Inorg. Chem. **1983**, *22*, 282-286

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Dinuclear Rhodium(III) Complexes: Synthesis and Crystal and Molecular Structures of Two Amine–Oxime Complexes of Rhodium(III)

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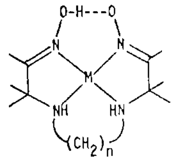
Received May 28, 1982

Dinuclear complexes are formed in the reaction of certain potentially tetradentate ligands with $RhCl_3$ in aqueous ethanol media. With the ligand 3,3′-(1,4-butanediyldiamino)bis(3-methyl-2-butanone) dioxime, the dinuclear complex (I) is bridged by the diamine portions of two ligands, forming a 14-membered heterocyclic ring containing both rhodium(III) atoms. In this complex very strong hydrogen bonds are formed between the two oxime oxygen atoms at each end of the complex (O---O = 2.387 (5) Å). Each rhodium has trans chloro ligands to complete the octahedral coordination. In contrast, with the ligand 3,3′-(1,2-ethanediyldiamino)bis(3-methyl-2-butanone) dioxime, the dinuclear complex (II) is bridged by two oxime groups from separate ligands and by a chloro ligand while the remainder of the octahedral coordination sphere of each rhodium atom is completed by two amine nitrogens and one oxime nitrogen of one of the organic ligands. No intramolecular hydrogen bond is present. Complex I crystallizes in monoclinic space group $P2_1/n$ (a = 8.223 (2) Å, b = 16.440 (2) Å, c = 14.209 (3) Å, β = 102.73 (2)°). There is a center of symmetry at the middle of the 14-membered heterocyclic ring. The structure of I was refined with 2417 observed data above 2σ to a final R of 0.036. Complex I crystallizes in monoclinic space group $C2/c$ (a = 20.813 (8) Å, b = 17.527 (8) Å, c = 13.484 (8) Å, β = 118.36 (5)°). There is a twofold axis passing through the bridging chloride ion. The structure of II was refined with 1710 observed data above 2σ to a final R of 0.036.

Introduction

Oxime and amine–oxime ligands are known to form stable complexes with Co(III).[1-3] A short intramolecular hydrogen bond between cis oxime groups is typical. As part of our continuing study of these hydrogen-bonded complexes, we are examining the effect of ligand steric effects, e.g., the number of bridging methylene groups in



as well as the effect of metal size. Toward this goal we have prepared a number of complexes of Co(III) and Rh(III) with variable numbers of methylene groups (n = 2–4) and have determined their molecular structures by X-ray diffraction. Herein we present the results on two of the rhodium complexes, which have unexpected dinuclear structures.

Experimental Section

Synthesis. Ligands. The ligands 3,3′-(1,2-ethanediyldiamino)-bis(3-methyl-2-butanone) dioxime (EnAO) and 3,3′-(1,4-butanediyldiamino)bis(3-methyl-2-butanone) dioxime, (BnAO) were prepared as described by Murmann.[4]

[Rh(EnAO-1.5H)Cl$_{1/2}$]$_2$Cl$_2$·11H$_2$O. To 1.45 mmol (0.381 g) of $RhCl_3 \cdot 3H_2O$ in 10 mL of water was added 1.77 mmol (0.520 g) of EnAO·HCl. This was followed by addition of 1 equiv of KOH. After 15 min of refluxing, another equivalent of KOH was added to the clear red solution. Refluxing continued for $2^1/_2$ h, giving an orange solution with a small amount of dark solid, which was removed by filtration. Yellow crystals of the desired product were then obtained by slow evaporation. The infrared spectrum showed bands characteristic of the ligand, e.g., C–H (~2950 cm^{-1}), N–H (~3150 cm^{-1}), and lower frequency bands, but no band characteristic of a short O–H–O hydrogen bond in the 1700–1800-cm^{-1} region.

[Rh(BnAO-H)Cl$_2$]$_2$. To an aqueous solution (10.0 mL) of $RhCl_3 \cdot 3H_2O$ (0.97 mmol) was added an ethanolic solution of BnAO (1.0 mmol). The resulting slurry was heated under reflux for $^1/_2$ h, at which point it was clear and orange. A 1.1-mmol quantity of KOH was added, yielding a lighter orange solution. After 45 min of stirring at reflux, the solution was filtered hot. After allowing half the solvent to evaporate over 3 weeks at room temperature, the solution was again warmed and yielded a yellow precipitate on cooling (~45% yield). This yellow solid was recrystallized from dimethyl sulfoxide to give the crystals for the X-ray determination. Important ^{1}H NMR chemical shifts (integration) were 1.2 (3), 1.4 (3), 2.1 (3), 2.5 (4), 4.35 (broad, ~1), and 19.5 (~0.5) ppm. These are relative to Me_4Si. The infrared spectrum had the normal C–H (~3000 cm^{-1}) and N–H (~3200 cm^{-1}) bands, numerous lower frequency ligand vibrations, and the characteristic broad, shallow O–H–O band at 1792 (5) cm^{-1}.

NMR Spectra. The spectra were recorded on a Varian EM-360 spectrometer with tetramethylsilane (Me_4Si) as an internal standard.

Infrared Spectra. Solid-state infrared spectra were measured on a Perkin-Elmer 180 spectrophotometer using Fluorolube mulls.

Collection and Reduction of X-ray Data. Diffraction data were collected at 22 (1) °C on an Enraf-Nonius CAD4 automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Lattice constants were measured by a least-squares fit of 25 carefully centered reflections on each compound. The intensities of three standard reflections measured after every 6000 s of X-ray exposure showed no significant variation. Orientation was checked after every 300 reflections with use of 3 orientation standards. Recentering, using 25 reflections, was done if any of the orientation standards was found to be significantly off center. A summary of cell data, data collection parameters, and refinement results is included in Table I.

Solution and Refinement of the Structures. Both structures were solved by conventional Patterson and Fourier methods. In each case only half of each dimer is symmetry independent. For compound I a center of symmetry is present at the middle of the 14-membered heterocyclic ring while compound II has a twofold axis passing through the bridging chloride ligand. The full-matrix least-squares refinement minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma^2(F_o^2) = \sigma_{\text{counting}}^2 + (0.03F_o^2)^2$. Atomic scattering factors were taken from ref 5 and included anomalous scattering contributions. Hydrogen atoms (no water hydrogen atoms) were included in fixed positions from difference Fourier syntheses or in chemically reasonable positions for compound II while for compound I their positional parameters were allowed to refine. The maximum electron density on both final difference Fourier syntheses was <0.9 e/Å^3 and was in the near vicinity of the rhodium atom position.

The final positional parameters for the non-hydrogen atoms are included in Tables II and III for compounds I and II, respectively.

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(2) Murmann, R. K.; Schlemper, E. O. *Inorg. Chem.* **1973**, *12*, 2625.
(3) Schlemper, E. O.; LaPlaca, S. J.; Davis, B. R.; Hamilton, W. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 918.
(4) (a) Vassain, E. G.; Murmann, R. K. *Inorg. Chem.* **1967**, *6*, 2043. (b) Murmann, R. K. *J. Am. Chem. Soc.* **1958**, *80*, 4174.
(5) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.

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Table I. Crystal Data, Data Collection Parameters, and Refinement Details for Compounds I and II

	I	II
formula	$(C_{14}H_{29}Cl_2N_4O_2Rh)_2$	$[(C_{12}H_{24.5}Cl_{1/2}N_4O_2)_2Rh_2]Cl_2 \cdot 11H_2O$
fw	918.44	1008.0
space group	$P2_1/n$	$C2/c$
a, Å	8.223 (2)	20.813 (8)
b, Å	16.440 (2)	17.527 (8)
c, Å	14.209 (3)	13.484 (8)
β, deg	102.73 (2)	118.36 (5)
V, Å^3	1873.6 (5)	4328 (1)
Z	2 dimers	4 dimers
D_{exptl}, g/cm^3	1.628	1.437
cryst size, mm	~0.13 × 0.16 × 0.30	~0.2 × 0.3 × 0.3
λ(Mo Kα), Å	0.7107	0.7107
monochromator	graphite	none (β filter)
μ, cm^{-1}	11.9	10.8
abs cor	none (est trans range 2% based on ψ scans)	none (est trans range 2% based on ψ scans)
scan method	θ–2θ step	θ–2θ step
scan range, θ, deg	$0.85 + 0.35 \tan\theta$	$0.65 + 0.35 \tan\theta$
scan speed	variable to obtain 3% counting statistics to a max scan time of 90 s	variable to obtain 3% counting statistics to a max scan time of 90 s
no. of reflctns measd	4941	5872
no. of indep reflctns	3293	2090
no. of reflectns above 2σ	2415	1710
no. of variables	296	236
$R(F) = \Sigma \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / \Sigma F_o$	0.036	0.036
$R_w(F) = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w F_o^2]^{1/2}$	0.047	0.051
max shift/error on last cycle	<0.20	<0.20

Table II. Atomic Positional Parameters[a] for Compound I

atom	x	y	z	atom	x	y	z
Rh	0.12414 (4)	−0.11581 (2)	0.27691 (3)	C(4)	−0.0156 (6)	−0.1915 (3)	0.4391 (4)
Cl(1)	−0.0524 (2)	−0.00531 (9)	0.2814 (1)	C(5)	0.1874 (7)	−0.0525 (4)	−0.0054 (4)
Cl(2)	0.3106 (2)	−0.22170 (9)	0.2735 (1)	C(6)	−0.2471 (7)	−0.2819 (4)	0.3310 (5)
O(1)	−0.0222 (5)	−0.1419 (2)	0.0736 (3)	C(7)	0.3036 (11)	0.0776 (4)	0.1500 (5)
O(2)	−0.1415 (5)	−0.2226 (3)	0.1807 (3)	C(8)	0.5030 (8)	−0.0383 (6)	0.1567 (5)
N(1)	0.0988 (5)	−0.1014 (2)	0.1349 (3)	C(9)	−0.1319 (7)	−0.1320 (4)	0.4739 (5)
N(2)	−0.0594 (5)	−0.1958 (3)	0.2682 (3)	C(10)	0.0235 (9)	−0.2624 (4)	0.5096 (5)
N(3)	0.3195 (5)	−0.0325 (3)	0.2724 (3)	C(11)	0.3647 (8)	0.0298 (3)	0.3482 (4)
N(4)	0.1386 (5)	−0.1500 (3)	0.4247 (3)	C(12)	0.5392 (8)	0.0524 (4)	0.3765 (4)
C(1)	0.1997 (6)	−0.0586 (3)	0.1001 (3)	C(13)	0.5981 (7)	0.1087 (4)	0.4509 (4)
C(2)	−0.1065 (6)	−0.2228 (3)	0.3425 (4)	C(14)	0.7799 (8)	0.1035 (4)	0.4900 (4)
C(3)	0.3327 (6)	−0.0126	0.1704				

[a] Estimated standard deviations from the least-squares refinement are included in parentheses in this and subsequent tables.

Table III. Atomic Positional Parameters for Compound II

atom	x	y	z	atom	x	y	z
Rh	0.06983 (2)	0.19146 (3)	−0.27616 (4)	N(4)	0.1727 (2)	0.1394 (3)	−0.2020 (4)
Cl(1)	0.0000 (0)	0.0940 (1)	−0.2500 (0)	C(1)	−0.0071 (3)	0.3204 (4)	−0.4048 (5)
Cl(2)	0.2612 (1)	0.1125 (1)	0.0684 (1)	C(2)	0.1144 (3)	0.0811 (4)	−0.3904 (5)
O(1)	−0.0831 (2)	0.2466 (2)	−0.3652 (3)	C(3)	0.0683 (3)	0.3325 (4)	−0.3949 (5)
O(2)	0.0078 (2)	0.1345 (3)	−0.5141 (3)	C(4)	0.1738 (3)	0.0713 (4)	−0.2720 (5)
O(3)	0.1251 (3)	0.1798 (4)	0.0809 (5)	C(5)	−0.0680 (4)	0.3755 (5)	−0.4695 (7)
O(4)	0.7768 (3)	0.1747 (4)	0.0216 (5)	C(6)	0.1090 (4)	0.0307 (5)	−0.4813 (6)
O(5)	0.1760 (3)	0.4543 (4)	0.4568 (5)	C(7)	0.0926 (4)	0.4153 (4)	−0.3645 (6)
O(6)	0.9307 (4)	0.3953 (5)	0.2464 (6)	C(8)	0.0680 (4)	0.3106 (4)	−0.5030 (5)
O(7)	0.1193 (5)	0.2414 (8)	0.2646 (7)	C(9)	0.1564 (4)	0.0002 (4)	−0.2240 (6)
O(8)	0.0000 (0)	0.1532 (9)	0.2500 (0)	C(10)	0.2486 (4)	0.0599 (4)	−0.2636 (6)
N(1)	−0.0168 (2)	0.2594 (3)	−0.3600 (4)	C(11)	0.1901 (3)	0.2568 (4)	−0.2888 (5)
N(2)	0.0643 (3)	0.1305 (3)	−0.4075 (4)	C(12)	0.2234 (3)	0.2049 (4)	−0.1888 (6)
N(3)	0.1203 (2)	0.2828 (3)	−0.2970 (4)				

Parameters for the hydrogen atoms, thermal parameters, and listings of observed and calculated structure factors are available as supplementary material.

Results and Discussion

The structure of compound I is discrete, dinuclear, neutral rhodium complexes with the rhodium(III) atom in a slightly distorted-octahedral configuration (Figure 1). The octahedron about each rhodium is completed by two nitrogen atoms from each of the two bridging tetradentate amine–oxime ligands and two chloro ligands in trans positions. The 1,4-diamine portion of each BnAO ligand bridges between the two rhodium atoms, forming a 14-membered, centrosymmetric heterocyclic ring. The rhodium atom is slightly (~0.06 Å) out of the best plane through the four nitrogen atoms toward Cl(1). The bond distances are shown in Figure 1. The two Rh–Cl distances are significantly different (Δ = 0.008 Å) as are the chemically equivalent Rh–N(amine) distances (Δ = 0.029 Å) and, to a lesser extent, the Rh–N(oxime) distances (Δ = 0.013 Å). The Cl(2)–HN(3) and Cl(2)–HN(4) distances of 2.73 (5) and 2.59 (5) Å, respectively, are less than the sum of the van der Waals radii, suggesting weak hydrogen bond interactions (N(3)–HN(3)---Cl(2) = 108 (4)°, and N(4)–NH4---Cl(2) = 120 (4)°). This hydrogen bonding may relate to the asymmetry

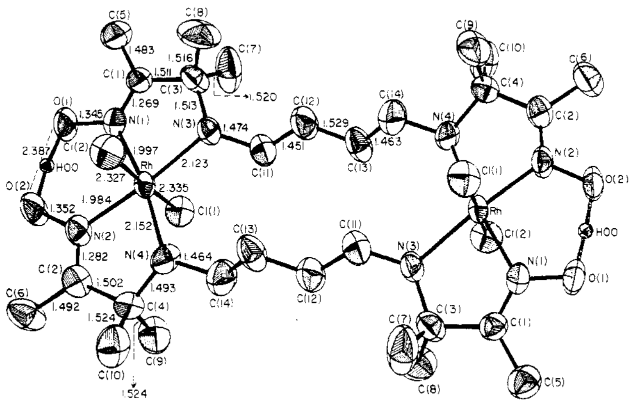

Figure 1. Molecular structure, atom labeling, and bond distances (Å) for compound I. Ellipsoids are drawon at the 50% probability level. Standard deviations are as follows: Rh–N, ±0.003–0.004 Å; Rh–Cl ±0.001 Å; C–C, C–N, N–O, O–O, ±0.004–0.007 Å.

Table IV. Intramolecular Bond Angles (deg) in Compound I

Cl(1)–Rh–Cl(2)	177.31 (5)	Rh–N(4)–C(14)	126.1 (4)
Cl(1)–Rh–N(1)	90.5 (1)	C(4)–N(4)–C(14)	111.9 (4)
Cl(1)–Rh–N(2)	92.8 (1)	N(1)–C(1)–C(3)	117.5 (4)
Cl(1)–Rh–N(3)	88.8 (1)	N(1)–C(1)–C(5)	121.7 (4)
Cl(1)–Rh–N(4)	94.4 (1)	C(3)–C(1)–C(5)	120.8 (4)
Cl(2)–Rh–N(1)	89.4 (1)	N(2)–C(2)–C(4)	117.0 (4)
Cl(2)–Rh–N(2)	89.9 (1)	N(2)–C(2)–C(6)	120.2 (4)
Cl(2)–Rh–N(3)	88.6 (1)	C(4)–C(2)–C(6)	122.8 (4)
Cl(2)–Rh–N(4)	86.0 (1)	N(3)–C(3)–C(1)	109.3 (4)
N(1)–Rh–N(2)	96.1 (1)	N(3)–C(3)–C(7)	110.6 (5)
N(1)–Rh–N(3)	78.7 (1)	N(3)–C(3)–C(8)	109.0 (5)
N(1)–Rh–N(4)	171.2 (2)	C(1)–C(3)–C(7)	107.6 (5)
N(2)–Rh–N(3)	174.6 (2)	C(1)–C(3)–C(8)	109.3 (5)
N(2)–Rh–N(4)	76.5 (2)	C(7)–C(3)–C(8)	111.1 (6)
N(3)–Rh–N(4)	108.6 (2)	N(4)–C(4)–C(2)	107.3 (4)
Rh–N(1)–O(1)	119.6 (3)	N(4)–C(4)–C(9)	111.4 (4)
Rh–N(1)–C(1)	121.8 (3)	N(4)–C(4)–C(10)	112.1 (4)
O(1)–N(1)–C(1)	118.5 (4)	C(2)–C(4)–C(9)	107.1 (4)
Rh–N(2)–O(2)	119.5 (3)	C(2)–C(4)–C(10)	109.2 (4)
Rh–N(2)–C(2)	122.8 (3)	C(9)–C(4)–C(10)	109.6 (5)
O(2)–N(2)–C(2)	117.6 (4)	N(3)–C(11)–C(12)	117.1 (5)
Rh–N(3)–C(3)	112.4 (3)	C(11)–C(12)–C(13)	119.2 (5)
Rh–N(3)–C(11)	119.8 (3)	C(12)–C(13)–C(14)	108.5 (5)
C(3)–N(3)–C(11)	119.4 (4)	N(4)–C(14)–C(13)	117.1 (5)
Rh–N(4)–C(4)	112.8 (2)		

in metal–ligand distances as well as to the displacement of the rhodium atom from the plane of the four nitrogen atoms. The two rhodium–nitrogen coordination planes are parallel and deviate from coplanarity by only about 0.2 Å. All of the carbon and oxygen atoms except for the methyl carbon atoms C(3) and C(4) are within 0.8 Å of both of these planes.

The bond angles are generally as would be expected (Table IV). Because of the displacement of the rhodium atom out of the nitrogen plane toward Cl(1), the N–Rh–Cl(1) angles average slightly larger than 90° while the N–Rh–Cl(2) angles are slighly less than 90°. The smallest of the angles in the coordination sphere are the N–Rh–N angles in the 5-membered chelate rings (76.5 (2) and 78.7 (1)°) while the N(3)–Rh–N(4) angle in the 14-membered ring opens to 108.6 (2)°. As a result the hydrogen bond on the opposite side of the rhodium atom is quite short, an O(1)- - -O(2) distance of 2.387 (5) Å, which is the shortest found in any of the amine–oxime complexes yet reported. The hydrogen atom however refines to an asymmetric position (O(1)–HOO = 0.96 (5), Å and O(2)–HOO = 1.44 (5) Å). From previous experiences, where hydrogen atoms have been located and refined with both X-ray and neutron diffraction data, we conclude that these X-ray values should not be taken very seriously. Some asymmetry in the direction indicated by these distances however is consistent with the shorter intermolecular contacts (Table V) involving O(2) compared with O(1). These contacts can be seen in the stereoview of the unit cell (Figure 2). The closest contact between carbon atoms within the molecule across the 14-membered ring is C(11)–C(13) (3.502 (6) Å).

Table V. Intermolecular Contacts (Å) Less than 3.8 Å in Compound I

Cl(1)–C(8)	3.734	O(2)–C(14)	3.759
Cl(2)–C(7)	3.661	N(1)–C(5)	3.663
O(1)–C(5)	3.524	C(1)–C(5)	3.660
O(1)–C(7)	3.650	C(5)–C(5)	3.565
O(2)–C(10)	3.257	C(5)–C(6)	3.696
O(2)–C(13)	3.491		

Table VI. Proposed Hydrogen Bonds (Å) in Compound II

Cl(2)---O(3)	3.147	O(4)---O(4)	2.816
Cl(2)---O(5)	3.152	O(4)---O(7)	2.902
Cl(2)---N(4)	3.243	O(4)---O(5)	2.921
Cl(2)---N(3)	3.425	O(5)---O(6)	2.780
O(1)---O(3)	2.864	O(6)---O(6)	2.837
O(2)---O(3)	2.591	O(6)---O(7)	2.880
O(2)---O(8)	3.124	O(7)---O(8)	2.845
O(3)---O(7)	2.751		

Table VII. Selected Bond Angles (deg) in Compound II

Cl(1)–Rh–N(1)	93.5 (1)	Rh–N(1)–C(1)	117.3 (4)
Cl(1)–Rh–N(2)	88.1 (1)	O(1)–N(1)–C(1)	119.4 (4)
Cl(1)–Rh–N(3)	173.0 (1)	N(1)–C(1)–C(3)	117.2 (5)
Cl(1)–Rh–N(4)	100.1 (1)	C(1)–C(3)–N(3)	105.9 (4)
Cl(1)–Rh–O(1)	91.3 (1)	Rh–N(3)–C(3)	112.0 (3)
N(1)–Rh–N(2)	99.1 (2)	Rh–N(3)–C(11)	107.8 (3)
N(1)–Rh–N(3)	80.6 (2)	C(3)–N(3)–C(11)	120.7 (4)
N(1)–Rh–N(4)	166.2 (2)	N(3)–C(11)–C(12)	105.9 (5)
N(1)–Rh–O(1)	86.1 (2)	C(11)–C(12)–N(4)	110.9 (5)
N(2)–Rh–N(3)	96.6 (2)	Rh–N(4)–C(12)	102.9 (3)
N(2)–Rh–N(4)	78.9 (2)	Rh–N(4)–C(4)	110.0 (3)
N(2)–Rh–O(1)	174.8 (2)	C(4)–N(4)–C(12)	116.8 (4)
N(3)–Rh–N(4)	86.0 (2)	N(4)–C(4)–C(2)	108.8 (5)
N(3)–Rh–O(1)	84.6 (2)	C(4)–C(2)–N(2)	117.1 (5)
N(4)–Rh–O(1)	96.1 (2)	Rh–N(2)–O(2)	124.0 (4)
Rh–O(1)–N(1)	110.2 (3)	Rh–N(2)–C(2)	119.6 (4)
Rh–N(1)–O(1)	123.2 (3)	C(2)–N(2)–O(2)	116.3 (5)

The infrared spectrum of this compound shows the characteristic broad, weak band at 1792 (5) cm^{-1}, normally found for this type of hydrogen bond. The ^1H NMR spectrum reveals a resonance for the hydrogen-bonded proton at 19.5 (1) ppm downfield from Me_4Si, which is characteristic of these strong hydrogen bonds.[6] Methyl and methylene proton chemical shifts are normal but not all well resolved.

The crystal structure of compound II (Figure 3) consists of discrete, dinuclear, distorted octahedrally coordinated rhodium(III), complex cations (Figure 4), chloride anions, and waters of hydration. The dinuclear rhodium ion (Figure 4) apparently has a 2+ charge since there are two chloride ions for each rhodium complex. The rhodium atoms are bridged by a chloride ligand and one deprotonated oxime group from each of the amine–oxime ligands. All four nitrogens of a particular amine–oxime ligand are coordinated to the same rhodium atom, and the six-coordination is completed by the bridging oxygen from the amine–oxime on the other rhodium and by the bridging chloride. A twofold axis passes through the bridging chloride and relates the halves of the dinuclear complex. The 2+ charge of the complex requires that only three protons are lost from the four oxime groups. The remaining proton appears to be distributed between the two uncoordinated oxime oxygen atoms (O(2)). There are 11 waters of hydration for each dimeric rhodium cation. Hydrogen atoms on these were not located. Elaborate hydrogen

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[6] Guillard, R. D.; Wilkinson, G. *J. Chem. Soc.* **1963**, 6041.

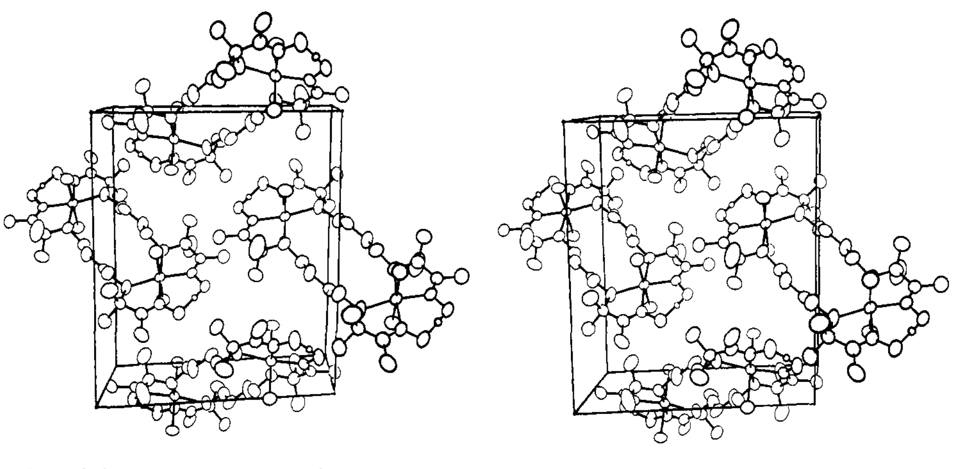

Figure 2. Stereoscopic view of the unit cell contents of compound I (hydrogen atoms except the hydrogen bond omitted for clarity).

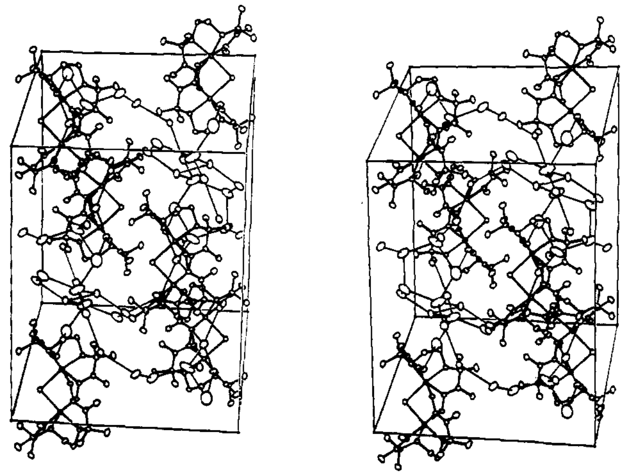

Figure 3. Stereoscopic view of the unit cell contents of compound II (hydrogen atoms omitted). Hydrogen bonds are illustrated.

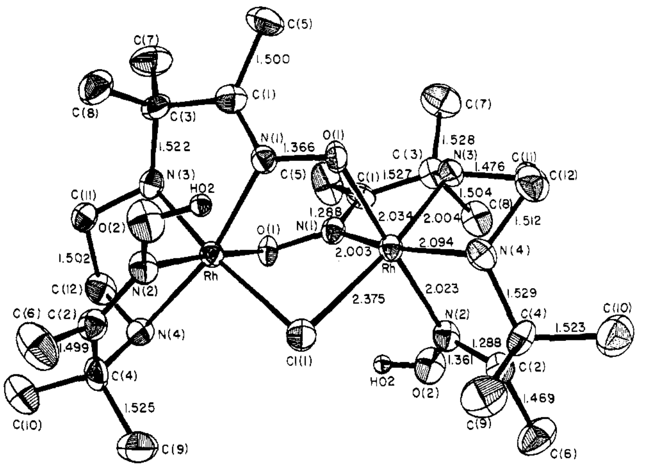

Figure 4. Molecular structure, atom labeling, and bond distances (Å) for compound II. Ellipsoids are drawn at the 50% probability level. Standard deviations are as follows: Rh–N, Rh–O, ±0.004–0.005 Å; Rh–Cl, ±0.002 Å; C–C, C–N, N–O, ±0.005–0.009 Å.

bonding (Table VI, Figure 3) includes all the water molecules, the ionic chloride, the oxime oxygens, and the amine nitrogens. The shortest of these is the O(2) oxime–O(3) water hydrogen bond of 2.591 Å (O(3)- - -HO(2) = 1.732 Å).

The bond distances are given in Figure 4 and the bond angles in Table VII. The Rh–N(oxime) distances are nearly identical (2.003 and 2.023 (4) Å) but are slightly longer than those (1.984–1.997 (3) Å) in I, where the oxime groups are involved in the strong intramolecular hydrogen bond. The latter are near those (1.98 (1) Å) in $[Rh(Ph_3Sb)Cl(DMG)_2]$,[7] which are comparable to those in $[ClRh(DMG)_2(PPh_3)]$,[8] where the average distance is Rh–N(oxime) = 1.988 Å. In contrast the Rh–N(amine) distances are quite different (2.004 and 2.094 (4) Å) and are shorter than those (2.123 and 2.152 (3) Å) in I. The former are similar to those (2.063 (9) Å) in $[(+)\text{-}Cr(en)_3\text{-}(+)\text{-}Rh(en)_3]Cl_6 \cdot 6H_2O$[9] and those (2.076 (4) Å) in (+)-tris[*trans*-1(*R*),2(*R*)-diaminocyclohexane]rhodium(III) nitrate trihydrate.[10] Thus those in compound I appear to be unusally long. The shorter Rh–N(amine) distance in II is that which is trans to the bridging chloride while the longer is trans to the nitrogen of the bridging oxime. The bridging Rh–Cl distance (2.375 (2) Å) is comparable to those observed in other studies, e.g., (2.380 (2) and 2.406 (2) Å) in $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]$.[11] These are considerably longer than those (2.327 (1) and 2.335 (1) Å) for the nonbridging chloro ligands in I. These are comparable to that (2.331 (1) Å) in $[Rh(py)_4Cl_2][H(NO_3)_2]$.[12]

Compound II fails to form the usual strong intramolecular hydrogen bond between cis oxime oxygen atoms. In the Ni(II) complex of this ligand[13] the O- - -O distance is 2.478 (5) Å, indicative of some lengthening because of the steric restrictions imposed by the ethylene bridge opposite the hydrogen bond. The dimeric Cu(II) complex[14] shows a more dramatic lengthening to 2.698 (6) Å. Thus it is not surprising that the larger Rh(III) gives a complex with no such hydrogen bond. Formation of the dimeric complex with BnAO (compound I) is more surprising. This is the first case we have observed where a tetradentate oxime ligand that is sterically able to wrap around one metal ion to form the strong intramolecular hydrogen bond instead chooses to bridge two metal ions to form the strong hydrogen bonds. This might be a reflection of the slow substitution rate on Rh(III). Thus it is possible that one pair of nitrogen atoms (an amine and an oxime) substitute on one rhodium and before the other end of the ligand is kinetically able to substitute on the same metal a second Rh(III) ion preferentially coordinates to the other half of the BnAO ligand. This proposal would suggest a Rh(III) concentration dependence and a possibility of forming the

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monomeric complex at lower Rh(III) concentration. An examination of this postulation is planned.

Acknowledgment. We acknowledge the financial support of the National Science Foundation, Grant No. CHE81-06795.

Registry No. I, 83633-48-1; II, 83633-51-6.

Supplementary Material Available: Listings of hydrogen atom positions, general temperature factor expressions, and observed and calculated structure factors for compounds I and II (24 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal and Molecular Structure of Bis(nitrato)[diisopropyl (*N*,*N*-diethylcarbamyl)methylenephosphonate]dioxouranium(VI)

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Received May 26, 1982

The title complex $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$ (1) was prepared by the addition of $UO_2(NO_3)_2{\cdot}6H_2O$ to the carbamylmethylenephosphonate ligand in ethanol. The compound has been characterized by infrared, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. A single-crystal X-ray analysis of **1** has been completed at -28 °C, and the complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.520$ (4) Å, $b = 10.963$ (4) Å, $c = 20.033$ (8) Å, $\beta = 103.79$ (3)°, $Z = 4$, $V = 2243.7$ Å^3, and $\rho_{calcd} = 1.99$ g cm^{-3}. The structure was solved with use of heavy-atom techniques, and blocked least-squares refinement converged with $R_F = 4.1\%$ and $R_{wF} = 3.9\%$ for 4153 independent reflections with $F \geq 4\sigma(F)$. The molecular structure of **1** consists of a linear UO_2^{2+} ion surrounded at its equator by four oxygen atoms from two bidentate nitrate ions and the phosphoryl and carbonyl oxygen atoms from a bidentate phosphonate ligand. Several important bond distances include U-O(uranyl)$_{av}$ = 1.756 (6) Å, U-O(phosphoryl) = 2.420 (4) Å, U-O(carbonyl) = 2.406 (5) Å, U-O(nitrate)$_{av}$ = 2.512 (5) Å, P-O(phosphoryl) = 1.485 (5) Å, and C-O(carbonyl) = 1.260 (8) Å.

Introduction

The potentially multifunctional carbamylmethylenephosphonate (CMP) ligands, $(RO)_2P(O)CH_2C(O)NEt_2$, are known to act as efficient extractants of lanthanide and actinide ions from acidic radioactive waste solutions.[1,2] Despite intensive study of this important separations chemistry,[1,2] the details of the extraction mechanism and the stoichiometries and structures of metal-CMP complexes have not been fully revealed. Recently, synthetic and structural studies in our laboratory have begun to provide a greater understanding of this coordination chemistry. For example, it has been observed that CMP ligands coordinate with metal ions in at least three modes. Mercury(II)[3] and cadmium(II)[4] promote loss of a methylene proton at the carbon atom bridging the phosphoryl and carbonyl groups with the subsequent formation of M_2L_2 complexes in which the metal ions bond with the methine carbon atom of one ligand and the phosphoryl and carbonyl oxygen atoms of the second ligand. Thorium(IV)[5] and La(III) through Gd(III)[6] interact with two neutral CMP ligands, forming bidentate chelates through lanthanide-phosphoryl oxygen and -carbonyl oxygen atom interactions. However, the lanthanides Tb(III) through Er(III)[6] bond only with the phosphoryl oxygen atoms of two neutral ligands. This interesting variation in coordination ability of the CMP ligands is consistent with differences in extraction efficiencies under certain conditions, and additional structural studies of relevant waste-metal-CMP complexes are of interest.

Uranium species are an important constituent in many acidic radioactive waste solutions, and Schulz and McIsaac[2,7] observed that UO_2^{2+} is extracted by CMP ligands under process conditions. Elaborating on this study, Horwitz and co-workers[8] recently suggested that dihexyl (*N*,*N*-diethylcarbamyl)methylenephosphonate (DHDECMP) acts as a neutral extractant toward UO_2^{2+}, and on the basis of distribution ratios, an extraction stoichiometry DHDECMP:UO_2^{2+} = 2 was proposed. In addition, infrared and thermodynamic data were used to suggest that the CMP ligand functions only as a monodentate ligand through uranium atom-phosphoryl oxygen atom interactions.

As part of our studies of the coordination properties of CMP ligands with transition, lanthanide, and actinide metal ion species, we have explored the chemistry of diisopropyl (*N*,*N*-diethylcarbamyl)methylenephosphonate (DiPDECMP) with UO_2^{2+} in nitric acid solution. We report here, the formation, spectroscopic characterization, and single-crystal X-ray diffraction analysis of the resulting complex $UO_2(NO_3)_2$(DiPDECMP).

Experimental Section

General Information. The DiPDECMP ligand was prepared by literature methods.[1] $UO_2(NO_3)_2{\cdot}6H_2O$ was obtained from City Chemical Corp. Infrared spectra were recorded on a Nicolet Model 6000 FT IR spectrometer from KBr pellets. NMR spectra were recorded on a Varian FT-80 spectrometer operating at 32.2 MHz (^{31}P), 20.0 MHz (^{13}C), and 80.0 MHz (^1H). The samples, dissolved in an internal deuterium lock solvent, were contained in 5-mm tubes. Spectral standards were 85% H_3PO_4 (^{31}P) and Me_4Si (^{13}C and ^1H). Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

Preparation of the Complex. The complex was prepared by addition of 12 mmol of $UO_2(NO_3)_2{\cdot}6H_2O$ to 24 mmol of DiPDECMP in ethanol. The mixture was heated, and a milky yellow solution was obtained immediately. The solution was filtered, and a light yellow solid was collected. The solid was washed with ethanol and redissolved

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