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### COMPARISON OF THE HYDROGEN BONDING IN TRANS-DICHLORO(3,3'-(1,3-PROPANEDIYL-DINITRIL)O)BIS(2-BUTANONE)DIOXIMATO) COBALT(III) AND RHODIUM(III)

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## COMPARISON OF THE HYDROGEN BONDING IN TRANS-DICHLORO(3,3'-(1,3-PROPANEDIYL- DINITRILLO)BIS(2-BUTANONE)DIOXIMATO) COBALT(III) AND RHODIUM(III)

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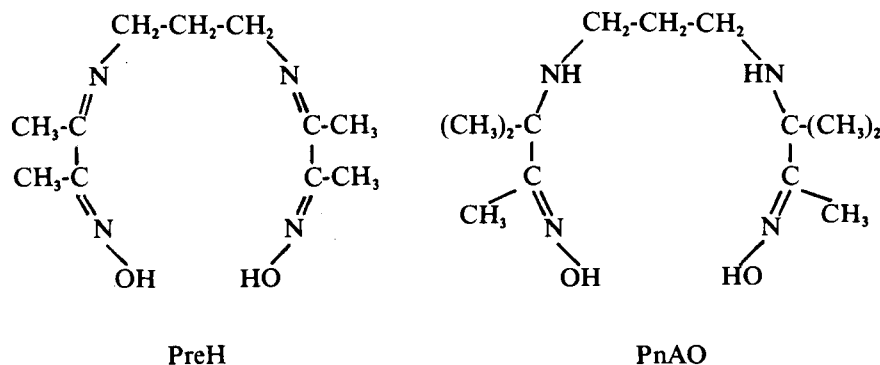
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Comparison of the hydrogen bonding in the isomorphous complexes, *trans*-dichloro(3,3'-(1,3-propanediyl)dinitrilo)bis(2-butanone)dioximato)-cobalt(III) and rhodium(III) provides an excellent example of the effect of metal ion size on the intramolecular O---O hydrogen bond (O---O=2.448(5)Å for Co and 2.626(4)Å for Rh). The lengthening of the O---O distance can be correlated with the increasing M-N distances from Co to Rh (Co-N(imine)=1.917(4)Å; Rh-N(imine)=2.00(2)Å; Co-N(oxime)=1.887(4)Å; Rh-N(oxime)=1.976(3)Å). The hydrogen bond appears to be much more asymmetric in the rhodium case with O-H distances of 0.88(4) and 1.75(4) Å compared with 1.20(6) and 1.31(6) Å in the cobalt case. The Rh-Cl distances (av. 2.335(2) Å) are also significantly longer than the Co-Cl distances (av. 2.239(1) Å). The results obtained for the cobalt complex in this study are compared with those in an earlier study.

The compounds crystallize ( $Z = 4$ ) in the monoclinic space group  $P 2_1/n$  with the following parameters for Co[Rh]:  $a = 9.846(1)[9.952(3)]$ ;  $b = 13.748(5)[13.751(2)]$ ;  $c = 11.648(2)[11.780(3)]$  Å;  $\beta = 95.46(1)[96.43(3)]^\circ$ ; and  $D_x = 1.562(2)[1.713(2)]$  g/cm<sup>3</sup>. The structures were refined with 1643[2435] independent reflections with  $I > 2\sigma(I)$  to final agreement factors of 0.042[0.027].

### INTRODUCTION

A series of related dichloro and dinitro cobalt(III) and rhodium(III) complexes<sup>1-3</sup> of bidentate  $\alpha$ -amineoxime and tetradentate  $\alpha$ -amineoxime ligands with intramolecular hydrogen bonds has been prepared and studied by x-ray diffraction and spectroscopic techniques to obtain information about the roles of the metal and ligand on the nature of the hydrogen bond (e.g., the O-O distance). The present study allows comparison of the effects of metal size (Co  $\rightarrow$  Rh) on the O-O hydrogen bond with the same constrained tetradentate ligand (PreH). In addition a comparison is made with the previously reported results on the Co(III)<sup>2</sup> and Rh(III)<sup>3</sup> complexes of a related saturated tetradentate ligand (PnAO).



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During the course of this study the structure of the cobalt(III) complex appeared<sup>4</sup> in the literature, and a comparison of the two studies is included in this paper.

## EXPERIMENTAL

[Co(PreH)Cl<sub>2</sub>]<sup>5,6</sup> and [Rh(PreH)Cl<sub>2</sub>]<sup>7</sup> were prepared as described in the literature. Dark green hexagonal plates of [Co(PreH)Cl<sub>2</sub>] were formed on slow evaporation of a water-acetone mixture of the complex at room temperature. For [Rh(PreH)Cl<sub>2</sub>] the yellow parallelepiped shaped crystals were obtained by evaporation of a dichloromethane solution of the complex. Crystals of the two compounds were found to be isomorphous in the monoclinic crystal system. The crystal data, data collection, and refinement results are included in Table I, along with previous results<sup>4</sup> for the cobalt complex in square brackets.

No explanation is apparent for the large discrepancy in cell dimensions in the two studies of the cobalt(III) complex. Our instrument was calibrated with an Enraf-Nonius ammonium hydrogen tartrate standard crystal.

For each complex a set of three dimensional intensity data was collected on an Enraf-Nonius CAD4 diffractometer. The integrated intensities were corrected for background and directly reduced to a set of relative squared structure amplitudes by the application of the standard of Lp factors. Individual estimated standard deviations ( $\sigma$  counting) were derived based on counting statistics. Three standard reflections

TABLE I  
Crystal Data, Data Collection, and Refinement Parameters for [Rh(PreH)Cl<sub>2</sub>] and [Co(PreH)Cl<sub>2</sub>]

	Rh(PreH)Cl <sub>2</sub>	Co(PreH)Cl <sub>2</sub>
formula	RhCl <sub>2</sub> O <sub>2</sub> N <sub>4</sub> C <sub>11</sub> H <sub>19</sub>	CoCl <sub>2</sub> O <sub>2</sub> N <sub>4</sub> C <sub>11</sub> H <sub>19</sub>
formula weight	413.11	396.14
space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> , Å	9.952(3)	9.846(1) [9.900(6)]
<i>b</i> , Å	13.751(2)	13.748(5) [13.812(17)]
<i>c</i> , Å	11.780(3)	11.648(2) [11.702(10)]
$\beta$ , degrees	96.43(3)	95.46(1) [95.47(6)]
<i>Z</i>	4	4
<i>D<sub>m</sub></i> , g/cm <sup>3</sup>	1.72(1)	1.55(1) [1.55]
<i>D<sub>c</sub></i> , g/cm <sup>3</sup>	1.713(2)	1.562(2) [1.539]
crystal size, mm	0.30 x 0.26 x 0.13	0.2 x 0.2 x 0.1
$\nu$ , MoK $\alpha$ (Å)	0.7107	0.7107
monochromator	graphite	graphite
$\mu$ , cm <sup>-1</sup>	13.8	14.8
absorption correction	empirical ( $\psi$ scans)	none (estimated range of transmission about 2% based on $\psi$ scans)
scan method	$\theta-2\theta$	$\theta-2\theta$
scan range, $\theta$ (deg)	0.70 + 0.35tan $\theta$	0.65 + 0.35tan $\theta$
scan speed	variable to obtain 3% counting	variable to obtain 3% counting
	statistics to a maximum scan time of	statistics to a maximum scan time of
	60 sec	90 sec
No. of refl. measured	3122	3032 [3590]
No. of indep. refl.	2815	2463
No. of refl. above 2 $\sigma$	2435	1643 [1754]
No. of variables	239	239
$R = \Sigma   F_o  -  F_c   / \Sigma F_o$	0.027	0.042[0.043]
$wR = [\Sigma w( F_o  -  F_c )^2 / \Sigma wF_o^2]^{1/2}$	0.048	0.049
maximum shift/error on last cycle	0.15	0.16

measured after every 7200 seconds of X-ray exposure showed no systematic variation with time. The data sets verify the isomorphism of the two compounds.

The structure of the cobalt complex was solved by Patterson and Fourier methods. Initially, hydrogen atoms were placed in "ideal" C-H positions (C-H = 0.95 Å and with idealized angles) but consistent with difference Fourier positions. The hydrogen bond hydrogen atom was also located on a difference Fourier map in a slightly asymmetric position. For the rhodium complex the starting parameters for the nonhydrogen atoms were taken from the refined cobalt structure, and hydrogen atoms were located from a difference Fourier synthesis with the hydrogen bond hydrogen found in a very asymmetric position. Full-matrix least-squares refinement for each structure minimized the function  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma^2(F_o)$ ,  $\sigma(F_o) = \sigma(F_o^2)/2F_o$ ,  $\sigma(F_o^2) = [\sigma^2_{\text{counting}} + (pF_o)^2]^{1/2}$ ,  $p = 0.05$  for Co, and  $p = 0.03$  for Rh. Hydrogen atoms were refined with fixed isotropic temperature factors ( $B = 5\text{Å}^2$ ). Only the data above  $2\sigma$  were used in the least squares refinements and agreement factor calculations. The final error in observation of unit weight was 1.23(1.96 for Rh). A final difference Fourier synthesis revealed no residual density greater than  $0.54\text{e}/\text{Å}^3$  ( $0.65$  for Rh).

The atomic positional parameters for the Co and Rh complex are included as Table II and III respectively. Hydrogen parameters, anisotropic thermal parameters, and tables of  $F_o$  and  $F_c$  are available as supplemental material from the Editor upon request.

TABLE II  
Atomic Positional Parameters for [Co(PreH)Cl<sub>2</sub>]

Atom	X	Y	Z	Atom	X	Y	Z
CO	0.11961(6)	-0.22925(5)	0.14240(6)	C(1)	0.0929(5)	-0.2770(4)	0.3643(4)
CL(1)	0.3356(1)	-0.2818(1)	0.1735(1)	C(2)	0.1219(5)	-0.2918(4)	-0.0909(5)
CL(2)	-0.0982(1)	-0.1815(1)	0.1125(1)	C(3)	0.1314(5)	-0.1760(4)	0.3671(4)
O(1)	0.0266(4)	-0.4024(3)	0.2411(3)	C(4)	0.1628(5)	-0.1899(4)	-0.0904(4)
O(2)	0.0522(4)	-0.4111(3)	0.0344(4)	C(5)	0.0513(6)	-0.3337(5)	0.4679(5)
N(1)	0.0709(4)	-0.3122(3)	0.2612(4)	C(6)	0.1161(7)	-0.3573(5)	-0.1822(5)
N(2)	0.0919(4)	-0.3186(3)	0.0199(4)	C(7)	0.1551(8)	-0.1231(5)	0.4786(5)
N(3)	0.1512(4)	-0.1405(3)	0.2692(4)	C(8)	0.1948(6)	-0.1437(5)	-0.1906(5)
N(4)	0.1687(4)	-0.1478(3)	0.0185(3)	C(9)	0.2012(6)	-0.0414(4)	0.2527(5)
				C(10)	0.2154(5)	-0.0472(4)	0.0372(5)
				C(11)	0.1555(6)	0.0003(4)	0.1363(5)

TABLE III  
Atomic Positional Parameters for [Rh(PreH)Cl<sub>2</sub>]

Atom	X	Y	Z	Atom	X	Y	Z
RH	0.12062(3)	-0.23282(2)	0.13542(3)	C(1)	0.0765(4)	-0.2837(3)	0.3588(4)
CL(1)	0.3440(1)	-0.28664(9)	0.1708(1)	C(2)	0.1250(5)	-0.2906(3)	-0.0957(4)
CL(2)	-0.1044(1)	-0.18299(9)	0.1015(1)	C(3)	0.1269(5)	-0.1820(3)	0.3656(4)
O(1)	0.0284(3)	-0.4087(2)	0.2313(3)	C(4)	0.1677(4)	-0.1862(3)	-0.0899(4)
O(2)	0.0574(4)	-0.4151(2)	0.0126(3)	C(5)	0.0448(5)	-0.3402(4)	0.4601(4)
N(1)	0.0692(3)	-0.3199(3)	0.2568(3)	C(6)	0.1261(6)	-0.3532(4)	-0.1977(4)
N(2)	0.0968(4)	-0.3210(3)	0.0022(3)	C(7)	0.1421(6)	-0.1316(4)	0.4767(4)
N(3)	0.1499(4)	-0.1444(3)	0.2699(3)	C(8)	0.1980(5)	-0.1379(4)	-0.1978(4)
N(4)	0.1717(3)	-0.1468(3)	0.0077(3)	C(9)	0.2012(6)	-0.0459(3)	0.2542(4)
				C(10)	0.2185(5)	-0.0469(3)	0.0360(4)
				C(11)	0.1558(4)	-0.0043(3)	0.1366(4)

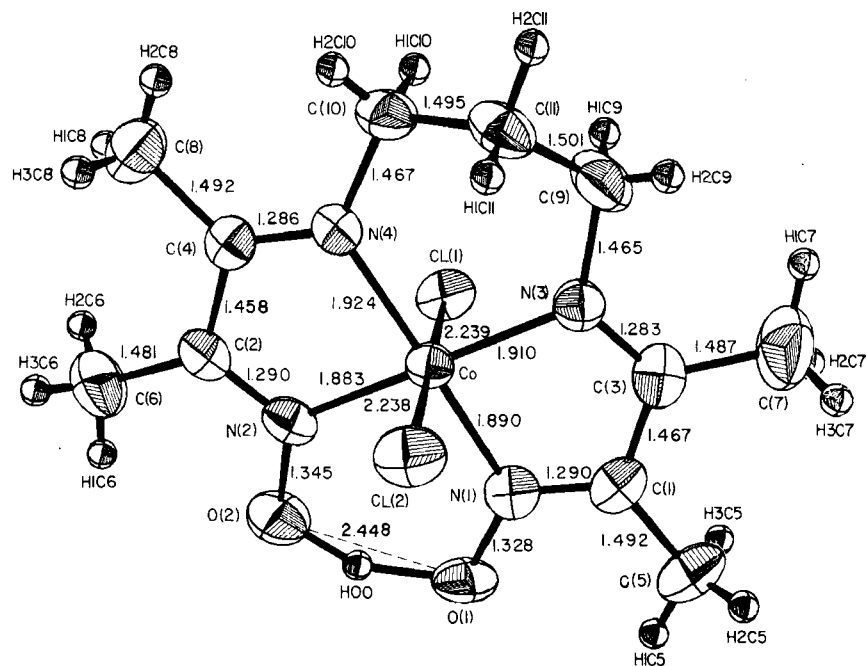


FIGURE 1 Perspective view of  $[\text{Co}(\text{PreH})\text{Cl}_2]$  showing thermal ellipsoids (50% probability), atom labelling, and bond distances. Standard deviations are Co-Cl, 0.001Å; Co-N, 0.004Å, N-O, C-N, C-C, and O-O, 0.005-0.009Å.

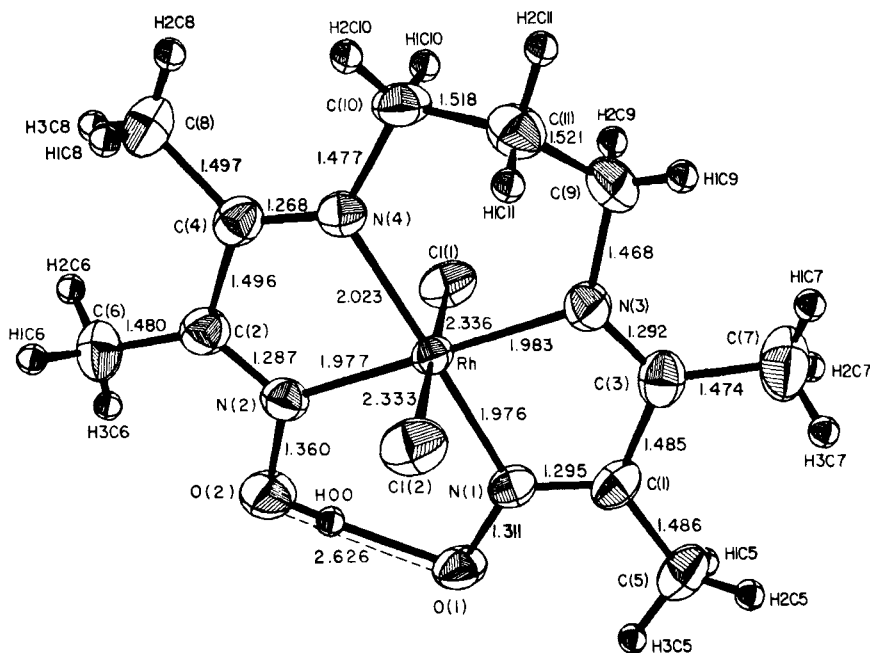
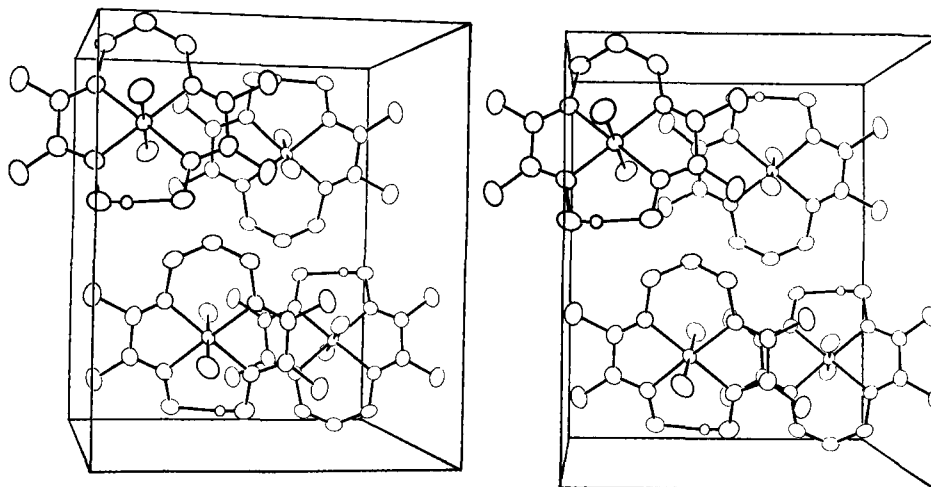


FIGURE 2 Perspective view of  $[\text{Rh}(\text{PreH})\text{Cl}_2]$  showing thermal ellipsoids (50% probability), atom labelling, and bond distances. Standard deviations are Rh-Cl, 0.001Å; Rh-N, 0.002-0.003Å; N-O, C-N, C-C, and O-O, 0.004-0.006Å.

FIGURE 3 Stereoscopic view of the unit cell of  $[\text{Rh}(\text{PreH})\text{Cl}_2]$ .

## RESULTS AND DISCUSSION

The bond distances and orientations of the ellipsoids are shown in Figure 1 (Co) and Figure 2 (Rh). The central metal atom in each complex is coordinated to four nitrogen atoms of the imineoxime ligands and two *trans* chloro ligands, resulting in distorted octahedral geometry. A stereoscopic view of the unit cell is shown in Figure 3. All intermolecular distances (ignoring hydrogens) under  $3.8 \text{ \AA}$  are compared in Table IV. A short intermolecular O(2)-O(2) distance ( $2.743(7)$  in Co and  $2.630(5) \text{ \AA}$  in Rh) is observed as in the earlier study.<sup>4</sup>

TABLE IV  
Intermolecular Contacts Less Than  $3.8 \text{ \AA}$  in  $[\text{Co}(\text{PreH})\text{Cl}_2]$ 

Distance	Value, $\text{\AA}$	Distance	Value, $\text{\AA}$
O(2)-O(2)	2.743(7)	Cl(1)-C(5)	3.703(7)
O(1)-C(9)	3.288(8)	Cl(1)-C(9)	3.708(6)
O(1)-C(8)	3.493(8)	Cl(2)-C(10)	3.725(6)
O(1)-C(11)	3.575(7)	C(5)-C(10)	3.730(9)
Cl(1)-C(6)	3.630(8)	Cl(1)-C(11)	3.731(6)
O(1)-C(6)	3.630(8)	O(2)-C(9)	3.757(7)
Cl(2)-C(5)	3.700(7)		

Intermolecular Contacts Less than  $3.8 \text{ \AA}$  in  $[\text{Rh}(\text{PreH})\text{Cl}_2]$ 

Distance	Value, $\text{\AA}$	Distance	Value, $\text{\AA}$
O(2)-O(2)	2.603(5)	Cl(1)-C(9)	3.712(4)
O(1)-C(9)	3.275(5)	C(5)-C(8)	3.740(7)
O(1)-C(8)	3.534(5)	C(4)-C(5)	3.751(5)
O(1)-C(11)	3.596(5)	Cl(1)-C(11)	3.755(4)
Cl(1)-C(6)	3.606(5)	Cl(2)-C(7)	3.766(5)
O(1)-C(6)	3.620(5)	O(1)-O(2)	3.782(4)
Cl(2)-C(10)	3.673(4)	Cl(1)-C(5)	3.783(4)
C(5)-C(10)	3.688(6)	C(5)-C(10)	3.796(6)
Cl(2)-C(5)	3.709(4)	Cl(2)-C(11)	3.799(4)

In  $[\text{Co}(\text{PreH})\text{Cl}_2]$  the cobalt atom and the four nitrogen atoms of the tetradentate ligand are planar within  $-0.020(4)\text{\AA}$  (N(2) and N(3)). All carbon atoms are on the C1(1) side of the cobalt-nitrogen plane ( $-0.02(1)$  to  $-0.24(1)\text{\AA}$ ) except C(11) which is  $0.650(6)\text{\AA}$  on the other side of the plane. The oxime oxygen atoms are on opposite sides of the plane ( $0.042(4)$  and  $-0.058(4)\text{\AA}$ ). These observations are in excellent agreement with the earlier study.<sup>4</sup> The hydrogen bonded hydrogen (HOO) atom is  $0.15(5)\text{\AA}$  from the plane defined by the cobalt, oxime-nitrogen, and oxime-oxygen atoms. The rhodium complex shows an almost identical arrangement with C(11)  $0.623(5)\text{\AA}$  out of the rhodium-nitrogen plane, N(2) and N(3) ( $-0.020(4)\text{\AA}$ ) from that plane, and O(1) and O(2) at  $0.037(3)$  and  $-0.054(3)\text{\AA}$ .

The intramolecular bond angles are shown in Table V. Bond distances and angles involving hydrogen atoms are deposited. The two Rh-Cl bond distances ( $2.336(1)$  and  $2.333(1)\text{\AA}$ ) are probably not significantly different, and the Co-Cl distances ( $2.239(1)$  and  $2.238(1)\text{\AA}$ ) are definitely equal. The values can be compared with Rh-Cl =  $2.329(1)\text{\AA}$  in  $[\text{Rh}(\text{AO})_2\text{-HCl}_2]^3$  and with Co-Cl =  $2.2588(8)\text{\AA}$  in  $[\text{Co}(\text{AO})_2\text{-HCl}_2]^1$ .

In  $[\text{Co}(\text{PreH})\text{Cl}_2]$  the average M-N(oxime) bond length  $1.887(4)\text{\AA}$  (Table VI) is significantly shorter ( $0.03\text{\AA}$ ) than the M-N(imine) bond  $1.917(4)\text{\AA}$  while in the Co(III) complexes of  $\text{AO}^1$  and  $\text{PnAO}^2$ , all M-N(Oxime) distances are  $0.056\text{--}0.077\text{\AA}$  shorter than the M-N(amine) distances irrespective of the steric requirements of the ligand. The shortening of the Co-N(imine) bond compared with the Co-N(amine) distance is undoubtedly related to multiple bonding at the  $\text{sp}^2$  imine nitrogen atom in the PreH ligand. Delocalization to some extent is present throughout the five-membered chelate ring. The same observations apply to  $[\text{Rh}(\text{PreH})\text{Cl}_2]$ , but because of the increased size of the metal, the M-N bonds are lengthened by about  $0.10\text{\AA}$ . In  $[\text{Ni}(\text{PnAO})\text{-7HNO}_2]^8$  (an oxidized form of the PnAO complex of  $\text{Ni}^{2+}$ ), the Ni-N(amine) bond is shorter than the Ni-N(oxime) distance by  $0.013\text{\AA}$ , and this was attributed to aromaticity in the six-membered oxidized chelate ring which includes the metal atom. The Co-N(oxime) distance is very constant among the AO complex ( $1.891(2)\text{\AA}$ )<sup>1</sup>, the PnAO complex ( $1.900(3)\text{\AA}$ )<sup>2</sup>, the DMG complex<sup>9</sup> ( $1.884(1)\text{\AA}$ ), and the present PreH complex ( $1.887(4)\text{\AA}$ ).

The C-C and C-N bond distances are normal. The Co complex, however, shows more delocalization of multiple bonding in the five-membered chelate rings resulting

TABLE V  
Comparison of Bond Angles in  $[\text{Co}(\text{PreH})\text{Cl}_2]$  and  $[\text{Rh}(\text{PreH})\text{Cl}_2]$ , in degrees

Cl(1)-M-Cl(2)	178.47(6)	178.52(3)	M-N(3)-C(3)	114.7(4)	115.5(2)
Cl(1)-M-N(1)	89.6(1)	89.84(8)	M-N(3)-C(9)	122.1(4)	119.5(2)
Cl(1)-M-N(2)	89.0(1)	88.53(8)	C(3)-N(3)-C(9)	123.1(5)	124.8(3)
Cl(1)-M-N(3)	98.9(1)	90.30(8)	M-N(4)-C(4)	114.7(3)	116.1(2)
Cl(1)-M-N(4)	90.2(1)	90.25(7)	M-N(4)-C(10)	122.3(3)	118.4(2)
Cl(2)-M-N(1)	89.1(1)	88.89(8)	C(4)-N(4)-C(10)	123.0(4)	125.4(3)
Cl(2)-M-N(2)	90.3(1)	90.96(8)	N(1)-C(1)-C(3)	112.1(4)	113.3(3)
Cl(2)-M-N(3)	90.9(1)	90.22(8)	N(1)-C(1)-C(5)	123.2(6)	123.3(3)
Cl(2)-M-N(4)	91.0(1)	91.00(7)	C(3)-C(1)-C(5)	124.7(3)	123.3(3)
N(1)-M-N(2)	97.6(2)	100.7(1)	N(2)-C(2)-C(4)	111.0(4)	111.1(3)
N(1)-M-N(3)	81.8(2)	79.8(1)	N(2)-C(2)-C(6)	123.8(5)	124.1(3)
N(1)-M-N(4)	178.4(2)	178.3(1)	C(4)-C(2)-C(6)	125.2(5)	124.5(3)
N(2)-M-N(3)	178.6(2)	178.7(1)	N(3)-C(3)-C(1)	114.6(4)	114.8(3)
N(2)-M-N(4)	80.8(2)	77.7(1)	N(3)-C(3)-C(7)	125.0(6)	125.7(4)
N(3)-M-N(4)	99.6(2)	101.9(1)	C(1)-C(3)-C(7)	120.4(5)	119.4(3)
M-N(1)-O(1)	122.4(3)	119.8(2)	N(4)-C(4)-C(2)	115.1(4)	115.6(3)
M-N(1)-C(1)	116.6(4)	116.5(2)	N(4)-C(4)-C(8)	125.7(5)	126.3(3)
O(1)-N(1)-C(1)	121.0(4)	123.6(3)	C(2)-C(4)-C(8)	119.2(5)	118.1(3)
M-N(2)-O(2)	123.0(3)	121.5(2)	N(3)-C(9)-C(11)	113.0(5)	112.4(3)
M-N(2)-C(2)	118.3(4)	119.6(2)	N(4)-C(10)-C(11)	112.6(4)	112.9(3)
O(2)-N(2)-C(2)	118.6(4)	118.9(3)	C(9)-C(11)-C(10)	115.1(5)	117.4(3)

TABLE VI  
Comparison of average bond distances and angles in related compounds.

Compound	O...O (Å)	M-N(oxime) (Å)	M-N(amine) (Å)	N(oxime)-M- N(amine) (deg)	N(oxime)- M-N(oxime) (deg)	N(amine)-M- N(amine) (deg)	Ref.
Co(AO) <sub>2</sub> (H)Cl <sub>2</sub>	2.422(3)	1.891(2)	1.947(2)	82.53(8)	99.0(1)	95.8(1)	1
Co(PnAO-H)(NO <sub>2</sub> ) <sub>2</sub>	2.432(3)	1.900(3)	1.977(3)	82.1(1)	98.6(1)	97.1(1)	2
Co(PreH)Cl <sub>3</sub>	2.449(5)	1.887(4)	1.917(4)	81.3(2)	97.6(2)	99.6(2)	this work
Rh(AO) <sub>2</sub> (H)Cl <sub>2</sub>	2.459(2)	1.990(1)	2.072(1)	80.23(4)	98.2(4)	101.2(4)	3
Rh(PnAO-H)Cl <sub>3</sub>	2.474(7)	1.987(5)	2.060(6)	80.3(3)	98.9(2)	100.3(3)	3
Rh(PreH)Cl <sub>3</sub>	2.626(4)	1.977(3)	2.003(3)	78.8(1)	100.7(1)	101.9(1)	this work

in a shortening of the C-C distances (av. 1.462(5)Å) compared with 1.490(6)Å in the Rh complex. Both of these values are significantly shorter than those observed in the PnAO complexes (1.512(4)Å for Co and 1.517(10)Å for Rh). The C-N(oxime) distances (av. 1.291(2)Å) and C-N(imine) distances (av. 1.282(7)Å) are very close to the values expected for a C-N double bond (1.287Å).<sup>10</sup>

An intramolecular O(1)-O(2) hydrogen bond distance of 2.448(5)Å is observed for [Co(PreH)Cl<sub>2</sub>]. This is similar to that observed for [CH<sub>3</sub>Co(PreH)(H<sub>2</sub>O)]ClO<sub>4</sub>.<sup>11</sup>



TABLE VII  
Comparison of Bond Distances for the two Determinations of  $[\text{Co}(\text{PreH})\text{Cl}_2]$

Bond	Value(Å)*	Bond	Value(Å)*
Co-Cl(1)	2.238(1)[2.242(2)]	N(3)-C(3)	1.283(6)[1.289(9)]
Co-Cl(2)	2.239(1)[2.236(2)]	N(4)-C(4)	1.286(6)[1.289(8)]
Co-N(1)	1.890(4)[1.891(6)]	N(3)-C(9)	1.465(7)[1.470(9)]
Co-N(2)	1.883(4)[1.892(6)]	N(4)-C(10)	1.467(7)[1.463(9)]
Co-N(3)	1.910(4)[1.915(6)]	C(9)-C(11)	1.501(9)[1.496(11)]
Co-N(4)	1.924(4)[1.921(6)]	C(10)-C(11)	1.495(9)[1.512(11)]
N(1)-O(1)	1.328(5)[1.317(7)]	C(1)-C(5)	1.492(9)[1.488(11)]
N(2)-O(2)	1.345(5)[1.344(7)]	C(2)-C(6)	1.481(9)[1.473(11)]
N(1)-C(1)	1.290(7)[1.307(9)]	C(3)-C(7)	1.487(9)[1.497(11)]
N(2)-C(2)	1.290(7)[1.285(9)]	C(4)-C(8)	1.492(9)[1.472(11)]
C(1)-C(3)	1.467(8)[1.457(10)]	O(1)-HOO	1.31(6)[1.40(10)]
C(2)-C(4)	1.458(8)[1.473(10)]	O(2)-HOO	1.20(6)[1.07(10)]

The values in square brackets are from the previous study<sup>4</sup> but using our cell dimensions.

(2.39(2)Å) and for  $[\text{Co}(\text{PreH})(\text{CH}_3)_2]^{12}$  (2.461(8)Å). The hydrogen bonded hydrogen appears to be nearly symmetrically disposed between the oxygen atoms with O(1)-HOO = 1.31(6)Å, O(2)-HOO = 1.20(6) Å, and O(1)-HOO-O(2) = 15(5)° (the earlier study<sup>4</sup> reported distances of 1.08(10)Å and 1.40(10)Å for the two O-H distances). The observed O---O distance is only slightly longer than in the less constrained  $[\text{Co}(\text{AO})_2\text{-H}]\text{Cl}_2$  complex (2.422(3)Å)<sup>1</sup> and the  $[\text{Co}(\text{PnAO-H})(\text{NO}_2)_2]$  complex (2.432(3)Å).<sup>2</sup> These observations for the Co complexes are in marked contrast with the observations for those containing the larger Rh(III) ion in which the AO and PnAO complexes<sup>3</sup> show nearly identical values (2.459(2) and 2.474(7)Å respectively). These are near the values observed for all the Co complexes, while the present PreH complex gives an O---O distance of 2.626(4)Å. The elongation of 0.180Å in going from the CoPreH complex to the RhPreH complex is a result of the larger Rh ion in the constrained geometry of the PreH tetradentate ligand. This can be seen in the N-M-N angles in Table VI where, for example, all other complexes have nearly identical N(oxime)-M-N(oxime) angles of 98.5(5)° while that in RhPreH opens to 100.7(1)°. The hydrogen atom lies asymmetrically between the oxygen atoms with O(1)-HOO = 1.75(4)Å, O(2)-HOO = 0.88(4)Å, and O(1)-HOO-O(2) = 174(5)°. As might be expected with a hydrogen bond this long, one of these is essentially a covalent O-H bond and the other is much weaker.

In Table VII the bond distances in the Co complex are compared with those from the earlier study calculated with the cell dimensions from this study. The agreement is in general quite good whereas before equalizing cell dimensions the differences were as large as 0.016Å (e.g., Co-Cl(1), 2.238(1)[2.254(2)Å]).

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