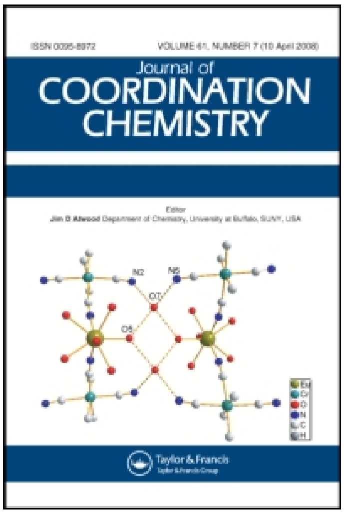

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PREPARATION, CHARACTERIZATION AND CRYSTAL STRUCTURES OF TWO AMINE-OXIME RHODIUM COMPLEXES

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PREPARATION, CHARACTERIZATION AND CRYSTAL STRUCTURES OF TWO AMINE-OXIME RHODIUM COMPLEXES

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Two amine-oxime complexes of rhodium(III) have been synthesized and structurally characterized as model compounds for a study of potential rhodium radiopharmaceuticals. Dichlorobis (2-acetylpyridineoxime)-rhodium(III) crystallizes in space group Pnma with $a = 13.462(4)$, $b = 12.496(2)$, $c = 9.661(2)$Å, $Z = 4$, $D_x = 1.819(2)$g/cm^3. The chloro ligands are *trans* (av Rh—Cl = 2.337(2)Å) in the octahedral Rh(III) complex. The oxime oxygens are involved in a short intramolecular hydrogen bond (O---O = 2.446(4)Å) with the hydrogen atom as well as the rhodium and two chlorine atoms on the mirror. Dichloro-[4,4′-(1,2-ethanediyldiimino)bis(4-methyl-2-pentanone-dioxime)]rhodium (III) crystallizes in space group $P2_12_12_1$ with $a = 14.435(3)$, $b = 7.638(9)$, $c = 16.596(3)$Å, $Z = 4$, $D_x = 1.667(2)$g/cm^3. The *trans* dichoro octahedral complex (av Rh—↓⧧ = 2.341(11)Å) has *cis* amine nitrogens (av Rh—N = 2.079(3)Å) and *cis* oxime nitrogens (av Rh—N = 2.030(3)Å). The oxime oxygen atoms are involved in a short intramolecular hydrogen bond (O---O = 2.423(3)Å). Synthesis and proton magnetic resonance results are included, along with a comparison with other rhodium(III) amine-oxime complex structures.

Keywords: rhodium, oxime, amine, multidentates, structures

INTRODUCTION

We are presently developing chelating ligands with additional functional groups as side chains for potential attachment to biological molecules for possible medical applications. In the course of this development of bifunctional chelates of Rh(III) as potential radiopharmaceuticals, we have prepared and characterized a bidentate oxime-aromatic amine rhodium(III) complex and a tetradentate aliphatic β-amine oxime complex. These are prepared and studied for comparison with earlier studies of bidentate and tetradentate aliphatic α-amine oxime complexes[1,2] and to serve as model complexes for the proposed radiopharmaceuticals which will be based on complexes of this type with appropriate functionalized side chains. To our knowledge these are the first reported structures of mononuclear metal complexes for each of these ligands. A dinuclear Cu(II) complex of the tetradentate ligand has been reported.[3]

EXPERIMENTAL

Preparation of Ligands

The ketone 4,4,9,9-tetramethyl-5,8-diazadodecan-2,11-dione was prepared as the diperchlorate salt.[4] The dioxime was prepared by dissolving about 1 gram of hydroxylamine hydrochloride in 3 cm^3 of H_2O. Then 2 cm^3 of 20% NaOH and 0.2 g of the diketone were added. The mixture was warmed on the steam bath for 10 minutes while adding NaOH solution dropwise to pH 9-10. The oxime crystallized immediately and was recrystallized from ethanol. The literature[5] and observed melting points of the oxime (H_2dddO) were 160–161.5°C.

The ligand 2-acetylpyridine oxime (PyAOH) was prepared as reported[6] and was recrystallized from ethanol.

Preparation of the Rhodium Complexes

(1) [Rh(HdddO)Cl_2]

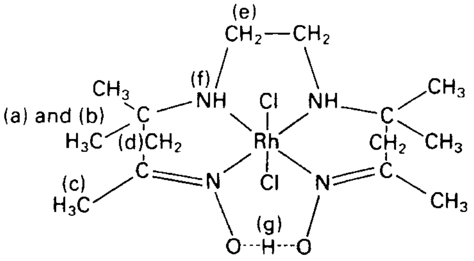
The complex was prepared using a procedure similar to that used for the tetradentate α-amine complex, [Rh(PnAO–H)Cl_2].[1] A solution of rhodium trichloride trihydrate (0.1417 g, 0.55 mmoles in 1.25 cm^3 of H_2O) was heated with an ethanolic solution of H_2dddO (0.1670 g, 0.62 mmoles in 2.5 cm^3 of ethanol) under reflux for about three hours. The pH at this point was about 2. A solution of KOH was added (0.724 M, 0.90 cm^3, 0.65 mmoles) to give a neutral pH. The solution was warmed and stirred for 45 minutes and filtered warm. A yellow-orange precipitate formed on cooling which was recrystallized from DMSO to obtain X-ray quality crystals. The compound can also be recrystallized from nitromethane.

(2) [Rh(PyAO)(PyAOH)Cl_2]

To an aqueous solution of hydrated rhodium trichloride trihydrate (0.10 g, 0.38 mmoles in a minimum amount of water) was added an ethanolic solution of PyAOH (0.1144 g, 0.84 mmoles in a minimum amount of ethanol). The resulting solution had a pH of about 1.5–2.0. The solution was warmed for about 30 minutes with the color changing from reddish-brown to yellow. On cooling a yellow-orange precipitate formed and was recrystallized from DMSO.

Proton Nuclear Magnetic Resonance

Spectra of the complexes were obtained on a JEOL FX90Q Fourier transform NMR Spectrometer with TMS as an internal standard in d_6-DMSO. The spectra are summarized here [Rh(PyAO)(PyAOH)Cl_2], 2.62s, 6H; 7.72–7.76t, 2H; 8.11–8.16d, 2H; 8.27–8.33t, 2H; 9.42–9.46d, 2H; 19.41s, 1H. The first is the methyl resonance and the last is the strongly hydrogen bonded oxime hydrogen. Those from 7.72–9.46 are the pyridine protons with the 9.42–9.46 peaks assigned to the proton on C2, and on the basis of coupling constants the proton at C3 is observed at 7.72–7.76. The assignments are consistent with those for Py–CH=NOH.[7] [Rh(HdddO)Cl_2], (a) and (b) 1.19s, 6H and 1.34s, 6H; (c) 2.16s, 6H; (d) 2.85s, 4H; (e) 3.02, 4H; (f) 5.25s, 2H; (g) 19.65s, 1H. (a) and (b) are different because of ring puckering on coordination.



X-ray Diffraction

(1) [Rh(PyAO)(PyAOH)Cl$_2$]

The light-yellow orange parallelepiped-shaped crystal was obtained by cooling a saturated DMSO solution and was mounted in random orientation on an Enraf-Nonius CAD4 diffractometer. Twenty five reflections were located by automatic search of reciprocal space and recentred twice. These setting angles were used to obtain the cell dimensions which are included in Table I with other crystal data and structure solution and refinement parameters.

The intensities were collected with Mo$K\alpha$ radiation ($\lambda = 0.7107$Å) obtained from a graphite monochrometer. The data were collected at a rate to obtain 3% counting statistics to a maximum of 90 seconds. To check instrument and crystal stability, three standard reflections were recorded after every 7200s of X-ray exposure and showed no significant decay or fluctuation. Three orientation standard reflections were checked after every 300 reflections, and all 25 orientation reflections were recentered to obtain a new orientation matrix if necessary. Statistical analysis of the intensities gave better agreement with the centrosymmetric space group *Pnma* than the acentric space group $Pn2_1a$. Structure solution confirmed this choice. The data were reduced in the normal manner[1]; absorption correction was deemed unnecessary because of the small variation in ψ scan intensities ($< 2\%$). All calculations were done on a PDP11/34 or PDP11/24 computer using SDP programs.[8]

Structure solution was accomplished by Patterson and Fourier methods, and refinement was by full-matrix least-squares (nonhydrogen atoms anisotropic and

TABLE I
Crystal data for the complexes

	[Rh(PyAO)(PyAOH)Cl$_2$]	*Rh(HdddO)Cl$_2$]*
a(Å)	13.462(2)	14.435(3)
b(Å)	12.496(2)	7.638(10)
c(Å)	9.661(2)	16.596(3)
Z	4	4
d_x(g/cm^3)	1.819(2)	1.667(2)
d_m(g/cm^3)	1.81(1)	1.65(1)
empirical formula	$RhC_{14}H_{15}Cl_2N_4O_2$	$RhC_{14}H_{29}Cl_2N_4O_2$
GFW	445.1	459.2
μ(cm^{-1})	13.8	12.3
scan method	θ–2θ	θ–2θ
scan range (θ) (deg)	$0.7 + 0.35 \tan \theta$	$0.7 + 0.35 \tan \theta$
scan limits (2θ)(deg)	2–55°	4–48°
hkl range	hkl and $hk\bar{l}$($2\theta = 2 - 23°$) hkl(23–55°)	hkl and $\bar{h}kl$($2\theta = 4$–$40°$) hkl, $\bar{h}kl$, $\bar{h}\bar{k}\bar{l}$ and $h\bar{k}\bar{l}$ ($2\theta = 4$–$24°$)
number of reflections measured	1707	3194
number of independent reflections measured	1120	2390
number of above 2σ used in structure deter.	1006	2227
function minimized	$\Sigma w(\lvert F_0 \rvert - \lvert F_c \rvert)^2$	$\Sigma w(\lvert F_0 \rvert - \lvert F_c \rvert)^2$
w	$4F_o^2/(\sigma^2_{\text{counting}} + (0.04F_o^2))$	$4F_o^2/(\sigma^2_{\text{counting}} + (0.04F_o^2)$
R	0.020	0.034
wR	0.029	0.043
S	1.16	1.54
max shift error	0.01	0.15
max dif. density	0.30 e/Å^3	1.3e/Å

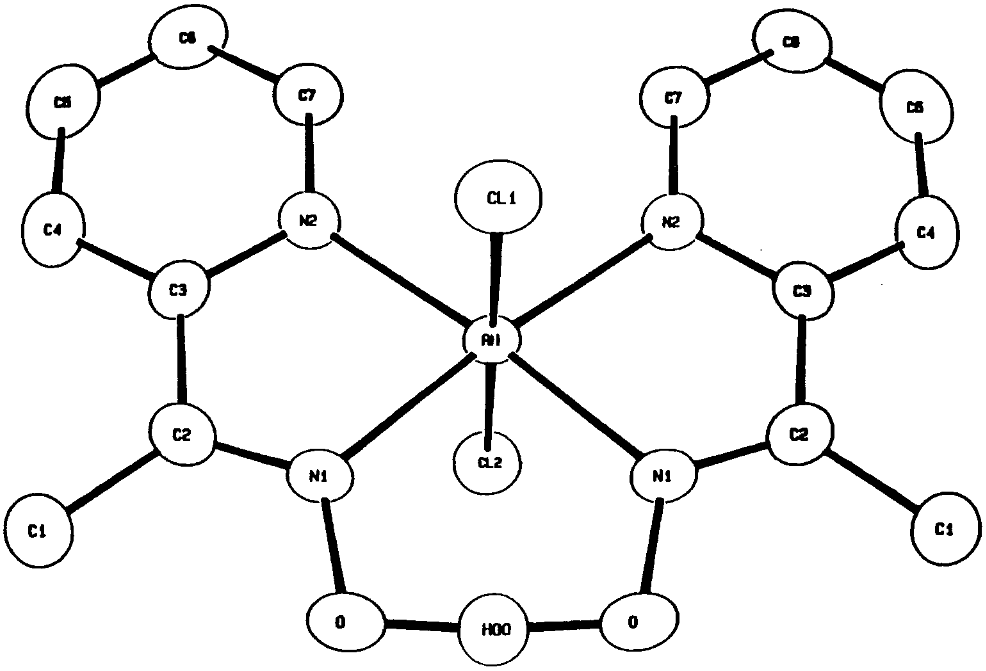


FIGURE 1 Perspective drawing of [Rh(PyAO)(PyAOH)Cl$_2$]

hydrogens isotropic). The chlorine atoms, the rhodium atom, and the hydrogen atom between the oxime oxygen atoms lie on the mirror plane.

The final positional parameters and isotropic equivalent parameters are included in Table II. The molecular structure is shown in Figure 1, and important bond distances and angles are given in Table III.

(2) [Rh(HdddO)Cl$_2$]

The light yellow-orange parallelepiped-shaped crystal was obtained on cooling of a saturated hot DMSO solution. Data collection, reduction, and structure solution

TABLE II
Positional parameters and their estimated standard deivations for [Rh(PyAO)(PyAOH)CL$_2$]

Atom	*x*	*y*	*z*	*B*(Å^2)
Rh	0.22791(2)	0.250	0.07739(3)	2.034(6)
Cl1	0.17145(7)	0.250	−0.1511(1)	3.19(2)
Cl2	0.29184(7)	0.250	0.3025(1)	3.22(2)
N1	0.3208(2)	0.1308(2)	0.0329(2)	2.43(4)
N2	0.1411(2)	0.1154(2)	0.1194(2)	2.45(4)
O	0.4126(1)	0.1521(2)	−0.0116(2)	3.48(4)
C1	0.3556(2)	−0.0613(2)	0.0174(3)	3.53(6)
C2	0.2929(2)	0.0330(3)	0.0491(3)	2.70(5)
C3	0.1915(2)	0.0221(2)	0.0994(3)	2.51(5)
C4	0.1467(2)	−0.0752(2)	0.1260(3)	3.58(6)
C5	0.0498(2)	−0.0791(3)	0.1700(3)	3.97(6)
C6	−0.0015(2)	0.0142(3)	0.1852(3)	3.59(6)
C7	0.0460(2)	0.1096(2)	0.1602(3)	3.21(6)

TABLE III

Bond distances in angstroms for [Rh(PyAO)(PyAOH)Cl_2]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Rh	Cl1	2.335(1)	N1	C2	1.289(4)	C4	C4	1.382(4)
Rh	Cl2	2.339(1)	N2	C3	1.363(4)	C4	C5	1.374(5)
Rh	N1	1.992(2)	N2	C7	1.341(4)	C5	C6	1.363(5)
Rh	N2	2.088(2)	C1	C2	1.481(4)	C6	C7	1.375(4)
N1	0	1.335(3)	C2	C3	1.455(5)			

Bond angles in degrees for [Rh(PyAO)(PyAOH)Cl_2]

Atom1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Cl1	Rh	Cl2	177.41(3)	0	N1	C2	119.9(2)	N2	C3	C2	115.8(2)
Cl1	Rh	N1	90.02(6)	Rh	N2	C3	112.5(2)	N2	C3	C4	120.6(3)
Cl1	Rh	N2	90.09(6)	Rh	N2	C7	129.4(2)	C2	C3	C4	123.7(3)
Cl2	Rh	N1	88.27(6)	C3	N2	C7	118.1(3)	C3	C4	C5	120.3(3)
Cl2	Rh	N2	91.44(6)	N1	C2	C1	124.3(3)	C4	C5	C6	119.0(4)
N1	Rh	N2	77.95(9)	N1	C2	C3	113.8(2)	C5	C6	C7	119.1(3)
Rh	N1	0	120.1(2)	C1	C2	C3	121.9(3)	N2	C7	C6	122.9(3)
Rh	N1	C2	120.0(2)								

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

were as above except as noted. ψ scans were used to apply an empirical absorption correction before averaging symmetry-equivalent data (transmission range 0.92–0.99). Systematic absences indicated space group $P2_12_12_1$.

In the least-squares refinement, hydrogen atoms were assigned fixed isotropic thermal parameters (4.0–5.0Å^2). The larger residuals in the final difference Fourier were within 1.2Å of the rhodium atom. The correct direction of the polar axis was obtained by refinement of both possibilities.

The final positional and isotropic equivalent thermal parameters for nonhydrogen atoms are in Table IV. The molecular structure is shown in Figure 2. The important bond distances and angles are given in Table V.

Supplemental material for both compounds includes hydrogen atom parameters, anisotropic thermal parameters, additional bond distances and angles, and F_0 and F_c values (x10) are available from the Editor on request.

RESULTS AND DISCUSSION

The crystal structure of [Rh(PyAO)(PyAOH)Cl$_2$] consists of discrete, distorted octahedral, neutral rhodium(III) complex molecules (Figure 1) with two chloro ligands in *trans* positions and four nitrogen atoms from the two PyAO ligands (oxime nitrogens *cis*) completing the coordination. The mirror symmetry makes the two bidentate ligands identical and the short O---O oxime hydrogen bond (2.446(4)Å) symmetric. The entire plane containing the Rh(III) ion and the two bidentate organic ligands is almost perfectly planar (max. deviation 0.085(3)Å for C4). The two Rh–Cl distances agree within 0.004Å, and all bond distances and angles are rather normal.

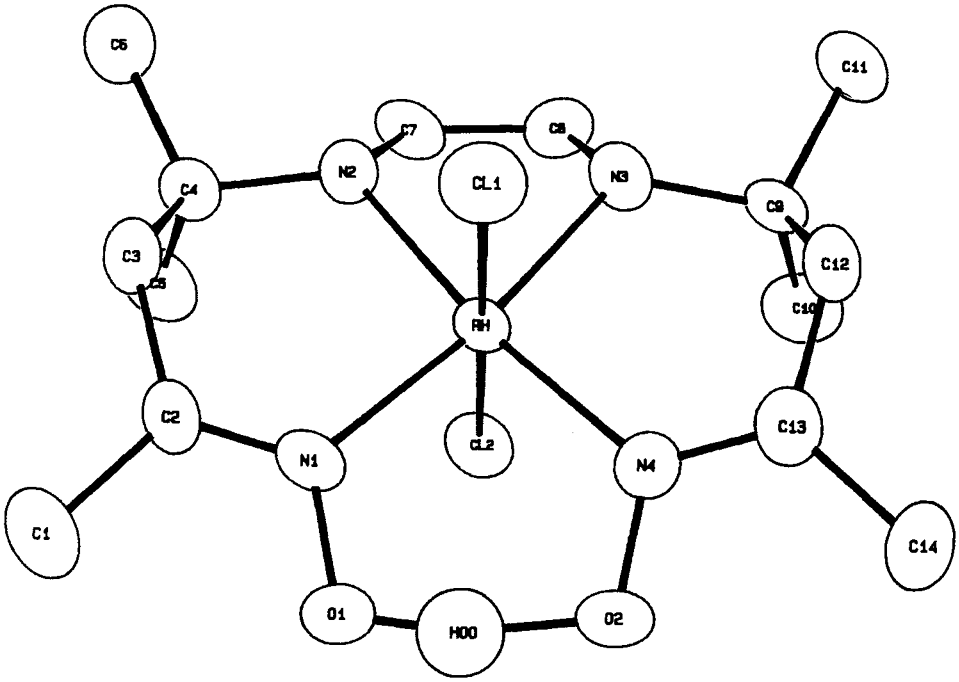


FIGURE 2 Perspective drawing of [Rh(HdddO)Cl$_2$]

TABLE IV
Positional parameters and their estimated standard deviations for $[\mathrm{Rh(HdddO)Cl_2}]$

Atom	*x*	*y*	*z*	$B(\mathrm{Å}^2)$
Rh	0.84974(3)	0.89992(6)	0.87458(3)	1.974(7)
Cl1	0.9447(1)	0.7739(2)	0.7749(1)	3.40(3)
Cl2	0.7551(1)	1.0149(2)	0.9750(1)	3.23(3)
O1	0.8253(3)	0.6016(6)	0.9836(3)	3.18(9)
O2	0.7059(3)	0.6292(5)	0.8818(3)	3.41(9)
N1	0.8901(4)	0.7162(6)	0.9561(3)	2.4(1)
N2	0.9577(4)	1.0693(7)	0.9021(3)	2.6(1)
N3	0.8258(4)	1.1092(7)	0.7969(3)	3.1(1)
N4	0.7409(4)	0.7579(7)	0.8335(3)	2.8(1)
C1	0.9882(5)	0.591(1)	1.0580(4)	4.1(2)
C2	0.9699(4)	0.7130(8)	0.9899(4)	2.5(1)
C3	1.0446(5)	0.8294(8)	0.9631(4)	2.8(1)
C4	1.0267(4)	1.0282(8)	0.9690(4)	2.7(1)
C5	0.9886(6)	1.0694(9)	1.0505(4)	4.0(2)
C6	1.1176(5)	1.125(1)	0.9530(5)	4.4(2)
C7	0.9234(5)	1.2504(8)	0.9011(4)	3.0(1)
C8	0.8488(5)	1.2741(9)	0.8378(4)	3.4(1)
C9	0.7403(4)	1.1107(9)	0.7449(4)	3.0(1)
C10	0.6539(6)	1.159(1)	0.7917(5)	4.8(2)
C11	0.7555(6)	1.239(1)	0.6750(5)	4.6(2)
C12	0.7329(5)	0.925(1)	0.7103(4)	3.4(1)
C13	0.6994(5)	0.7842(9)	0.7664(4)	3.3(1)
C14	0.6163(5)	0.681(1)	0.7423(5)	4.7(2)

Because of the bite of the ligand and the intramolecular O---O hydrogen bond the N—Rh—N angles deviate significantly from "ideal" 90° values (Table III). The parameters for the short hydrogen bond are O1— HOO = 1.225(4)Å, O1---HOO---O1 = 174°, and N1—O1—HOO = 104°. Comparison with other amine oxime complexes is given below.

The crystal structure of $(\mathrm{Rh(HdddO)Cl_2}]$ consists of discrete, slightly distorted, neutral octahedral rhodium(III) complex molecules (Figure 2) with *trans* chloro ligands and *cis* amine and *cis* oxime nitrogen atoms from the tetradentate *β*-amine oxime ligand. There are no unusually short intermolecular contacts; the shorter contacts are between methyl and methylene groups so there are no intermolecular hydrogen bonds. There is considerable puckering of the chelate rings but C4 and C9 are nearly in the Rh, 4N plane with their methyl carbon atoms on opposite sides of that plane. 01, 02, C8 and C7 are on Cl2 side of that plane while the amine hydrogen atoms, C2, C3, C12, and C13 are on the Cl1 side. These hydrogen atoms appear to be weakly intramolecularly hydrogen bonded to Cl1 (Cl1—N2 = 3.096(5)Å, Cl1—HN2 = 2.68Å, Cl1—N3 = 3.104(5)Å, Cl1—HN3 = 2.69A, Cl1---HN2—N2 = 109°, and Cl1---HN3—N3 = 109°). This is accompanied by a longer Rh—Cl1 (2.354(1)Å) than Rh—Cl2(2,328(1)Å) distance as might be expected. The 0---0(2.423(3)Å) hydrogen bond is quite short but slightly asymmetric with H00—01 = 1.08Å, H00—02 = 1.36Å, and O1---HOO---O2 = 165°.

The only other reported crystal structure[3] of a metal complex of HdddO is that of the dinuclear Cu(II) complex $[\mathrm{Cu(HddO)}]_2$ where each Cu(II) ion is in trigonal bipyramidal coordination with four nitrogen atoms from one HdddO ligand and an oxime oxygen atom from the other Hddd0 ligand. This oxygen atom occupies an equatorial position. The oxygen atoms of the oxime groups of each ligand are

TABLE V

Bond distances in angstroms for $[Rh(HdddO)Cl_2]$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Rh	Cl1	2.354(1)	N2	C4	1.525(7)	C4	C6	1.530(8)
Rh	Cl2	2.328(1)	N2	C7	1.469(7)	C7	C8	1.515(9)
Rh	N1	2.034(4)	N3	C8	1.469(7)	C9	C10	1.515(9)
Rh	N2	2.076(4)	N3	C9	1.507(7)	C9	C11	1.534(8)
Rh	N3	2.062(5)	N4	C13	1.280(7)	C9	C12	1.531(8)
Rh	N4	2.027(5)	C1	C2	1.487(8)	C12	C13	1.505(9)
01	N1	1.361(6)	C2	C3	1.466(9)	C13	C14	1.491(9)
02	N4	1.366(6)	C3	C4	1.544(8)			
N1	C2	1.282(6)	C4	C5	1.493(8)			

Bond angles in degress for $[Rh(HdddO)Cl_2]$

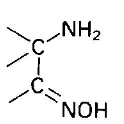
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Cl1	Rh	Cl2	178.01(6)	N1	Rh	N2	93.9(2)	Rh	N2	C4	121.5(3)
Cl1	Rh	N1	91.1(1)	N1	Rh	N3	171.4(2)	Rh	N2	C7	109.4(3)
Cl1	Rh	N2	88.4(1)	N1	Rh	N4	94.4(2)	C4	N2	C7	115.0(4)
Cl1	Rh	N3	88.6(1)	N2	Rh	N3	77.4(2)	Rh	N3	C8	109.5(3)
Cl1	Rh	N4	89.8(1)	N2	Rh	N4	171.5(2)	Rh	N3	C9	119.8(4)
Cl2	Rh	N1	87.3(1)	N3	Rh	N4	94.2(2)	C8	N3	C9	116.3(5)
Cl2	Rh	N2	92.7(1)	Rh	N1	O1	118.0(3)	Rh	N4	O2	118.4(3)
Cl2	Rh	N3	93.2(1)	Rh	N1	C2	124.2(4)	Rh	N4	C13	124.8(4)
Cl2	Rh	N4	89.3(1)	O1	N1	C2	117.3(4)	O2	N4	C13	116.7(5)
N1	C2	C1	120.3(5)	C3	C4	C6	108.7(5)	C10	C9	C11	110.6(5)
N1	C2	C3	121.1(6)	C5	C4	C6	111.8(5)	C10	C9	C12	111.1(6)
C1	C2	C3	118.6(5)	N2	C7	C8	111.1(5)	C11	C9	C12	108.5(5)
C2	C3	C4	117.0(5)	N3	C8	C7	112.3(5)	C9	C12	C12	117.0(5)
N2	C4	C3	105.4(4)	N3	C9	C10	112.5(5)	N4	C13	C12	120.1(5)
N2	C4	C5	112.1(5)	N3	C9	C11	108.7(5)	N4	C13	C14	121.8(6)
N2	C4	C6	109.5(4)	N3	C9	C12	105.3(5)	C12	C13	C14	118.3(5)
C3	C4	C5	109.1(5)								

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

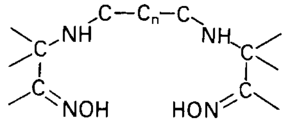
intramolecularly hydrogen bonded (O---O = 2.54(1)Å). That structure is similar to that observed for $[Cu_2(EnAO)_2](ClO_4)_2$ (see diagram of EnAO below) which has the four nitrogens and the oxime oxygen in square pyramidal coordination,[9] rather than trigonal bipyramidal coordination, around the Cu(II) ion.

The PMR spectra of the complexes are not unusual and show the usual down-field signal characteristic[1,2] of similar short O---O hydrogen bonds (19.7 ppm for $[Rh(HdddO)Cl_2]$ and 19.4 ppm for $[Rh(PyAO)(PyAOH)Cl_2]$) indicative of the highly deshielded symmetrical or nearly symmetrical nature of this hydrogen bond.

Previous amine-oxime rhodium(III) complex structures[1,2] were of the bidentate ligand AOH, $[Rh(AO)(AOH)Cl_2]$, the tetradentate ligand PnAOH, $[Rh(PnAO)Cl_2]$, and the bridging tetradentate ligand BnAOH$[Rh_2(BnAO)_2Cl_4]$, where each BnAO ligand bridges the two rhodium atoms through the amine nitrogen atoms to give a fourteen-membered $RH_2N_4C_8$ ring with short O---O intramolecular hydrogen bonds at both ends of the dinuclear complex. In addition, with EnAOH, a nonhydrogen bonded dinuclear complex was observed.[2]



AOH



EnAOH(n=0), PnAOH(n=1) and BnAOH(n=2)

The present structures are very similar to those of the AOH and PnAOH ligands.[1] The significant differences are as follows.

All four mononuclear complexes contain the short O---O hydrogen bond but there is a range of 0---0 distances from 2.423(3) to 2.474(7)Å. The order of increasing length is HdddO < PyAO < AO < PnAO, but all are longer than in the dinuclear BnAO complex (2.387(7)Å). The latter is among the shortest O---O hydrogen bonds reported.

The Rh—Cl bonds show little variation in the five complexes with average values from 2.331(1) to 2.341(1)Å, but there is a much wider variation in Rh—N distances. The Rh—N (oxime) distance in the mononuclear complexes ranges from 1.987(5) to 2.031(5)Å but only the HdddO complex has a distance significantly different from 1.99Å. Thus it appears that the oxime nitrogen of the β-amine oxime is more weakly bonded to Rh(III) than that of any of the α-amine oximes including the aromatic PyAO species. For the Rh—N (amine) bonds there is an indication of decreasing bonding strength from the aliphatic α-amine complexes (RhPnAO, 2.060(6)Å and RhAO, 2.072(1)Å) to the aliphatic β-amine oxime (RhHdddO, 2.079(5)Å) to the aromatic α-amine oxime (RhPyAO, 2.088(2)Å). Thus overall, based on bond lengths, the aliphatic α-amine oximes are most tightly bound, followed by the aromatic α-amine complex, and finally by the aliphatic β-amine oxime complex. The N—Rh—N angles can be rationalized in terms of chelate ring size, steric effects of the aromatic rings, and the strength of the O---O hydrogen bond.

In summary, all of these amine-oxime Rh(III) complexes appear to be good model complexes for the proposed bifunctional rhodium(III) complexes to be used as potential radiopharmaceuticals. Although no kinetic or thermodynamic properties were measured, the complexes appear to be quite stable and inert. In solution, heating to 60°C for approximately thirty minutes showed no significant decomposition, as indicated by the consistent colour of the solution. In the solid state the complexes seem to be stable indefinitely. We are currently designing similar ligands with functionalized side chains.

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