen-bonded to each HL^2 ligand is essentially coplanar with it.

The structure shows strong evidence that there is appreciable multiple character in the Ru–N bonds as a result of π-donation from the metal dπ orbitals (t_{2g} orbitals in a truly octahedral complex) to the ligand π* system. It is well-known that the Ru^{2+} ion is an excellent π-donor.[17] In this case, the uniformly short Ru–N bonds provide perhaps the most direct indication that such bonding occurs. Further evidence is found in a comparison of the intraligand bond lengths with those previously reported[18] for the similar molecule HL^1. In the ruthenium complex the N=C and N=N distances are somewhat longer and the N–C distances slightly shorter than in the HL^1 molecule, as a result of electron density having entered one or more ligand π* orbitals. It should be noted that the meridional arrangement of the ligands is an optimal one for such metal to ligand π-bonding. Each ligand is oriented to have full access to one dπ orbital, and the third d orbital is available to both ligands.

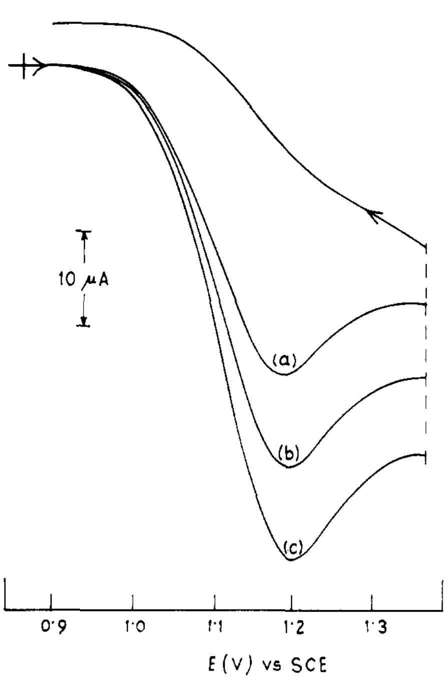

Figure 3. Cyclic voltammograms of $RuCl_2(HL^2)_2$ in MeCN (0.1 M in TEAP) at various scan rates: (a) 20, (b) 40, (c) 60 mV s^{-1} (solute concentration $\sim 10^{-3}$ M; platinum electrode).

Selected Reactions. Dehydrohalogenation and Ligand Insertion. Attempted deprotonation of $RuX_2(HL)_2$ invariably leads to dehydrohalogenation. This is a chemical manifestation of the proven close proximity of oxime H and Cl. Thus, addition of base to $RuX_2(HL)_2$ leads to the loss of two molecules of HX. With use of benzene as the solvent and NEt_3 as the base crystalline $NEt_3{\cdot}HX$ can be isolated quantitatively from the reaction mixture. The resulting brown solution reacts with a variety of neutral ligands, giving nonelectrolyic heterochelates of the type $RuL_2L'_2$, where L'_2 is either a pair of monodentate (e.g., pyridine) or one bidentate (e.g., bpy) ligand(s) (eq 2). The detailed chemistry of such heterochelates will be reported separately.

$$\mathrm{RuX_2(HL)_2} \xrightarrow[\text{(ii) L}'_2]{\text{(i) NEt}_3} \mathrm{RuL_2L'_2} \tag{2}$$

Cyclic Voltammetry. In MeCN (0.1 M in TEAP) $RuX_2(HL)_2$ displays a well-defined cyclic voltammetric response near 1.2 V vs. SCE at a platinum electrode. On scan reversal no cathodic response is observed either due to irreversibility of the electrode process or due to decomposition of the oxidized complex (Figure 3). Anodic peak potentials at a scan rate of 50 mV s^{-1} are as follows: $RuCl_2(HL^1)_2$, 1.21 V; $RuCl_2(HL^2)_2$, 1.20 V; $RuBr_2(HL^2)_2$, 1.19 V; $RuCl_2(HL^3)_2$, 1.22 V; $RuBr_2(HL^3)_2$, 1.17 V. The electrode process is undoubtedly

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(16) The deviation in brackets is calculated as $[\sum_i \Delta_i^2/n(n-1)]^{1/2}$, in which Δ_i is the deviation of the *i*th of *n* values from the arithmetic mean of the sample.

(17) Richardson, D. E.; Walker, D. D.; Sutton, J. E.; Hodgson, K. O.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2216.

(18) Roy, T.; Sengupta, S. P. *Cryst. Struct. Commun.* **1980**, *9*, 965.

due to the oxidation of $RuX_2(HL)_2$ to the corresponding ruthenium(III) complex. The formal potential ($E°_{298}$) of the couple (3) is estimated[19] to be 1.15 V. That the anodic peak

$$Ru^{III}X_2(HL)_2^+ + e^- \rightleftharpoons Ru^{II}X_2(HL)_2 \qquad (3)$$

corresponds to a one-electron stoichiometry was established by comparing its current height with that of an equimolecular solution of $Ru(bpy)_3^{2+}$ (here ruthenium(II) → ruthenium(III) oxidation occurs[14,20] near 1.3 V).

It is instructive to compare the formal potentials and average Ru–N bond distances (*l*) of $RuCl_2(HL)_2$ with those of *cis*-$RuCl_2(bpy)_2$ and *cis*-$RuCl_2(pap)_2$. All the three complexes have π-bonding ligands and the *cis*-$RuCl_2N_4$ coordination sphere. The $E°_{298}$ values of the ruthenium(III)–ruthenium(II) couple of the bpy and pap complexes are 0.30[14] and 1.05[15] V, respectively. In *cis*-$RuCl_2(bpy)_2$ *l* is estimated[21,22] to be 2.06 Å and in *cis*-$RuCl_2(pap)_2$ *l* is[23] 2.02 Å. Thus *l decreases* in the order bpy > pap > HL probably due to a parallel *increase* in the π-acceptor strength of ligands. Significantly the formal potentials of the complexes increase in the ligand order bpy < pap < HL. The high formal potential of $RuX_2(HL)_2$ is thus linked with the strong Ru–HL π-interaction which stabilizes the t_2 orbital. This orbital is involved in the electron-transfer process.

Concluding Remarks

All the $RuX_2(HL)_2$ complexes are found to occur in only one isomeric form. It is very probable that this form has the same gross stereochemistry (**3**) as that of $RuCl_2(HL^2)_2$. Significantly intramolecular X···HL hydrogen bonding is maximized in **3**. In **5** only one such bond can occur, and in **4** no such bonding is possible. In this context we note that *cis*-$RuCl_2(pap)_2$, in which the question of hydrogen bonding does not arise, exists in at least two isomeric forms whose backbones have been X-ray crystallographically characterized to be similar to **3** and **5** (oxime nitrogen replaced by pyridine nitrogen).[15,23] It would appear that isomeric stability in the case of $RuX_2(HL)_2$ is intimately related to the extent of X···HL hydrogen bonding. When the structures of $RuX_2(HL)_2$ (**3**) and $RuX_2(HL)(L)$ (**2**) are considered collectively, the role of intramolecular hydrogen bonding of one kind or another as a dominant factor controlling the stereochemistry of the dihalobis(arylazo oxime)ruthenium moiety comes to a sharper focus. The relative stabilities of the cis and trans geometries for the $RuCl_2$ fragment seemingly depend on the metal oxidation number. The isomerization[24] cis → trans has been shown to accompany electrochemical metal oxidation (Ru(II) → Ru(III)) in a diphosphine complex of dichlororuthenium. The mutual relationship of $RuX_2(HL)_2$ and $RuX_2(HL)(L)$ is somewhat similar, but electrochemical conversion of one to the other is not achievable.

Experimental Section

Table IV. Summary of Crystallographic Parameters for *cis*-$RuCl_2(HL^2)_2$

formula	$RuCl_2(N(Ph){=}NC(Ph){=}NOH)_2$
fw	622.5 for $RuCl_2O_2N_6C_{26}H_{22}$
space group	$Pc2_1n$
a, Å	11.879 (3)
b, Å	12.155 (3)
c, Å	18.418 (3)
V, Å^3	2659 (3)
Z	4
d_{calcd}, g/cm^3	1.55
cryst size, mm	0.20 × 0.20 × 0.20
μ(Mo Kα), cm^{-1}	8.13
data collection instrument	Enraf-Nonius CAD-4
radiation	Mo Kα ($\lambda_\alpha = 0.71073$ Å) (graphite monochromated)
scan method	ω-2θ
data collection range	$+h, +k, +l$; $4 < 2\theta < 50°$
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	1500
no. of parameters refined	412
R^a	0.0309
$R_w{}^b$	0.0356
quality-of-fit indicator^c	0.971
largest shift/esd, final cycle	0.26

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{observns} - N_{parameters})]^{1/2}$.

Starting Materials. Arylazooximes were prepared by following literature methods.[25] $RuCl_3 \cdot 3H_2O$ was purified as before.[10] Electrochemically pure acetonitrile solvent and tetraethylammonium perchlorate (TEAP) were obtained as described earlier.[8,10] Commercially available ethanol was dried by using a standard procedure. All other reagents (BDH, India) were of analytical grade. Elemental analyses and molecular weight determinations were carried out by CSIRO, Australia.

Physical Measurements. UV–vis, IR, far-IR, and ^1H NMR spectra were recorded with Cary 17D, Beckman IR-20, Beckman IR-720 and Varian T-60A spectrometers, respectively. Solution electrical conductivity was measured with use of a Philips PR9500 bridge. Cyclic voltammetric measurements were made with a PAR Model 175 universal programmer for sweep generation and PAR Model 174A polarographic analyzer. A three-electrode cell system, PAR Model 377A, which includes a planar Beckman Model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE), was used. Electrochemical results were obtained at 298 K and are uncorrected for junction potentials.

Preparation of Complexes. Dichlorobis(arylazo oxime)ruthenium(II), $RuCl_2(HL)_2$. All dichloro complexes were prepared by using the same general procedure. The yield of $RuCl_2(HL)_2$ is ~20%. Experimental details are given below for the preparation of $RuCl_2(HL^2)_2$.

Dichlorobis(α-(phenylazo)benzaldoxime-*N*,*N*′)ruthenium(II), $RuCl_2(HL^2)_2$. A 65-mg (0.25 mmol) quantity of $RuCl_3 \cdot 3H_2O$ was dissolved in 10 mL of absolute ethanol in a 50-mL three-necked flask fitted with a dinitrogen inlet tube. The solution was flushed with dinitrogen for 15 min. To this solution was added 123 mg (0.50 mmol) of HL^2. The mixture was boiled for 2 h while its color changed from brown to pink. The solution thus obtained was cooled to room temperature, and the shining dark colored crystals of the complex were filtered and washed thoroughly with water and finally with diethyl ether. The compound thus obtained was dried in vacuo over P_4O_{10}. Anal. Calcd for $RuC_{26}H_{22}N_6O_2Cl_2$: C, 50.20; H, 3.70; N, 13.20; Cl, 11.00. Found: C, 50.36; H, 3.68; N, 13.45; Cl, 11.70. Molecular weight in benzene: calcd, 622; found, 585.

Dichlorobis(1-(phenylazo)acetaldoxime-*N*,*N*′)ruthenium(II), $RuCl_2(HL^1)_2$. This was prepared by using the procedure as described above except that 1.0 mmol of $RuCl_3 \cdot 3H_2O$ was reacted with 2.0 mmol of HL^1 in 15 mL of absolute ethanol. Anal. Calcd for $RuC_{16}H_{18}N_6O_2Cl_2$: C, 38.24; H, 3.58; N, 16.73; Cl, 14.14. Found: C, 38.42; H, 4.12; N, 16.45; Cl, 14.20.

Dichlorobis(α-(*p*-tolylazo)benzaldoxime-*N*,*N*′)ruthenium(II), $RuCl_2(HL^3)_2$. This was prepared by using the method given above for the preparation of $RuCl_2(HL^2)_2$. Anal. Calcd for $RuC_{28}H_{26}N_6O_2Cl_2$: C, 51.68; H, 4.00; N, 12.92; Cl, 10.92. Found: C, 51.96; H, 4.43; N, 13.04; Cl, 11.10.

Dibromobis(arylazo oxime)ruthenium(II), $RuBr_2(HL)_2$. The dibromo complexes were prepared by following the procedure used in the case of the chloro complex except that $RuCl_3 \cdot 3H_2O$ was stirred for 10 min with 500 mg of LiBr prior to the addition of HL. The

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(19) For a one-electron reversible reaction we have $E°_{298} = E_{pa} - 30$ mV, where $E°_{298}$ and E_{pa} are respectively formal potential and anodic peak potential.

(20) Brown, G. M.; Weaver, T. R.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 190.

(21) The estimate is made by considering observed distances[22] in $Ru(bpy)_3^{2+}$ and $Ru(bpy)_2(CO)Cl^+$.

(22) Rillema, D. P. Jones, D. S.; Levy, H. A. *J. Chem. Soc., Chem. Commun.* **1979**, 849. Clear, J. M.; Kelly, J. M.; O'Connell, C. M.; Vos, J. G.; Cardin, C. J.; Costa, S. R. *Ibid.* **1980**, 750.

(23) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 602.

(24) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1037.

(25) Bamberger, E.; Pemsel, W. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 85. Kalia, K. C.; Chakravorty, A. *J. Org. Chem.* **1970**, *25*, 2231.

Table V. Positional and Isotropic-Equivalent Thermal Parameters and Their Estimated Standard Deviations for *cis*-$RuCl_2(HL^2)_2$[a]

atom	x	y	z	B, Å^2
Ru	0.81251 (5)	1.000	0.77673 (3)	3.147 (9)
Cl(1)	0.6741 (2)	0.9333 (2)	0.6920 (1)	5.11 (5)
Cl(2)	0.8494 (2)	0.8151 (2)	0.8146 (1)	4.95 (5)
O(1)	0.6729 (5)	0.9338 (6)	0.9045 (3)	5.0 (1)
O(2)	0.9091 (5)	0.9617 (5)	0.6296 (3)	5.1 (2)
N(1)	0.6964 (4)	1.0129 (7)	0.8538 (3)	3.3 (1)
N(2)	0.6551 (5)	1.1736 (6)	0.7973 (3)	3.3 (1)
N(3)	0.7449 (6)	1.1478 (5)	0.7608 (3)	3.2 (1)
N(4)	0.9307 (5)	0.9883 (6)	0.7006 (3)	3.5 (1)
N(5)	1.0463 (5)	1.0394 (5)	0.7908 (3)	3.4 (1)
N(6)	0.9522 (5)	1.0497 (5)	0.8253 (3)	3.0 (1)
C(1)	0.6291 (6)	1.0977 (7)	0.8495 (4)	3.3 (2)
C(2)	0.5316 (7)	1.1230 (7)	0.8973 (4)	3.5 (2)
C(3)	0.5316 (8)	1.1069 (8)	0.9706 (4)	4.8 (2)
C(4)	0.4403 (9)	1.1336 (9)	1.0111 (5)	5.4 (3)
C(5)	0.3457 (8)	1.1788 (9)	0.9803 (5)	5.5 (3)
C(6)	0.3450 (8)	1.1972 (9)	0.9058 (6)	5.5 (3)
C(7)	0.4364 (7)	1.1701 (8)	0.8651 (5)	4.5 (2)
C(8)	0.7734 (7)	1.2284 (7)	0.7073 (4)	3.5 (2)
C(9)	0.6899 (7)	1.2861 (8)	0.6720 (4)	4.2 (2)
C(10)	0.7233 (8)	1.3636 (9)	0.6211 (5)	5.1 (2)
C(11)	0.8338 (9)	1.3839 (9)	0.6062 (6)	5.8 (3)
C(12)	0.9126 (8)	1.327 (1)	0.6433 (6)	6.3 (3)
C(13)	0.8862 (9)	1.2480 (9)	0.6926 (5)	5.4 (2)
C(14)	1.0366 (6)	1.001 (1)	0.7210 (4)	3.5 (1)
C(15)	1.1390 (7)	0.9821 (7)	0.6802 (4)	4.2 (2)
C(16)	1.1474 (8)	0.906 (1)	0.6228 (5)	5.4 (2)
C(17)	1.250 (1)	0.8886 (9)	0.5904 (5)	6.9 (3)
C(18)	1.3410 (9)	0.944 (1)	0.6128 (7)	7.8 (3)
C(19)	1.3372 (8)	1.016 (1)	0.6666 (7)	8.1 (3)
C(20)	1.2368 (8)	1.0332 (8)	0.6999 (5)	5.8 (3)
C(21)	0.9651 (6)	1.1028 (7)	0.8938 (4)	3.2 (2)
C(22)	1.0311 (8)	1.1956 (8)	0.8999 (4)	4.4 (2)
C(23)	1.0448 (8)	1.2444 (9)	0.9657 (5)	5.2 (2)
C(24)	0.9944 (8)	1.204 (1)	1.0243 (4)	6.0 (3)
C(25)	0.9230 (9)	1.113 (1)	1.0198 (5)	6.2 (3)
C(26)	0.9109 (8)	1.0638 (8)	0.9531 (4)	4.5 (2)
H(3)	0.595 (6)	1.079 (6)	0.994 (4)	4 (2)*
H(4)	0.440 (7)	1.125 (8)	1.069 (4)	8 (3)*
H(5)	0.292 (6)	1.174 (7)	1.016 (4)	4 (2)*
H(6)	0.291 (6)	1.220 (8)	0.879 (4)	6 (2)*
H(7)	0.436 (5)	1.188 (5)	0.818 (3)	2 (1)*
H(9)	0.619 (5)	1.274 (5)	0.692 (3)	2 (1)*
H(10)	0.678 (6)	1.396 (6)	0.594 (3)	4 (2)*
H(11)	0.849 (7)	1.434 (8)	0.575 (4)	6 (2)*
H(12)	0.985 (5)	1.346 (5)	0.628 (3)	2 (1)*
H(13)	0.937 (4)	1.205 (5)	0.718 (3)	1 (1)*
H(16)	1.078 (6)	0.877 (6)	0.608 (4)	4 (2)*
H(17)	1.257 (6)	0.826 (6)	0.559 (4)	3 (2)*
H(18)	1.392 (6)	0.930 (6)	0.596 (3)	4 (2)*
H(19)	1.391 (8)	1.044 (9)	0.695 (4)	9 (3)*
H(20)	1.238 (4)	1.066 (5)	0.735 (3)	1 (1)*
H(22)	1.067 (5)	1.218 (6)	0.855 (3)	3 (1)*
H(23)	1.083 (6)	1.304 (7)	0.967 (4)	4 (2)*
H(24)	0.998 (4)	1.242 (4)	1.069 (3)	1 (1)*
H(25)	0.891 (8)	1.074 (8)	1.049 (5)	7*
H(26)	0.884 (5)	1.005 (7)	0.951 (3)	2 (1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

yield of dibromo species was 25%.

Dibromobis(α-(phenylazo)benzaldoxime-*N*,*N*′)ruthenium(II), $RuBr_2(HL^2)_2$. Anal. Calcd for $RuC_{26}H_{22}N_6O_2Br_2$: C, 43.97; H, 3.10; N, 11.81. Found: C, 44.03; H, 3.23; N, 12.16. Molecular weight in benzene: calcd, 711; found, 700.

Dibromobis(α-(*p*-tolylazo)benzaldoxime-*N*,*N*′)ruthenium(II), $RuBr_2(HL^3)_2$. Anal. Calcd for $RuC_{28}H_{26}N_6O_2Br_2$: C, 45.46; H, 3.52; N, 11.37. Found: C, 45.78; H, 3.74; N, 11.43.

Diiodobis(α-(phenylazo)benzaldoxime-*N*,*N*′)ruthenium(II), $RuI_2(HL^2)_2$. Here $RuCl_3\cdot 3H_2O$ was stirred for 10 min with 2 g of NaI prior to the addition of HL^2. The remaining procedure is the same as that used for the synthesis of $RuCl_2(HL^2)_2$. The yield of the complex is only 15%. Anal. Calcd for $RuC_{26}H_{22}N_6O_2I_2$: C, 38.75; H,2.73; N, 10.43. Found: C, 38.56; H, 2.71; N, 9.90.

In order to obtain pure products uncontaminated by $RuX_2(HL)(L)$, it is essential that the ethanol solvent used be as dry as possible. In case of contamination purification can be achieved by column chromatography on silica gel (60–120 mesh) with benzene as the eluant. The contaminant moves out as a black-violet band. The pink second band is then eluted out and collected. From this pure crystals deposit on evaporation under reduced pressure.

X-ray Data Collection, Structure Solution, and Refinement. A black crystal of approximate dimensions 0.20 × 0.20 × 0.20 mm was attached in a random orientation to a glass fiber and mounted on an Enraf-Nonius CAD-4 automated diffractometer. Procedures used to collect and process data were essentially the same as reported previously.[26]

The automatic search routine of the diffractometer was used to locate and center 25 reflections in the range $15 < 2\theta < 33°$. These reflections were used for determination and least-squares refinement of the unit-cell parameters. The orthorhombic cell (Table IV) was found to have dimensions consistent with the presence of four molecules in the unit cell.

Graphite-monochromated Mo Kα radiation ($\lambda\alpha = 0.71073$ Å) was used for intensity data collection, during which the positions of 2664 reflections in the range $4 \leq 2\theta \leq 50°$ were scanned with an ω–2θ motion. Three standard reflections, measured after every hour of X-ray exposure, showed no significant loss of intensity during the course of data collection. Lorentz and polarization corrections were applied, and after the corrected intensities were converted to structure factors and equivalent data were averaged, the remaining 1500 unique reflections whose magnitudes satisfied the condition $F_o^2 \geq 3\sigma(F_o^2)$ were used to solve and refine the structure.[27] Systematic absences of the type $(0kl)$, $l = 2n + 1$, and $(hk0)$, $h + k = 2n + 1$ indicated that the space group could be either $Pc2_1n$ or $Pcmn$. Successful solution and refinement established $Pc2_1n$ as the correct choice.[28]

The position of the ruthenium atoms was determined from the three-dimensional Patterson map and refined by least-squares methods. The rest of the structure was revealed by alternate calculations of difference Fourier maps and cycles of refinement. In this way all atoms except the two hydrogen atoms bound to the oxygen atoms were located. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined with isotropic temperature factors. The refinement converged with final residuals (summarized and defined in Table IV) $R = 0.031$ and $R_w = 0.035$ and a quality-of-fit indicator equal to 0.97. The final refinement cycle did not shift any parameter by more than 0.26 times its estimated standard deviation. A difference Fourier map at the end of refinement had no peak more dense than 0.45 e/Å^3.

Table V gives the coordinates and isotropic-equivalent thermal parameters for all refined atoms. Tables II and III list the more important bond distances and bond angles, respectively. Complete lists of anisotropic thermal parameters, bond distances and angles, and structure factors are available as supplementary material. Figure 2 shows the atom-labeling scheme as well as the 50% probability ellipsoids for non-hydrogen atoms.

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Registry No. $RuCl_2(HL^1)_2$, 85505-02-8; $RuCl_2(HL^2)_2$, 85505-03-9; $RuBr_2(HL^2)_2$, 85421-93-8; $RuI_2(HL^2)_2$, 85421-94-9; $RuCl_2(HL^3)_2$, 85421-95-0; $RuBr_2(HL^3)_2$, 85421-96-1.

Supplementary Material Available: Tables of anisotropic thermal parameters, all bond lengths and angles, root-mean-square amplitudes of thermal vibration, and the observed and final calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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(26) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

(27) Computing was done on the PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX, with software from the Enraf-Nonius Structure Determination Package.

(28) Space group $Pc2_1n$ is the (bca) setting of space group No. 33 $(Pna2_1)$ of: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1965; Vol. I.