Table V. Effect of Varying Concentration of Substrate at Different Temperatures[a]

temp, °C	$10^3 \times$ $[N_2H_5^+]$, M	$10^4 \times$ k_{obsd}, s^{-1}	$10^4 \times$ k_{calcd}, s^{-1}	% error
30	3	1.12	1.10	−2.0
	4	1.31	1.32	+0.5
	5	1.51	1.50	−0.3
	6	1.65	1.66	+0.6
	7	1.77	1.78	+0.9
	8	1.88	1.89	+0.6
	10	1.98	2.07	+4.7
	14	2.44	2.32	−4.8
35	2	0.98	0.99	+1.2
	3	1.44	1.37	−4.5
	4	1.75	1.70	−2.6
	5	1.92	1.98	+3.1
	6	2.19	2.23	+1.6
	8	2.59	2.64	+1.7
	10	2.97	2.96	−0.4
40	2	1.27	1.29	+1.7
	3	1.92	1.82	−5.0
	4	2.34	2.31	−1.5
	5	2.69	2.74	+2.0
	6	3.14	3.13	−0.3
	8	3.84	3.82	−0.5
	10	4.49	4.39	−2.1
45	2	1.69	1.67	−1.6
	3	2.51	2.40	−4.4
	4	3.17	3.08	−2.7
	5	3.55	3.71	+4.4
	6	4.34	4.29	−1.1
	8	5.30	5.34	+0.7
	10	5.95	6.25	+5.1

[a] $[Ir(IV)] = 1.04 \times 10^{-4}$ M and $[H^+] = 1.0 \times 10^{-1}$ M.

behaves as a 1-equiv oxidant in the oxidations of some organic[7,8,18] and inorganic compounds.[19]

The rates are found to depend not on the nature of the anions of the added salts but on the ionic strength. Again, for a reaction between ions of opposite charge, the rate would decrease with an increase in ionic strength. The results obtained in this study are, therefore, not in conformity with what might be predicted from the Brønsted–Bjerrum relation based on the Debye–Hückel theory. Added salts often exhibit specific effects, and numerous apparent anomalies are known in the literature.[20–22] The anomalies may arise because of the ion pairing of the reactants in the reaction mixture. However, the equilibrium constant would be much smaller than that which has been obtained in this study, if the two ions associate by electrostatic interactions. Consequently, the ion pairing between the reactants may not take place. Alternatively, it may be that the activitiy coefficient of the activated complex is very much different[23] from that given by the simplifying assumption of the Debye–Hückel theory and hence opposite results are not unexpected.

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Registry No. $N_2H_5^+$, 18500-32-8; $IrCl_6^{2-}$, 16918-91-5.

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Oxygen-17 Nuclear Quadrupole Resonances in Molecular Oxygen Reversibly Bonded to Iridium Carrier

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A proton nuclear magnetic double-resonance technique has been used to detect the pure nuclear quadrupole resonances of $^{17}O-^{17}O$ reversibly bonded to Vaska's iridium compound, $IrO_2Cl(CO)(P[C_6H_5]_3)_2$. Two sets of lines are observed, corresponding to $e^2qQ = 16.9$ MHz with $\eta = 0.7$ and to $e^2qQ = 15.6$ MHz with $\eta = 0.9$. The inequivalence of the charge distributions about each O atom which is revealed by these results, and which is not evident in the X-ray internuclear distances, may provide new insight into the mechanism of reversible oxygen bonding.

Introduction

In recent years some efforts to understand the electronic structure of the reversible dioxygen bond in the proteins hemoglobin and myoglobin have focused on relatively small synthetic transition-metal compounds which also combine reversibly with one molecule of oxygen.[1] An early member of this class is Vaska's iridium compound[2] whose crystal structure determination[3] confirmed that the dioxygen bond

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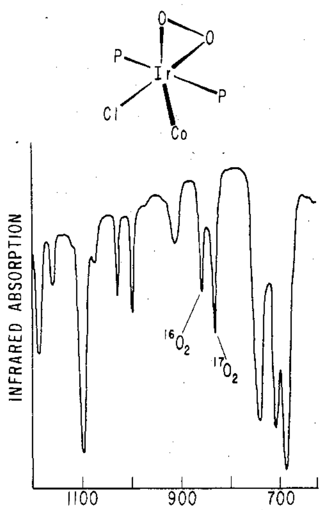

Figure 1. Upper: oxygen-binding site in Vaska's iridium molecule, $IrO_2Cl(CO)[P(C_6H_5)_3]_2$. The three phenyl groups attached to each P atom are not shown. Ir, O(1), O(2), CO, and Cl atoms are coplanar, and the P atoms are at nearly perpendicular distances above and below the plane. Br may be substituted for the Cl ligand. See Figure 1 in ref 3 for a complete perspective drawing. Lower: a portion of the $IrO_2Cl(CO)[P(C_6H_5)_3]_2$ infrared absorption spectrum (solid) showing $^{16}O_2$ and $^{17}O_2$ stretching peaks at about 858 cm^{-1}.

Table I. ^{17}O Pure Nuclear Quadrupole Resonance Frequencies in Vaska's Iridium Compound, $IrO_2Cl(CO)[P(C_6H_5)_3]_2$[a]

$^1/_2 \leftrightarrow {}^3/_2$	$^3/_2 \leftrightarrow {}^5/_2$	e^2qQ	η
3.50	4.70	16.9	0.65
3.89	4.20	15.6	0.91

[a] Transition frequencies and e^2qQ are in MHz. The coupling constants (e^2qQ) are probably too large for conventional ^{17}O NMR spectroscopy. An attempt to detect ^{17}O-free induction decay at 8.1 MHz (chloroform solvent) failed.

has the side-on coordination that Griffith proposed for oxyhemoglobin[4] (see Figure 1). We report here the pure nuclear quadrupole resonance (NQR) spectrum of ^{17}O–^{17}O bonded to Vaska's compound (Figure 2 and Table I). This work supplements the X-ray data in revealing that the charge distributions about each O atom differ significantly. This is also the first observation of NQR in a species of molecular oxygen and, in this case, may help provide a sensitive test for theoretical models of the reversible bond.

Experimental Section

Crystalline samples of the deoxygenated compound were prepared according to Vaska.[2] The yellow crystals were then dissolved in chloroform and stirred for several hours in a sealed atmosphere of oxygen gas (90% ^{17}O enrichment) at about 100 mm pressure. The chloroform was then slowly evaporated at about −15 °C, and the orange crystals of the oxygenated compound were washed and stored under vacuum in sealed tubes at 77 K. Compounds with both chloride and bromide ligands (Figure 1) were prepared. $^{17}O_2$ uptake was confirmed by recording the infrared absorption spectrum (Figure 1) which exhibits an O–O stretching line at about 858 cm^{-1}.[1]

The ^{17}O–^{17}O NQR spectrum was obtained with a double-resonance technique[5-7] which may be schematized as follows. The protons of the sample are first polarized in a large static magnetic field. The magnetic field is then adiabatically turned off in a time which is short compared to the proton spin–lattice relaxation time. The spin–spin ordering of the protons is now very large, but a phase-modulated radio-frequency field at frequency ν_B applied in zero field will continuously decrease the proton spin order when ν_B matches an ^{17}O quadrupole transition. This occurs through the dipolar spin interaction between ^{17}O and nearby proton spins. The loss in proton order is observed by adiabatically remagnetizing the protons and exciting a proton-free induction signal with a resonant radio-frequency pulse. The frequency ν_B of the phase-modulated field is then advanced and the cycle is repeated to record the entire quadrupole resonance spectrum. Double-resonance cross-relaxation between ^{17}O and proton spins may also be excited in small, nonzero, magnetic fields, but in zero field the quadrupole transition frequencies are uniquely determined by molecular electric field gradients, and broadening of transitions by the magnetic field is absent.

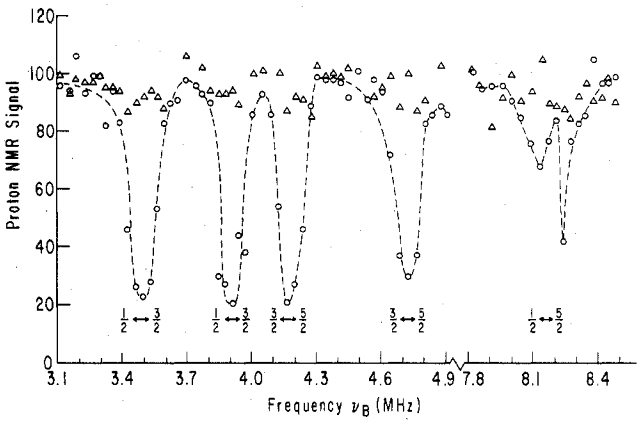

Figure 2. Pure nuclear quadrupole resonances of ^{17}O–^{17}O ($I = {}^5/_2$, 90% enrichment) reversibly bound to a synthetic iridium molecule, $IrO_2Cl(CO)[P(C_6H_5)_3]_2$. There are three resonances for each O atom, corresponding to $\nu_{1/2\leftrightarrow3/2}$, $\nu_{3/2\leftrightarrow5/2}$, and the weakly allowed sum transition $\nu_{1/2\leftrightarrow5/2}$. Resonances were observed at 4.2 K in about 50 mg of polycrystalline powder with a proton nuclear magnetic double-resonance technique. Triangles correspond to irradiation in zero applied magnetic field at frequency ν_B without phase modulation; open circles correspond to irradiation with a 180° phase shift every 833 μs. In both cases the magnitude, H_1, of the irradiating field was about 18 G, and the irradiation time was 0.4 s. The spectrum is only slightly changed (±10 kHz) when Br is substituted for the Cl ligand (see Figure 1), and no resonances have been detected in a sample with natural-abundance ^{17}O.

Results and Discussion

^{17}O, with a nuclear spin $I = {}^5/_2$, has two allowed quadrupole resonance transitions in zero magnetic field, which may be denoted by use of magnetic quantum numbers as $\nu_{5/2\leftrightarrow3/2}$ and $\nu_{3/2\leftrightarrow1/2}$, with $\nu_{3/2\leftrightarrow1/2} \leq \nu_{5/2\leftrightarrow3/2}$. From these transition frequencies, the coupling constant e^2qQ/h and the electric field gradient asymmetry parameter η can be determined.[8] An additional transition $\nu_{5/2\leftrightarrow1/2}$, which is the sum of $\nu_{5/2\leftrightarrow3/2}$ and $\nu_{3/2\leftrightarrow1/2}$, is forbidden for an axially symmetric electric field gradient ($\eta = 0$) but allowed for $\eta \neq 0$. This transition has been observed here and is the basis for the identification of the transitions listed in Table I.

The O–O internuclear distance in the Ir compound (1.30 Å) suggests a transfer of about one electron from Ir to the O_2 molecule,[1,3] and the large asymmetry in the charge distributions about each O atom, as evidenced by the parameters η (Table I), is consistent with the added charge residing mainly in a π^* O_2 orbital. However, while Ir–O bond lengths show two oxygen atoms equidistant from the iridium atom,[3] the asymmetry parameters η indicate a significant difference in the symmetry of the charge distributions about the two oxygens. The same inequivalence may also be evident in the X-ray electron density contours.[3] While different bonding between iridium and its carbonyl and chloride ligands (Figure 1) could account for the inequivalence, arguing against this are the following: (i) the NQR spectrum is unchanged (within ±10 kHz) when bromide is substituted for chloride[9] and (ii) significant asymmetry is evident in the electron density contours even though the Cl and CO ligands randomly occupy their positions in the crystal.[3] We suggest then that the inequivalence is due primarily to unequal charge-transfer interactions between the O atoms and a nearby phenyl ring. The orientation and distance of one ring[10] appears to allow some overlap between oxygen orbitals and the ring's π orbital.

Two distinct measures of electronic structure have been known for the iridium–dioxygen bond: the O–O and O–Ir internuclear distances[3] and the O–O stretching frequency.[1] We have now added a third, the ^{17}O nuclear quadrupole resonances. Taken together, these experimental observations may decide whether the π-bonding model of Griffith[4] or the two-electron oxidative addition model of Gray[11] is the better formulation of the reversible O_2 bond in this system. Whether the inequivalence of the oxygen atoms' charge distributions is incidental or essential to reversible bonding is also an interesting question that similar experiments on other synthetic oxygen carriers may help answer.

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Registry No. $Ir(^{17}O{=}^{17}O)Cl(CO)(P[C_6H_5]_3)_2$, 35599-61-2.

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Oxygen-17 Nuclear Magnetic Resonance Spectra of Certain Oxomolybdenum(VI) Complexes and the Influence of the Multiplicity of the Mo–O Bond

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The line widths and the paramagnetic chemical shifts of the ^{17}O NMR signals for a series of mononuclear oxomolybdenum(VI) complexes are discussed. The chemical shifts are shown to be related to both the force constants for Mo–O stretching vibrations and the Mo–O bond distances. These relationships are attributed to a dependency of the chemical shift on the π-bond order of these bonds. In addition, enrichment of the complexes with both ^{17}O and ^{18}O has allowed a complete confirmation of some previous assignments of Mo–O stretching frequencies.

Introduction

Complexes of molybdenum are dominated by the presence of oxo ligands when that metal is in its higher oxidation states.[1,2] To a large degree, the stability of the Mo–O fragments is undoubtedly due to extensive multiple bonding between the constituent atoms which is indicated by the short Mo–O bond distances[1,2] and the large stretching force constants.[3] The possible importance of these fragments in the chemistries of the molybdo enzymes has been recognized.[1,4] Because of the prevalence of the oxo ligand, we have undertaken a study of the ^{17}O NMR spectra of simple, diamagnetic complexes as a complement to their known chemistries. The advent of Fourier transform techniques and convenient methods for ^{17}O enrichment from readily available sources remove many of the earlier difficulties experienced in ^{17}O NMR spectroscopy. These advantages are mitigated somewhat by the ever-present quadrupole moment of the ^{17}O nucleus which will result in a broadened NMR resonance when the electron distribution about the oxygen atom is not symmetric. Unless the molybdenum atom is at a site of cubic symmetry, the large[5] quadrupole moments of ^{95}Mo ($I = {}^5/_2$, 15.7%) and ^{97}Mo ($I = {}^5/_2$, 9.5%) can also induce efficient relaxation at an ^{17}O nucleus which will cause further broadening of the ^{17}O NMR resonance. Nevertheless, Klemperer and his colleagues have shown[6] with condensed molybdates that usable NMR signals can still be obtained and that the ^{17}O chemical shifts are related to the types of oxo ligands in the molecule. The present study of oxomolybdenum(VI) complexes is concerned principally with empirical observations about the influence of multiple bonding within a Mo–O fragment on the chemical shifts of the ^{17}O NMR signal.

Table I. Chemical Shifts and Line Widths

complex	^{17}O, %	chemical shift,[a] ppm	$\Delta\nu_{1/2}$, Hz
$MoO_4{}^{2-}$	5	$532 \pm 1^{b,c}$	
$MoO_3(NTA)^{3-}$	1.5	$701 \pm 2^{b,d}$	81 ± 10
$MoO_3(IDA)^{2-}$	1.5	$698 \pm 2^{b,e}$	155 ± 10
$MoO_2(Etcys)_2$	12	921 ± 5^{f}	1250 ± 60
	2	919 ± 5^{g}	790 ± 60
$MoO_2(Et_2dtc)_2$	27	975 ± 5^{f}	362 ± 15
$MoO_2(acac)_2$	2	1025 ± 5^{g}	400 ± 30
$MoOCl_2(Etdtc)_2$	27	948 ± 5^{f}	258 ± 15
$MoOBr_2(Et_2dtc)_2$	27	947 ± 5^{f}	212 ± 15

[a] Downfield from external $H_2{}^{17}O$. [b] Measured in enriched water. [c] pH 10. [d] pH 8.4. [e] pH 7.0. [f] Measured in CH_2Cl_2. [g] Measured in DMF.

Experimental Section

Materials. Chemicals were reagent grade and used without further purification. Enriched water was purchased from Monsanto Research Corp., Mound Laboratory. The isotopic composition was 25.2% ^{16}O, 43.4% ^{17}O, and 31.4% ^{18}O.

Preparation of ^{17}O-Enriched Complexes. The enrichment of $MoO_4{}^{2-}$ was accomplished by dissolving $Na_2MoO_4{\cdot}2H_2O$ in diluted ^{17}O-enriched water. Enriched samples of $MoO_3(NTA)^{3-}$ (NTA = nitrilotriacetate ligand) and $MoO_3(IDA)^{2-}$ (IDA = iminodiacetate ligand) were prepared by adding the requisite amount of ligand to a 0.9 M solution of $MoO_4{}^{2-}$ in enriched water. The acidity of the solutions was then adjusted. Calculated enrichment levels and the pH of these solutions are included in Table I. Enrichment of the carboxylate oxygen atoms will not occur under these conditions because their exchange with the solvent is slow.[7]

The complexes which were examined in organic solvents were enriched and isolated prior to the NMR measurement. All of these complexes were identified by their infrared spectra. An enrichment of approximately 2% was achieved with $MoO_2(Etcys)_2$ (Etcys = ethyl ester of the cysteinate ligand) and $MoO_2(acac)_2$ (acac = acetylacetonate ligand) from solutions of $MoO_4{}^{2-}$ and the ligand in diluted ^{17}O-enriched water. Highly enriched $MoO_2(Et_2dtc)_2$ (Et_2dtc = diethyldithiocarbamate ligand) was prepared by an unpublished method.[8] An extensively dried sample of $MoO_2(Et_2dtc)_2$ (0.5 g) was dissolved in 100 mL of dichloroethane which had been distilled from P_2O_5. To this solution, 0.075 mL of 43.4% ^{17}O-enriched water was