Inorg. Chem. **1990**, *29*, 4831-4833

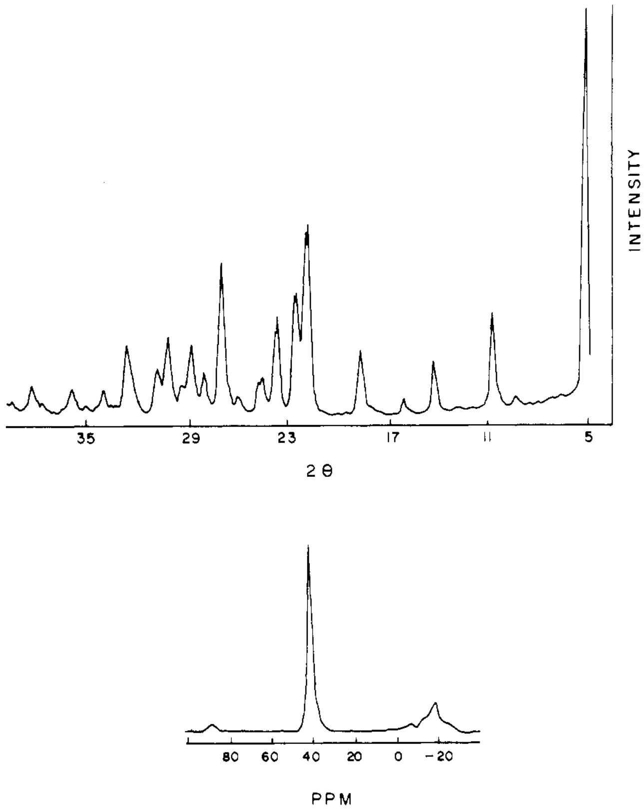

Figure 1. XRD pattern and ^{27}Al MASNMR spectrum of VPI-5.

common for both syntheses and the end products should therefore have the same identity.

Experimental Section

VPI-5 was synthesized by using *n*-dibutylamine as the template.

XRD patterns were recorded with a PW 1730 Philips instrument using nickel-filtered Cu Kα radiation. MASNMR spectra were recorded in the solid state with a Bruker MSL 300 spectrometer operating at a field of 7 T. ^{27}Al MASNMR spectra were run at 78.2 MHz, with a pulse length of 2 μs, a pulse interval of 500 ms, and a spinning speed of 3–5 kHz. The chemical shift was measured relative to aqueous $AlCl_3$ solution.

Samples of VPI-5 were calcined at different temperatures (388–773 K) in dry nitrogen or vacuum.

Results and Discussion

The VPI-5 sample, as synthesized, was air-dried and its identity confirmed by XRD and ^{27}Al MASNMR measurements. The XRD pattern matches closely with that reported;[5] the ^{27}Al MASNMR spectrum shows the presence of tetrahedrally and octahedrally coordinated Al in the ratio 2:1 (Figure 1).

Figure 2A shows the XRD pattern and ^{27}Al MASNMR spectrum of the sample calcined at 773 K. The former matches closely with the data reported for $AlPO_4$-8.[2] The MASNMR spectrum is devoid of the signal attributed to octahedral coordination of Al(VI), and it now shows only the Al(IV) signal at ~40 ppm characteristic of all $AlPO_4$ materials. The observations were identical with respect to samples calcined at intermediate temperatures. In the light of this study, it is suggested that the changes in the ^{31}P MASNMR spectra of VPI-5 on calcination reported by Grobet et al. may be associated with the transformation to $AlPO_4$-8. Recently, Davis et al. have examined $AlPO_4$-8 and shown that it is a distinct phase.[6]

A sample of VPI-5 after calcination at 773 K was cooled in dry atmosphere and exposed to moisture for rehydration. Figure 2B shows the XRD pattern and ^{27}Al MASNMR spectrum of the sample. The XRD pattern shows a shift in the *d* values and also a reduction in the peak intensity at d = ~16 Å. The multiple resonance maxima of the Al(IV) peak may be explained as being due to aluminum atoms in different crystallographic sites.[7] Rehydration also restores the Al(VI) peak in the MASNMR spectrum. These changes in the spectra may be interrelated and indicative of transformation of Al(IV) to Al(VI).[3a]

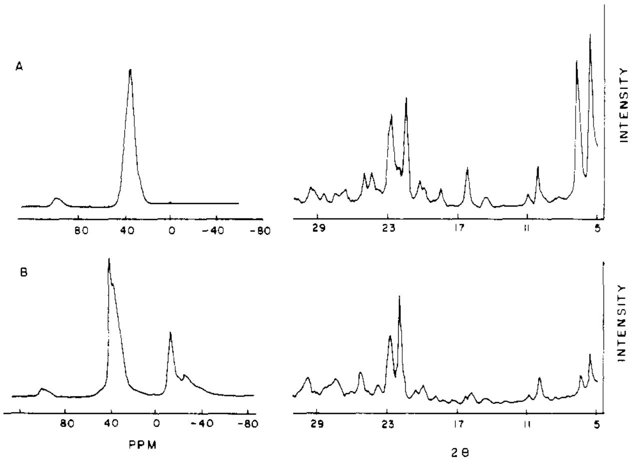

Figure 2. (A) XRD pattern and ^{27}Al MASNMR spectrum of calcined VPI-5 at 773 K in dry nitrogen. (B) XRD pattern and ^{27}Al MASNMR spectrum of calcined rehydrated VPI-5.

The effect of calcination and rehydration of the sample can be schematically represented as follows:

$$\text{VPI-5} \xrightarrow[-H_2O]{\text{heat}} AlPO_4\text{-8} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} AlPO_4\text{-8 (hydrated)}$$

It is significant to note, in this context, that there has been, as yet, no publication outside of the patent report on the synthesis of $AlPO_4$-8. If this fact is taken along with our observations, the conclusion that VPI-5 is only a precursor to $AlPO_4$-8, to which it transforms irreversibly upon calcination, seems justified. This would, of course, mean that the largest pore molecular sieve (VPI-5) was originally synthesized by Flanigen et al., who missed identifying it because the product was dried at 388 K!

Acknowledgment. We thank Dr. P. Rajamohanan for the MASNMR experiments and Dr. P. Ratnasamy for helpful discussions. S.P. thanks the CSIR for a fellowship.

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Molecular Structure of $Ru(CO)_3Cl_2H_2O$·Diglyme: Hydrogen Bonding of Diglyme to Coordinated Water

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During the course of an investigation of the reactions of ruthenium carbonyl chlorides adsorbed on metal oxide surfaces,[1] we obtained crystals of the complex $Ru(CO)_3Cl_2H_2O$-diglyme (**1**). This complex serves as a simple model for the structure of the surface species $Ru(CO)_3Cl_2$(surface).[1] The complex is also unique since water as a ligand in 18e organometallic complexes is rare. The recent report of water bound to iridium in $[IrH_2$-

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[1] Bergmeister, J. J., III; Hanson, B. E. *Inorg. Chem.* **1990**, *29*, 4055.

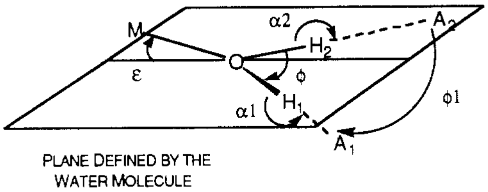

Figure 1. Parameters for coordinated water molecules after Ferrais and Franchini-Angela.[3]

$(THF)(H_2O)(PPh_3)_2]SbF_6{\cdot}THF$[2] prompts us to report the structure of **1**.

The structural characterization of water coordinated to transition metals has, for the most part, been confined to ionic complexes.[3] Water in crystals is always observed to form hydrogen bonds to an appropriate hydrogen bond acceptor in the crystal.[4] The geometry of oxygen in water coordinated to a single metal ion has been found to vary from pyramidal with nearly tetrahedral angles to trigonal planar with the metal atom in the same plane as the water molecule.

Recently water has found application as a solvent for some novel catalytic systems.[5] As noted above, one of the few organometallic complexes in which water acts as a ligand that has been structurally characterized is the hydrido aquo complex $[IrH_2(THF)(H_2O)(PPh_3)_2]SbF_6{\cdot}THF$.[2] This complex is unique in that it has both hydride and water as ligands. An unusual feature of this structure, as noted by the authors, is the apparent planar nature of both coordinated water and THF; although the hydrogen atoms in water could not be located directly, their position was inferred from the position of the hydrogen bond acceptor groups. The hydrogen atoms of the water molecule in **1** could be found by X-ray crystallography, and in contrast to the iridium complex, the water ligand is distinctly pyramidal.

Some of the structural features of interest in complexes of coordinated water are evidence for hydrogen bonding of the coordinated water, the degree of planarity of the $M{-}OH_2$ group, and the hydrogen bond angle at hydrogen.[3] Coordinated water is typically found to be hydrogen bonded through both hydrogen atoms to acceptor groups, A. Bond distances are the best direct evidence for hydrogen bonding; the distances of interest in the unit, M–O–H···A, where A is the hydrogen-bond acceptor, are d_{O-A} and when available d_{H-A}. Planarity of the $M{-}OH_2$ group is best measured by the angle, ϵ, that the M–O vector makes with the OH_2 plane. A review of structures that contain trigonally bound water reveals that ϵ varies from 0° in planar systems to 54.6° (approximately half the expected tetrahedral angle) in fully pyramidal systems.[3] The H–O–H angle, ϕ, is typically in the tetrahedral range, 103–115°, and is taken as a measure of the hybridization at oxygen. The O–H···A angle, α, for hydrogen-bonded systems varies from 155° to 180°. In the absence of a structurally determined hydrogen atom position, an assumption about this bond angle must be made to locate reasonable positions for the hydrogens. These parameters are defined pictorially in Figure 1.[3]

Experimental Section

Crystals of $Ru(CO)_3Cl_2H_2O{\cdot}$diglyme were grown from wet diglyme solutions of $[Ru(CO)_3Cl_2]_2$.[6] A nearly colorless crystal of dimensions 0.3 × 0.3 × 0.3 mm was mounted in epoxy at the end of a glass fiber. Indexing and data collection were performed on a Nicolet R3m/V diffractometer with Mo Kα radiation at −119 °C. The unit cell based on the least-squares fit of 25 reflections with $15° < 2\theta < 30°$ was determined to be a = 9.453 (9) Å, b = 15.312 (13) Å, c = 11.075 (16) Å, V = 1603 Å^3.

Table I. Crystal Data for **1**

$C_9H_{16}O_7Cl_2Ru$
a = 9.453 (9) Å
b = 15.312 (13) Å
c = 11.075 (16) Å
V = 1603 (3) Å^3
Z = 4
R_1 = 0.029
R_2 = 0.033
fw = 408.2
space group: *Pnma*
T = −119 °C
λ = 0.71073
ρ_{calcd} = 1.691 g cm^{-3}
μ(Mo Kα) = 1.315 mm^{-1}
transm = 0.7808–0.9571

Table II. Atomic Coordinates (×10^4)

	x	*y*	*z*
Ru(1)	2400 (1)	2500	1131 (1)
C(1)	2206 (5)	2500	2829 (4)
Cl(1)	4160 (1)	1392 (1)	1400 (1)
O(3)	2979 (4)	2500	−704 (3)
O(2)	263 (3)	3955 (2)	704 (3)
C(2)	1043 (4)	3403 (3)	880 (3)
O(5)	2439 (3)	969 (2)	−1839 (2)
C(3)	1250 (4)	1735 (2)	−3401 (3)
O(4)	2041 (4)	2500	−3200 (3)
C(4)	2151 (4)	960 (2)	−3097 (3)
C(5)	3165 (5)	208 (2)	−1459 (4)
O(1)	2270 (4)	2500	3850 (3)
H(3B)	395	1725	−2835
H(3A)	856	1717	−4210
H(4B)	2998	948	−3606
H(4A)	1566	454	−3247
H(5C)	3935	150	−1907
H(5B)	3456	288	−834
H(5A)	2639	−210	−1592
H(1)	2812 (51)	2059 (28)	−1017 (43)

Table III. Selected Distances (Å) and Angles (deg)

Ru(1)–C(1)	1.889 (5)	Ru(1)–Cl(1)	2.395 (3)
Ru(1)–O(3)	2.105 (4)	Ru(1)–C(2)	1.905 (5)
O(3)···O(5)	2.710 (5)	O(3)–H(1)	0.77 (5)
C(1)–Ru(1)–Cl(1)	86.8 (1)	C(1)–Ru(1)–O(3)	170.5 (2)
Cl(1)–Ru(1)–O(3)	86.5 (1)	C(1)–Ru(1)–C(2)	94.6 (2)
Cl(1)–Ru(1)–C(2)	178.0 (1)	O(3)–Ru(1)–C(2)	92.0 (1)
C(2)–Ru(1)–Cl(1A)	88.4 (1)	Cl(1)–Ru(1)–Cl(1A)	90.2 (1)
C(2)–Ru(1)–C(2A)	93.0 (2)	H(1)–O(3)–H(1A)	121 (7)

Data were collected at 152 K by the $\theta{-}2\theta$ scan technique in the range 3.5–55°. The scan rate varied with peak intensity, 10.1–19.5°/min. Three standard reactions were measured after every 200 reflections and showed no loss in intensity during data acquisition. A total of 5235 reflections were collected of which 1915 were independent (R_{int} = 2.25%). Of the independent reflections, 1790 had $F > 3\sigma(F)$; these reflections were used to determine the structure. The absorption coefficient, μ, for Mo Kα radiation was calculated to be 1.32 cm^{-1}; a semiempirical absorption correction was made. The minimum and maximum transmissions through the crystal were calculated to be 0.7808 and 0.9571 respectively. The crystal and refinement parameters are summarized in Table I, a more complete table is available with the supplementary material (Table S1).

All calculations were performed on a MicroVAX II with the SHELXTL PLUS crystallographic package provided by Nicolet. Neutral-atom scattering factors were obtained from the standard source, and the effects of anomalous dispersion were included in F_c.[7] The heavy atoms, ruthenium and chlorine, were located by direct methods. Refinement was accomplished by full-matrix least-squares methods to minimize the function $\sum w(F_o - F_c)^2$. Unit weights were used. The hydrogen atom bound to oxygen was found in an electron density difference map and refined so that esd's could be included with bonding parameters for this hydrogen; the hydrogen atom positions of diglyme were calculated and added to the refinement. The diglyme hydrogen atoms were refined with the riding model provided with the Nicolet software package with fixed isotropic thermal parameters, U. The final residuals were R_1 = 0.029 and R_2 = 0.033. Atomic coordinates are compiled in Table II. Atomic displacement parameters are available as Supplementary Material (Table

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Table IV. Parameters for Coordinated Water As Defined by Ferraris and Franchini-Angela^{a}

structure	d_{M-O}, Å	d_{O-H}, Å	d_{O-A_1}, Å	d_{O-A_2}, Å	ϕ, deg	$\phi1$, deg	$\alpha1$, deg	$\alpha2$, deg	ϵ, deg
18e Complexes									
1	2.105	0.77	2.71	2.71	121	119.8	178	178	39.6
$Ir(H_2O)^{b}$	2.258	na	2.73	2.92	na	90.1	180 (est)	180 (est)	16.7
Ionic Complexes^{c}									
$K_2CuCl_4(H_2O)_2{}^{d}$	1.972	0.956	3.116	3.116	109.7	100.3	173.3	173.3	0.1
$Mn(HCO_2)_2(H_2O)_2{}^{e}$	2.208	0.983	2.711	2.764	109	113.9	158	178	54.6
obsd range^{a}		0.86–1.00	2.6–3.2		103–115	71–147	130–179	130–179	0–54.6

^{a}Reference 3. $^{b}[IrH_2(H_2O)(THF)(PR_3)_2]^{+}$.[2] Hydrogen positions not determined; ϵ based on O, A_1, A_2 plane. ^{c}The ionic complexes shown for comparison are representative of planar and pyramidal geometry at oxygen. ^{d}Reference 10. ^{e}Reference 9.

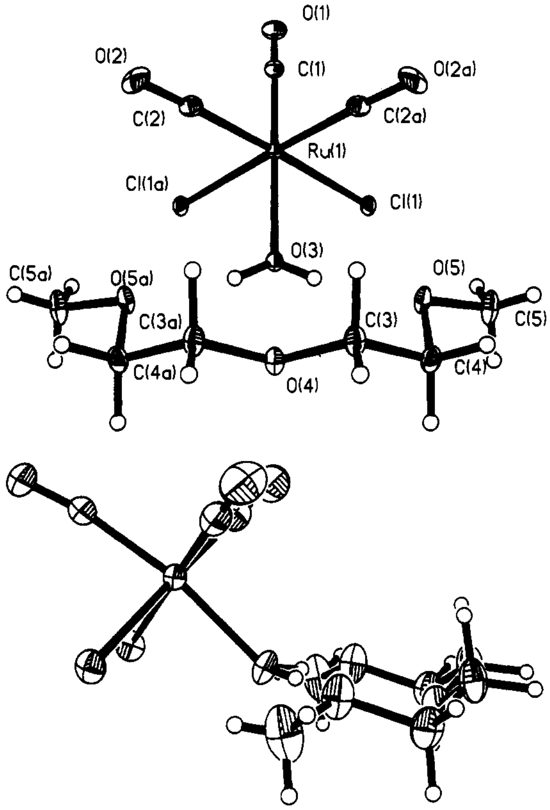

Figure 2. Thermal ellipsoid plots for two orientations of compound **1**. The view shown in part a (top) is a projection onto the Cl(1), Cl(1a), C(1) plane and defines the atomic numbering scheme. Part b (bottom) shows a "side-on" view of the molecule and illustrates that diglyme, Cl(1), Cl(1a), and O(3) are essentially coplanar.

S2). Selected bond distances and angles are given in Table III.

Results and Discussion

The molecular geometry and atomic numbering scheme for **1** are shown in Figure 2. The coordination geometry at ruthenium is octahedral, and the three carbonyl ligands are arranged facially. It has been suggested that adducts of the type $Ru(CO)_3Cl_2L$ may exist as both the facial or meridinal isomers.[8] No evidence for the meridinal form of **1** was obtained by IR either in solution or in the solid state as a KBr pellet. In the solid state the molecule occupies a site of mirror plane symmetry that includes Ru, O(3), C(1), and O(4) and bisects the Cl–Ru–Cl angle.

The parameters that define a hydrogen-bonded water (vide supra) are evaluated in Table IV for **1**, $[IrH_2(THF)(H_2O)(PPh_3)_2]SbF_6 \cdot THF$, and two representative coordination complexes, $K_2CuCl_4 \cdot 2H_2O$[9] and $Mn(O_2CH)_2 \cdot 2H_2O$[10] for which the geometry of coordinated water was determined by neutron diffraction. The O–H bond distance in **1** is 0.77 Å; this is shorter than observed in structures that were determined by neutron diffraction. However it is well-known that X-ray diffraction underestimates bond distances to hydrogen. The H–O–H bond angle is larger than typically observed for coordinated water in coordination complexes. For **1** the position of the hydrogen atoms on water is dictated in part by the presence of diglyme. The H–O–H angle is nearly identical with the O(5)···O(3)···O(5a) angle. The value of ϵ in **1** is 39.6; thus, the water molecule is nearly pyramidal. An ϵ value of 54.7° is expected for tetrahedral oxygen. The corresponding value for ϵ in $[IrH_2(THF)(H_2O)(PPh_3)_2]SbF_6 \cdot THF$ is 16.7°. It should be noted though that the latter value is based on the position of the acceptor atoms F and O and not the position of the hydrogen atoms since the hydrogens were not located.

Bond angles at two-coordinate oxygen atoms in silicate materials vary from 130 to nearly 180°.[11] Thus oxygen is quite flexible in its bonding capabilities, and to understand the bonding of oxygen in terms of hybridization, it is apparent that anything from sp^3 to sp hybridization at oxygen is possible. The high-pressure polymorph of silica, Stishovite, contains planar three-coordinate oxygen. Electron density mapping locates nonbonding electron density above and below the OSi_3 plane consistent with an sp^2 model for hybridization for trigonal-planar oxygen.[12]

Water coordinated to metals is best regarded as a two-electron donor regardless of whether it is planar or tetrahedral. However a planar water molecule does have the capacity to act as a two-electron π donor in a similar fashion to a halide; it is never suggested that terminally bonded halides in organometallic compounds contribute more than two electrons to the metal.

The function of the diglyme in **1** is to provide a hydrogen-bond acceptor for the coordinated water molecule. Thus the diglyme adopts a conformation that directs O(5) and O(5a) toward the protons of the coordinated water. In this conformation, diglyme has the appearance of a fragment of a cyclic polyether. Cyclic polyethers are well-known to behave as hydrogen bond acceptors. For example, 18-crown-6 complexes of quaternary amines have been structurally characterized and show the presence of N–H···O hydrogen bonds.[13] The O···O distance in **1** is 2.71 Å, which is in the range normally found for hydrogen-bonded water molecules. The hydrogen bonding and the crystal lattice serve to stabilize a conformation of diglyme that is not minimized with regard to intramolecular contacts.

Acknowledgment. Funds to purchase the X-ray diffractometer were provided by the State of Virginia. Partial support was provided by the NSF.

Supplementary Material Available: Tables S1 and S2, listing complete data acquisition and crystal parameters and thermal parameters for all atoms (4 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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