"electrostatic minimum energy configuration". If this is the case one might expect to get relatively little variation in the nonimposed short contacts but this is *not* the case as can be seen from the data presented.

The Tropolonato Ligands. Bond lengths and angles for the tropolonato ligands in this complex are given in Table V. Shown also in Table V are the mean values $\bar{l}$ of the bonds within the four ligands which are considered to be chemically equivalent and σ_s (the error based on the internal consistency of the structure, as defined earlier in the text). The corresponding values of $\bar{l}$ for all previously determined tropolonato complexes[1,4,5] are also listed, and, except in the case of the C_1–C_7 bond length, the mean values in the NbT_4^+ cation are, within the error expressed by $\sigma\bar{l}$, equal to the general mean values. Examination of the structural data available on tropolonato ligands[1,4,5] reveals that increasing strength of the complexing bonds is accompanied by lengthening of the C–O bonds and also some shortening of the C_1–C_7 bonds. The values of the C_1–C_7 bonds (Table V) do not differ significantly from values obtained for strongly complexing tropolonato ligands (e.g., 1.439 (15) Å in T_3SnCl).[16]

Three of the C_7 rings in the ligands are planar (relevant least-squares mean planes are given in Table VI), and in the fourth, the distortions are not chemically significant. Deviations of the corresponding oxygen atoms from these planes are small (0.001–0.057 Å), though larger deviations of the niobium atom from each plane (0.099–0.218 Å) are observed.

The $(O(H\cdots Cl)_3)^{2-}$ Anion. The arrangement of a flattened pyramidal hydroxonium ion (H_3O^+), triply bonded to three chlorine atoms at the vertices of the base of the pyramid (O···Cl = 2.87 (3) Å), has been found previously in the structures of hydrogen chloride monohydrate[24] (O···Cl = 2.95 (1) Å) and cesium chloride–0.33(hydroxonium bichloride) (O···Cl = 2.92 (2) Å).[25] It is interesting to note that the same type of disorder is proposed in all three structures, with equal probability that the oxygen will be above or below the plane formed by the three chlorine atoms. No evidence for the hydrogen atom positions in this anion was found from the data, which is not surprising in view of the occupancy numbers of 0.25 or 0.5 which would be assigned to them. Bond lengths and angles for this anion and for the acetonitrile molecules of crystallization are included in Table II.

Registry No. $(NbT_4)_2(O(H\cdots Cl)_3)\cdot CH_3CN$, 56630-15-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC503069-12-75.

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Coordination of Perrhenate Ion in a Five-Coordinate Square-Pyramidal Copper(II) Complex. Crystal Structure of Perrhenato-2,2'-(1,3-diaminopropane)bis(2-methyl-3-butanone oximato)copper(II)

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The crystal structure of perrhenato-2,2'-(1,3-diaminopropane)bis(2-methyl-3-butanone oximato)copper(II), [Cu(PnAO-H)(ReO_4)], has been determined from three-dimensional X-ray data collected with a scintillation counter. The orthorhombic unit cell dimensions are a = 11.989 (6), b = 12.430 (6), and c = 13.258 (7) Å. The density of 1.968 (2) g/cm^3 calculated for four molecules per unit cell agrees with the flotation density of 1.96 (2) g/cm^3. The space group is *Pmcn*. A full-matrix least-squares refinement gave a final conventional agreement factor of 5.2%. The structure consists of discrete five-coordinate square-pyramidal copper(II) neutral complexes. The tetradentate α-amine oxime ligand is bonded in a square plane about the copper with Cu–N(amine) = 1.99 (1) Å and Cu–N(oxime) = 1.96 (1) Å. The apical position of the square pyramid is occupied by a perrhenate oxygen (Cu–O = 2.40 (1) Å and Re–O(av) = 1.70 (3) Å). The copper atom is significantly (0.24 Å) out of the plane of the four nitrogens toward the perrhenate ion. The short intramolecular hydrogen bond involves a separation of oxime oxygens of 2.46 (2) Å.

Introduction

A comprehensive study of the short intramolecular hydrogen bonds in α-amine oxime complexes of metal ions is in progress in order to examine the effect of the O---O distance on the hydrogen atom position and the associated potential function. Previous structural studies have involved a bidentate α-amine oxime with Ni(II),[1,2] Pt(II),[3] and Co(III),[4] a tetradentate α-amine oxime (EnAO) with Ni(II),[5] and the present tetradentate α-amine oxime (PnAO) (Figure 1) with Co(III).[6] Changing steric requirements of the ligand and changing the

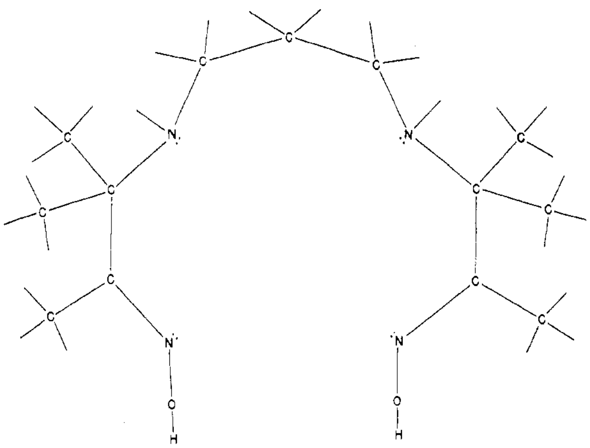

Figure 1. Neutral 2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone oxime) (PnAO).

size of the metal ion have produced O---O[1,6] distances ranging from 2.42 to 2.48 Å. The present study was undertaken to examine the effect on the O---O distance of the Cu(II) ion. The perrhenate complex was chosen for the study because precipitation of $[Cu(PnAO\text{-}H)]^+$ with perrhenate yielded an unusual-colored product compared with simple salts of the copper amine oxime complex such as $[Cu(PnAO\text{-}H)]NO_3$. Coordination of perrhenate ion to first-series transition metals has been reported earlier,[7,8] but no X-ray structural studies have been presented.

Experimental Section

A. Crystal Preparation. The purple complex $[Cu(PnAO\text{-}H)]^+$ was prepared as described by Vassian[9] and precipitated as $[Cu(PnAO\text{-}H)(ReO_4)]$ on addition of $NaReO_4$. The burgundy-colored crystals were then obtained by slow evaporation of aqueous solutions.

B. X-Ray Data. Perrhenate-2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone oximato)copper(II), $[Cu(C_{13}H_{27}N_4O_2)(ReO_4)]$ crystallizes in the orthorhombic crystal system with four molecules in a unit cell with $a = 11.989$ (6), $b = 12.430$ (6), and $c = 13.258$ (7) Å. These cell dimensions and their standard deviations were determined from a least-squares refinement[10] of the setting angles of 20 reflections, carefully centered using a narrow vertical slit in front of the detector and a low takeoff angle on a Picker four-circle X-ray diffractometer with Mo Kα_1 radiation. A measurement of the density by flotation in a CCl_4–CBr_4 solution gave 1.96 (2) g/cm³. A calculated density of 1.968 (2) g/cm³ is obtained assuming four formulas per unit cell. The choice of space groups *Pmcn* or $P2_1cn$ is based on the systematic extinctions for $h0l$, l odd, and $hk0$, $h + k$ odd. Subsequent refinement is consistent with the selection of space group *Pmcn*. Interchange of the a and c axes would yield the more conventional *Pnam* space group.

The crystal chosen for the intensity data collection was bounded by the $00\bar{1}$, 001, $\bar{1}10$, 110, $1\bar{1}0$, and $\bar{1}\bar{1}0$ faces and had approximate dimensions of 0.04 × 0.14 × 0.16 mm. The crystal was aligned on a Picker four-angle programmer system as previously described. The refined orientation and cell dimensions were used to calculate the setting angles for all measured reflections. The crystal was mounted with the 110 direction nearly along the ϕ axis of the diffractometer. For intensity data collection the diffracted X-rays were filtered through a niobium β filter. A takeoff angle of 2.5° was used to obtain the Mo Kα radiation. The receiving aperture was about 3 × 3 mm and was positioned 27 cm from the crystal. The θ–2θ scan technique ($2\theta = 0$–$40°$) was used with a scan rate of 1.0°/min and with a variable scan ranging from 1.00 to 1.30° to account for the α_1–α_2 splitting. Stationary-counter backgrounds were taken for 20 sec on each end of the scan. The count rate never exceeded 8000 counts/sec and was therefore in the linear range of the detector. The pulse height analyzer was set for about a 95% window, centered on the Mo Kα peak. The intensities of 2149 reflections were measured. These included all Friedel pairs out to $2\theta = 20°$. Three standard reflections were measured every 50 reflections as a check on crystal and instrument stability. The total change in intensity was less than 12%, and a correction was applied to all data for this decrease.

Table I. Hydrogen Atom Parameters

Atom	x	y	z
H1O1	$-^1/_4$	0.055	0.614
H1C5	0.035	0.395	0.445
H2C5	0.151	0.323	0.476
H3C5	0.072	0.355	0.563
H1C4	0.035	0.255	0.295
H2C4	−0.028	0.156	0.333
H3C4	0.096	0.174	0.363
H1C3	0.042	0.070	0.632
H2C3	0.115	0.065	0.540
H3C3	0.119	0.165	0.604
H1N2	−0.135	0.359	0.500
H1C6	−0.143	0.334	0.293
H2C6	−0.080	0.429	0.343
H1C7	$-^1/_4$	0.495	0.307
H2C7	$-^1/_4$	0.476	0.423

Table II. Atomic Positional Parameters[a]

Atom	x	y	z
Re	$-^1/_4$	0.04530 (8)	0.21595 (6)
Cu	$-^1/_4$	0.2141 (2)	0.4823 (2)
O1	−0.1477 (9)	0.0550 (8)	0.6138 (7)
O2	$-^1/_4$	0.104 (1)	0.334 (1)
O3	$-^1/_4$	−0.086 (1)	0.229 (1)
O4	−0.132 (1)	0.081 (1)	0.150 (1)
N1	−0.127 (1)	0.1375 (9)	0.5480 (8)
N2	−0.1263 (9)	0.3136 (9)	0.4459 (7)
C1	−0.026 (1)	0.167 (1)	0.530 (1)
C2	−0.013 (1)	0.259 (1)	0.453 (1)
C3	0.068 (2)	0.112 (2)	0.577 (1)
C4	0.026 (1)	0.209 (1)	0.353 (1)
C5	0.075 (1)	0.338 (1)	0.492 (1)
C6	−0.142 (1)	0.380 (1)	0.353 (1)
C7	$-^1/_4$	0.442 (2)	0.360 (2)

[a] Standard deviations from the least-squares refinement are included in parentheses in this and other tables.

Background and Lorentz–polarization corrections were made using the usual equations. Absorption corrections were made ($\mu = 76.4$ cm⁻¹) with the transmission factor ranging from 0.37 to 0.75. Equivalent and duplicate reflections were averaged, reducing the number of reflections to 1360, assuming equivalence of Friedel pairs. The agreement factor, $\sum|F^2 - F^2_{av}|/\sum F^2$, was 0.053, and there were no large discrepancies in intensities of Friedel pairs in keeping with the subsequent successful refinement in *Pmcn*. The 991 reflections with $F_o^2 > 2.5\sigma(F_o^2)$, where $\sigma(F_o^2) = [\sigma^2_{counting} + (0.05F_o^2)^2]^{1/2}$, were used in the structure solution and refinement.

C. Determination of the Structure. The rhenium and copper atoms were located from a Patterson synthesis and found to be on the mirror at $x = ^1/_4$. All other atoms were located from successive Fourier and difference Fourier syntheses. Refinement of positional and isotropic thermal parameters for all atoms except hydrogens converged with $R = \sum|F_o^2 - kF_c^2|/\sum F_o^2 = 0.146$ and $r = [\sum w(F_o^2 - kF_c^2)^2/\sum wF_o^4]^{1/2} = 0.219$, where $w = 1/\sigma^2(F_o^2)$ and k is a refinable scale factor. In this and all refinements the function $\sum w(F_o^2 - kF_c^2)^2$ was minimized. For C, N, and O scattering factors were taken from Ibers;[11a] those of H, from Stewart;[11b] and those of Cu and Re, from Cromer and Waber.[11c] Using the tabulated values[11d] of $\Delta f'$ and $\Delta f''$ for Cu and Re, the effects of anomalous dispersion were included in F_c.[11e] Refinement with anisotropic temperature factors reduced R to 0.075 and r to 0.120. Inclusion of hydrogen atoms from difference Fourier and chemically reasonable positions with isotropic temperature factors 1.0 Å² greater than those of the atom to which they were attached gave $R = 0.069$ and $r = 0.110$. Refinement with fixed hydrogen atoms and all other atoms anisotropic then gave $R = 0.067$ and $r = 0.106$. In the last cycle of refinement none of the parameters shifted by more than 0.10σ for that parameter. Inclusion of the hydrogen atom positional parameters in the refinement increased the number of variables from 122 to 165 and gave $R = 0.066$ and $r = 0.104$. This improvement proved to be insignificant,[12] and therefore the parameters from the preceding refinement are reported. The conventional agreement factor was 0.052. The standard deviation of an observation of unit weight was 1.30. The observed and calculated structure factors (×10) are available.[13] The hydrogen atom positions

Table III. Atomic Anisotropic Thermal Parameters[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	0.00852 (9)	0.00642 (8)	0.00295 (5)	0.0	0.0	0.00006 (6)
Cu	0.0054 (2)	0.0049 (2)	0.0033 (1)	0.0	0.0	0.0003 (1)
O1	0.011 (1)	0.0063 (8)	0.0051 (6)	0.0005 (8)	0.0000 (7)	0.0019 (6)
O2	0.006 (1)	0.014 (2)	0.0045 (9)	0.0	0.0	−0.002 (1)
O3	0.012 (2)	0.007 (1)	0.006 (1)	0.0	0.0	0.000 (1)
O4	0.014 (1)	0.012 (1)	0.009 (1)	−0.004 (1)	0.004 (1)	−0.002 (1)
N1	0.009 (1)	0.0034 (9)	0.0045 (7)	−0.0006 (9)	0.0007 (8)	−0.0010 (7)
N2	0.006 (1)	0.006 (1)	0.0040 (7)	0.0006 (8)	0.0006 (7)	−0.0006 (7)
C1	0.007 (2)	0.007 (1)	0.0047 (9)	−0.002 (1)	−0.003 (1)	0.000 (1)
C2	0.005 (1)	0.007 (1)	0.005 (1)	−0.002 (1)	0.001 (1)	−0.001 (1)
C3	0.008 (2)	0.015 (2)	0.008 (1)	0.003 (2)	−0.001 (1)	−0.002 (1)
C4	0.008 (2)	0.011 (2)	0.005 (1)	−0.001 (1)	0.002 (1)	0.000 (1)
C5	0.006 (1)	0.009 (2)	0.010 (1)	0.001 (1)	−0.002 (1)	−0.002 (1)
C6	0.008 (1)	0.007 (1)	0.004 (1)	0.000 (1)	0.001 (1)	0.002 (1)
C7	0.009 (2)	0.005 (2)	0.006 (1)	0.0	0.0	0.003 (1)

[a] The anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11}{}^2 + k^2\beta_{22}{}^2 + l^2\beta_{33}{}^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

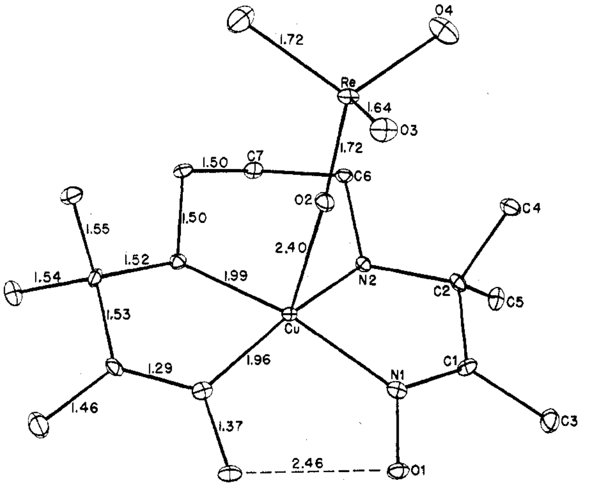

Figure 2. Perspective view of perrhenato-2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone oximato)copper(II), [Cu(PnAO-H)-(ReO_4)], showing bond distances. Standard deviations: Re–O, Cu–N, Cu–O, ±0.01 Å; C–C, C–N, N–O, ±0.01–0.02 Å.

Table IV. Intermolecular Distances

Dist	Value, Å	Dist	Value, Å
Cu-O4	3.67	C1-O4	3.73
O3-C4	3.86	O4-C5	3.40
O3-C5	3.72	O4-C2	3.57
C7-C6	3.48	O4-N1	3.75
O1-C6	3.27	O4-N2[a]	3.01

[a] This is the intermolecular hydrogen bond between the amine nitrogens and perrhenate oxygens.

Table V. Cu, N2, N1, O1 Least-Squares Plane: $2.186x - 7.026y - 10.667z + 7.195 = 0$

Atom	Dist, Å	Atom	Dist, Å
Cu	0.000 (2)	C3	0.40
N1	0.10 (1)	C4	2.02
N2	−0.04 (1)	C5	−0.27
O1	−0.06 (1)	C6	0.45
C1	0.31	C7	−0.29
C2	0.51	O2	2.36
H1N2	−0.96		

are given in Table I while the final positional and thermal parameters of all other atoms are included in Tables II and III.

Discussion

A. Nature of the Structure. The crystal structure consists of discrete neutral square-pyramidal copper(II) complexes (Figures 2 and 3). The square pyramid about the copper atom consists of four nitrogens of the tetradentate PnAO ligand and an oxygen atom from the perrhenate ion. The molecule has C_s symmetry with the mirror passing through the Cu, Re, C7, O2, O3, and H1O1 atoms. This is the first reported X-ray diffraction study of a perrhenate ion coordinated to a transition metal. The perrhenate ion has the expected near-tetrahedral geometry. There are no unusually short intermolecular contacts as can be seen from Table IV where all intermolecular distances (ignoring hydrogens) less than 3.9 Å are given. The structure is largely established by van der Waals interactions and the rather long intermolecular hydrogen bonds from perrhenate oxygens to amine nitrogens (O4---N2 = 3.01 Å and O4---H–N2 = 160°).

The square pyramid about the Cu(II) atom is significantly distorted. The copper atom is displaced approximately 0.24 Å out of the best plane through the four nitrogen atoms toward the coordinated perrhenate. The perrhenate oxygen to copper bond is not quite perpendicular to the nitrogen plane as evidenced by the O2–Cu–N2(amine) angle (99.0 (4)°) and the O2–Cu–N1(oxime) angle (95.0 (4)°) and by the O2–N2 (3.35 Å) and O2–N1 (3.23 Å) distances. The reason for this distortion is not clear unless it is to reduce interaction with the methylene C6 atoms (O2–C6 = 3.68 Å). This is probably

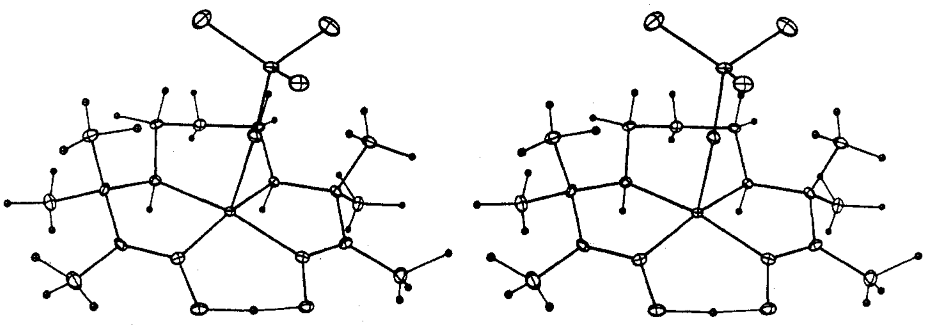

Figure 3. Stereoscopic view of [Cu(PnAO-H)ReO_4]. Hydrogen atoms are illustrated with small spheres. The atom labeling is shown in Figure 2.

Table VI. Root-Mean-Square Components of Thermal Displacement along the Principal Axes (Å)

Atom	Axis 1	Axis 2	Axis 3
Re	0.162 (2)	0.225 (1)	0.249 (1)
Cu	0.168 (4)	0.197 (4)	0.198 (4)
O1	0.18 (2)	0.25 (1)	0.28 (1)
O2	0.19 (2)	0.21 (2)	0.33 (2)
O3	0.23 (2)	0.24 (2)	0.30 (2)
O4	0.23 (2)	0.27 (2)	0.39 (2)
N1	0.15 (2)	0.20 (2)	0.26 (2)
N2	0.18 (2)	0.21 (2)	0.22 (2)
C1	0.14 (3)	0.23 (2)	0.27 (2)
C2	0.15 (3)	0.21 (2)	0.26 (2)
C3	0.22 (3)	0.25 (2)	0.36 (2)
C4	0.19 (2)	0.26 (2)	0.30 (2)
C5	0.20 (3)	0.24 (2)	0.32 (2)
C6	0.16 (3)	0.24 (2)	0.26 (2)
C7	0.15 (4)	0.25 (3)	0.27 (3)

Table VII. Intramolecular Bond Angles

Angle	Value, deg	Angle	Value, deg
O2-Re-O3	109.1 (7)	C6-C7-C6[a]	118 (2)
O2-Re-O4	110.5 (5)	C6-N2-Cu	117 (1)
O3-Re-O4	107.9 (5)	C6-N2-C2	115 (1)
O4-Re-O4[a]	110.8 (9)	C2-N2-Cu	112 (1)
N1-Cu-N1[a]	97.4 (8)	N1-C1-C2	116 (1)
N1-Cu-N2	81.4 (5)	N1-C1-C3	121 (1)
N1-Cu-N2[a]	166.0 (4)	C2-C1-C3	123 (1)
N2-Cu-N2[a]	96.3 (6)	N2-C2-C1	107 (1)
O2-Cu-N1	95.0 (4)	N2-C2-C4	113 (1)
O2-Cu-N2	99.0 (4)	N2-C2-C5	111 (1)
O1-N1-C1	120 (1)	C1-C2-C4	108 (1)
O1-N1-Cu	119 (1)	C4-C2-C5	110 (1)
C1-N1-Cu	110 (1)	O1-H1O1-O1	180
		N1-O1-H1O1	100

[a] Related by a mirror plane at $x = -^1/_4$ to that listed in Table II.

not the reason however, since a similar distortion was observed[14] in the square-pyramidal $[Cu(NH_3)_4(H_2O)]^{2+}$ ion in $[Cu(NH_3)_4(H_2O)]SO_4$ where the two independent O–Cu–N angles are 96.6 (3) and 91.4 (3)°. In that complex the Cu atom is 0.19 Å out of the plane of the ammonias toward the coordinated water.

The least-squares plane (Table V) through the copper, the oxime N and O, and the amine N on one side of the copper reveals the puckering of the PnAO ligand. These four atoms are nearly planar, but there is considerable deviation of the remainder of the ligand atoms from that plane. Interestingly all of the nonhydrogen atoms in that half of the PnAO ligand are above this plane except methyl carbon C5 and methylene carbon C7. This is the same side of the plane occupied by the perrhenate ion. This particular ligand configuration, which would appear to be sterically less favorable than that obtained by placing the amine hydrogens above the plane, does allow for the intermolecular hydrogen bond between the amine nitrogens (N2) and the perrhenate oxygens (O4). A similar but somewhat less pronounced puckering of the PnAO ligand was observed[6] in $[Co(PnAO\text{-}H)(NO_2)_2]$ where the two amine hydrogen atoms were intramolecularly hydrogen bonded to one of the nitro groups.

The shapes and orientations of the thermal ellipsoids can be seen in Figures 2 and 3, while the root-mean-square displacements along the principal axes are in Table VI. As might be anticipated, the thermal motion of the perrhenate oxygens is the largest. In all cases the maximum vibration of each terminal nonhydrogen atom is nearly perpendicular to the bond and the minimum is nearly along the bond.

B. Bond Distances and Angles Involving the Amine Oxime Ligand. The bond distances involving all atoms except hydrogens are given in Figure 2. Table VII contains the more significant bond angles. Hydrogen atoms were placed[15] to give C–H distances of 0.95 Å, an N–H distance of 0.90 Å, and tetrahedral angles.

As observed in other amine oxime complexes, such as the $[Co(PnAO\text{-}H)(NO_2)_2]$ complex,[6] the Cu–N(amine) distance (1.99 (1) Å) is longer than the Cu–N(oxime) distance (1.96 (1) Å). In the cobalt complex the difference (0.08 Å) is significantly greater. In the trimeric complex, μ_3-hydroxo-(oxo)-tri-μ-(2-propylamino-2-methyl-3-butanone oximato)-triaquotricopper(II),[16] the Cu–N(amine) distance is 2.03 (1) Å, and the Cu–N(oxime) distance, 1.96 (1) Å. In $[Cu(NH_3)_4H_2O]SO_4$ the Cu–N(amine) distance is 2.031 (6) Å. These comparisons suggest that the Cu–N(amine) distance in the present study is unusually short, possibly because of the steric requirement of the ligand. The cis N–Cu–N angles in this complex are in agreement, within experimental error, with the corresponding N–Co–N angles in $[Co(PnAO\text{-}H)(NO_2)_2]$.[6] All of the intraligand distances and angles are in reasonable agreement with those previously observed. As previously noted[6] there is considerable distortion in bond angles from the expected tetrahedral and trigonal-planar values, presumably required in order to achieve the tetradentate bonding. Displacement of the Cu atom by 0.24 Å from the nitrogen plane partially compensates for the apparent larger size of Cu(II) compared with Co(III), so that many features of the ligand geometry are quite similar in this complex and $[Co(PnAO\text{-}H)(NO_2)_2]$.

C. Nature of the Perrhenate Linkage. The perrhenate ion has the ability to coordinate to transition metal ions. The first report[7] of this by Lenz and Murmann involved the preparation of $[Co(NH_3)_5(ReO_4)]^{2+}$. Mayfield and Bull[8] suggested that ReO_4^- coordinates more strongly than BF_4^- or ClO_4^- but less strongly than Cl^- and Br^-, based on spectral studies of complexes $[ML_4(ReO_4)_2]$ where M = Co(II), Cu(II), Ni(II), Mn(II), or Zn(II) and L = pyridine (py) or 4-methylpyridine. In $[Cu(py)_4(ReO_4)_2]$ the authors reported splitting of the Re–O stretching mode in the infrared spectrum to give one band at about 928 cm^{-1} (ν_1) and three bands at 900, 907, and 918 cm^{-1} (ν_3). In the present compound these bands are observed at 922 and 898 cm^{-1}. The latter band has apparent shoulders at 902 and 908 cm^{-1} which are not well resolved on the Perkin-Elmer 237B spectrometer used.

Diffraction studies of the structure of ReO_4^- have been limited in both number and accuracy, the latter largely because of the dominance of the scattering by the rhenium. In $KReO_4$ the Re–O distance is 1.77 (3) Å.[17] Re_2O_7[18] and $Re_2O_7(OH_2)_2$[19] involve half the rhenium atoms in tetrahedral configuration and half in distorted octahedral configuration. In the tetrahedral portion of the polymeric Re_2O_7, the average Re–O distance is 1.74 (4) Å while in the dimeric $Re_2O_7(OH_2)_2$, the average tetrahedral Re–O distance is 1.76 (3) Å. In the compound $(CH_3)_3SiOReO_3$[20] the average Re–O distance is 1.62 (7) Å. In light of the other observations and the present average value of 1.70 (3) Å, the 1.62-Å value appears somewhat short. The reason for the short 1.64 Å Re–O3 distance in this study is not apparent. The Re–O4 distances might be expected to be slightly longer than the Re–O3 distance because of the O4---N2 hydrogen bond, but not by 0.08 Å as observed here. A careful study of the structure of another complex with coordinated perrhenate is required to establish any difference between the coordinated and noncoordinated Re–O distances. While there is a definite change in the solid color in going from $[Cu(PnAO\text{-}H)]ClO_4$ to $[Cu(PnAO\text{-}H)ReO_4]$, the extent of covalent interaction between the perrhenate ion and the Cu atom is not established and may be small.

D. The Short Intramolecular Hydrogen Bond. The displacement of the Cu atom from the tetradentate ligand plane probably facilitates a shorter O---O distance (2.46 (2) Å) than would have otherwise been observed. Because of the large standard deviation this distance is not significantly longer than that observed in [Co(PnAO-H)$(NO_2)_2$]^6 of 2.432 (3) Å or in bis(2-amino-2-methyl-butanone oximato)nickel(II) ion^2 of 2.420 (3) Å. In the latter, neutron diffraction revealed a nearly symmetrical hydrogen bond O1–H (1.187 (5) Å) and O2–H (1.242 (5) Å). In the present compound the space group symmetry places the hydrogen atom on a mirror with exactly equal O–H distances or randomly disordered on either side of the mirror. From the difference Fourier the hydrogen atom appears to be on the mirror or very close to it, but because of the rhenium atom, hydrogen atom positions are not well defined.

The infrared frequency associated with the O---H---O vibration is a broad band peaking at 1790 cm^{-1} with a shoulder at about 1855 cm^{-1}. In [Cu(PnAO-H)]NO_3 this band also occurs at 1800 cm^{-1} but without the shoulder. The position of these bands is similar to that reported for other α-amine oxime complexes.[21]

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Registry No. [Cu(PnAO-H)(ReO_4)], 56804-74-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC503226-12-75.

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Crystal and Molecular Structure of Chlorobis(3-butenyldiphenylphosphino)rhodium(I)[1]

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The structure of chlorobis(3-butenyldiphenylphosphino)rhodium(I) has been determined by three-dimensional X-ray diffractometer techniques. The compound crystallizes in the space group $P2_1/c$ with cell constants of a = 10.697 (5) Å, b = 9.832 (5) Å, c = 36.44 (2) Å, and β = 96.42 (3)°; Z = 4. The structure, solved by heavy-atom techniques, was refined by full-matrix least-squares methods using the 4218 reflections which had intensities 3σ above background to an unweighted R value of 5.1%. The coordination around the Rh(I) atom is best described as trigonal bipyramidal with one phosphorus and the midpoints of the two olefinic groups forming the equatorial plane which lies 0.13 Å toward the Cl atom from Rh(1). In spite of the different geometric constraint imposed by the butenyl chains, both olefinic groups lie in the equatorial plane (within 8.5°). This phenomenon and the placement of the best π acceptor in the equatorial plane are interpreted in terms of a synergetic cooperation between the π and σ bonding in this plane.

Introduction

Several transition metal complexes containing bidentate ligands in which one donor is a group 5 or 6 atom and the other an olefin have been prepared and a few reactions involving the olefin have been reported.[2,3] The chelate effect offers the opportunity to study weak metal–olefin interactions and the significance of these interactions in the mechanism of catalytic hydrogenation.

During studies concerning rhodium(I) species as homogeneous catalysts, the reaction of $(C_6H_5)_2PCH_2CH_2CH{=}CH_2$ with $[Rh(C_2H_4)_2Cl]_2$ in diethyl ether at room temperature yielded yellow-orange, air-stable crystals of $RhCl[(C_6H_5)_2PCH_2CH_2CH{=}CH_2]_2$. The infrared spectrum of this compound in methylene chloride has an absorption corresponding to unbonded olefin ($\nu_{C=C}$ 1642 cm^{-1}) in addition to an absorption at 1505 cm^{-1}, assigned as a C–H bending frequency, typical of metal–olefin bonding. In the solid state, however, the spectrum suggests that all olefins are coordinated. The complex is monomeric in chloroform and was thought to be four-coordinate in solution and five-coordinate in the solid state, with each olefin occupying a coordinate site.

The steric requirements of the bidentate ligand $(C_6H_5)_2PCH_2CH_2CH{=}CH_2$ are best met with a 90° angle, P–

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