is also much lower than other hemes with an imidazole ligand. This small V could result from opposing contributions of the two axial ligands or more likely from a decrease in the Fe–imidazole interaction caused by the large trans influence of the cyanide ligand.

The orientation of the **g** tensor has been determined from ESR measurements by Peisach, Blumberg, and Wyluda[37] and by Hori,[26] and from NMR measurements by Shulman, Glarum, and Karplus.[38] The measurements by Peisach et al. appear to be consistent with the NMR measurements but differ drastically from those of Hori. Peisach et al. find that in the cyanide complex the *largest* g value in the heme plane corresponds to the projection of the imidazole ring on the heme plane (while for the azide complex Helckê et al. found that the smallest g value corresponds to the projection of the imidazole ring). Hori, on the other hand, found that the **g** tensor orientations of the azide, cyanide, and imidazole complexes of myoglobin are very similar.

Further analysis of the magnetic resonance data will require additional consideration of both the protein structural data and magnetic resonance data for small-molecule cyanide complexes. Although X-ray data for the complex are available,[39] we do not as yet have specific information on the orientation of the cyanide ligand. Preliminary results in this laboratory indicate that the cyanide ligand, unlike any of the other ligands discussed above, functions as a π acceptor. Complete **g** tensor determinations of several (porphinato)iron(III) cyanide complexes now in progress should provide additional insight.

Conclusions

Electron spin resonance **g** tensor determinations for a series of low-spin (tetraphenylporphinato)iron(III) thiolate complexes demonstrate that while the relationship between axial ligand orientation and the orientation of the principal axes of the **g** tensor is not intuitively obvious, it is in complete accord with a simple model of metal–ligand bonding. Crystal field analysis of the principal g values for the series of complexes gives an excellent correlation between the tetragonality of the complex (Δ) and the pK_a of the corresponding thiol. The rhombicity (V/Δ) is found to be essentially constant over a wide range of acid strengths.

The bright prospect that single-crystal ESR measurements could provide a detailed picture of the electronic structure of heme proteins has to some extent fallen under a shadow cast by a collection of confusing and apparently inconsistent results. The present investigation suggests, however, that with proper interpretation based on control experiments with well-characterized small-molecule analogues, a wealth of information is indeed available from such measurements.

Acknowledgment. This work was supported by a grant from the National Science Foundation (No. CHE 81-10285) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. (S-3-Me-1-Bu)(HS-3-Me-1-Bu)FeTPP, 85565-22-6; (SBzl)(HSBzl)FeTPP, 85565-23-7; $(SPh)_2FeTPP^-$, 77321-78-9; (S-*m*-Tol)(HS-*m*-Tol)FeTPP, 85565-24-8; (SPh)(HSPh)$FeNH_2TPP$, 85565-25-9; (SPh)(HSPh)FeTPP, 54959-14-7; ferricytochrome *c*, 9007-43-6.

Supplementary Material Available: A table of the X-ray and ESR data used to generate Figure 5 (6 pages). Ordering information is given on any current masthead page.

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^{17}O NMR as a Tool for Studying Oxygenated Transition-Metal Derivatives: First Direct ^{17}O NMR Observations of Transition-Metal-Bonded Peroxidic Oxygen Atoms. Evidence for the Absence of Oxo–Peroxo Oxygen Exchange in Molybdenum(VI) Compounds

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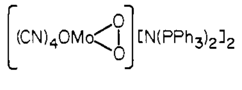
Abstract: The first high-resolution ^{17}O NMR observations of peroxidic oxygen atoms bonded to transition metals are reported for ^{17}O-enriched


$$\left[(CN)_4OMo\langle{}^{O}_{O}\right][N(PPh_3)_2]_2$$

as well as for nonenriched alkylperoxo derivatives of platinum. The chemical shifts of the oxo group in a series of Mo(VI) derivatives are also reported. The results are interpreted to evaluate the practicability of ^{17}O NMR as a tool to investigate the oxygen chemistry of the transition elements. In the case of the oxo–peroxo Mo(VI) derivative, direct ^{17}O NMR evidence is given that the oxo and peroxo groups do not exchange.

There exist a wide range of molecular transition-metal compounds containing oxygen atoms in their coordination sphere,[2] many of which are presently receiving considerable attention for their interest as reagents, catalysts, or key intermediates in selective

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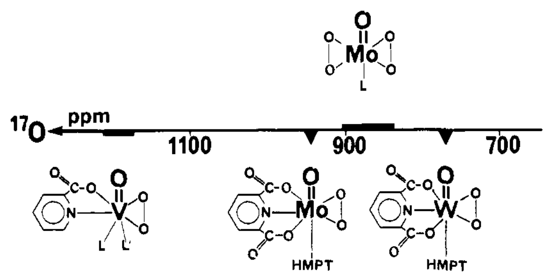
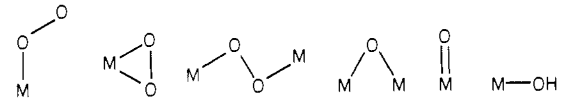


Figure 1. ^{17}O chemical shifts of the oxo group for oxoperoxometal (W, Mo, V) derivatives.

oxidations involving molecular dioxygen, hydrogen peroxide, and alkyl hydroperoxides as the source of oxygen. Others are studied in the hope of improving our understanding of biological oxygen transportation and oxidation processes.

Oxygen binding patterns I–VI can be obtained when dioxygen interacts with transition-metal complexes in low oxidation states.



superoxo I peroxo II μ-peroxo III μ-oxo IV oxo V hydroxo VI

All can be considered as potential sources of oxygen atoms liable to be transferred to reactive substrates.[3] Superoxo complexes (I) occur naturally in oxygen-carrying iron porphyrins; they are also involved in enzymatic monooxygenases. Peroxo (II) and μ-peroxo (III) metal derivatives are responsible for various selective oxidation reactions such as epoxidations (M = Mo, W, V, Ti, ...) or ketonizations (M = Rh, Pt, Pd, ...). They will be the prinicpal object of this paper.

Metal–μ-oxo complexes (IV) have been shown to be the active species in the oxidation of alcohols to ketones in the presence of copper, while oxo complexes (M = Cr, Mo, W, V, ...) (V) lead to epoxidation of olefins, oxidative cleavages, etc. Finally, hydroxo complexes (VI) are involved in Wacker-type oxidation processes (M = Pd).

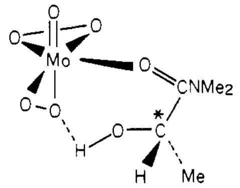
Although ligated oxygen is of such widespread importance in chemistry and has been the subject of numerous spectroscopic and crystallographic studies, it is only recently that ^{17}O has begun to be used to study transition-metal derivatives containing the I–VI moieties.[4-9]

The potentialities of ^{17}O as a structural NMR probe for investigating *oxo* and *μ-oxo* derivatives (IV and V) were first established in the chemistry of the polyoxyanions of the early transition elements. ^{17}O enrichment of the oxo group is easily obtained, and well-resolved ^{17}O NMR spectra can be measured. Thus ^{17}O NMR measurements performed on a large number of polymolybdates allowed Klemperer and co-workers[4] to construct a chemical shift scale for molybdenum-bonded oxygen, which shows a good correlation between the shielding of the ^{17}O nucleus and the number of molybdenum atoms bonded to oxygen. A similar trend was observed in polytungstates, polyniobates, polytantalates, and polyvanadates.[4]

More recently, the ^{17}O chemical shifts have been measured for a series of mononuclear mono-, di-, or trioxomolybdenum(VI) complexes: correlations have been established between these chemical shifts and both the Mo=O bond distance and the force constant of the Mo=O stretching vibrations.[5,6] ^{17}O NMR chemical shifts measured in complexes containing the $MoO_3{\cdot}L$ pattern were even found to be more sensitive than crystal structure distance determinations to the trans influence of ligand L.[7]

We have ourselves measured ^{17}O spectra on a series of oxo peroxo derivatives of the early transition metals.[8] The chemical shifts measured for the oxo resonance are reported in Figure 1. They were found to be closely dependent on the metal: the signals corresponding to the oxo oxygen atom in $MO(O_2)$(dipicolinate)·HMPA appear in the ^{17}O spectrum to be separated by more than 170 ppm when M = Mo (δ 946) or M = W (δ 772). The position of the oxo signal in the ^{17}O spectrum is also very sensitive to the metal's environment: when L is varied in $MoO(O_2)_2{\cdot}L$ derivatives, the Mo=O resonances were spread over a range of chemical shifts of more than 60 ppm.

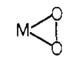
We also found that ^{17}O NMR spectroscopy was able to detect configurational differences in oxoperoxomolybdenum(VI) derivatives: the two diastereroisomers, which occur when both L and the metal are chiral, give distinct Mo=O signals in the ^{17}O spectra.[9]



However, all attempts that had been made previously to measure the resonance of the O_2 molecule in dioxygen—or *peroxo*—complexes of the transition metals (bonding patterns II or III) had failed. Despite the use of highly enriched $^{17}O_2$ (95%), no signal could be observed for either oxyhemoglobin or the Vaska type complexes $Ir(O_2)(CO)X(PY_3)$ (50% is $^{17}O_2$).[11,12] We were ourselves unable to detect any signal for the compounds $M(O_2)(PPh_3)_2$, M = Pt or Pd (10% $^{17}O_2$), even when recording the spectra on a high performance spectrometer.

This failure to observe signals in dioxygen adducts has been attributed in the case of the Ir complexes to extensive line broadening due to slow molecular tumbling.[11] We do not believe, in the case of $Pd(O_2)(PPh_3)_2$, that the correlation times of molecules of this size should be long enough to cause line broadening to such an extent that the ^{17}O signals become undetectable in the conditions we used.

The electric field around an oxygen atom "locked" in the



triangle is less symmetrical than it is around a terminal oxo-type (M=O) oxygen atom. The values of the nuclear quadrupolar constants, combined with the high-spin number, allow for the calculation of the line widths and show them to be ca. 2000 Hz for medium-sized molecules (vide infra): the lines should be easily detected.

Another possible source of line broadening could arise from the fact that these O_2 derivatives bind molecular oxygen reversibly, and that the resulting exchange between the complex and free molecular oxygen, which is paramagnetic, could indeed cause a dramatic broadening of the ^{17}O signal. To test this hypothesis, we turned to compounds **1** and **2**, where such an exchange is no longer possible.

This allowed us to observe, as reported here, the first high-resolution ^{17}O NMR resonances of peroxidic oxygen atoms bonded

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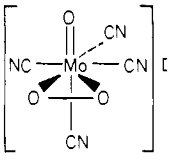

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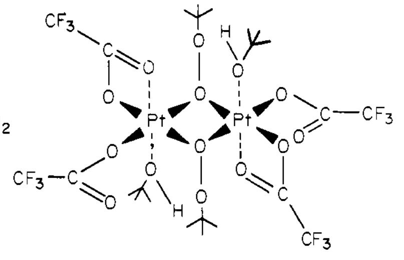
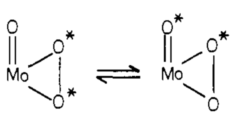


2

to transition metals. In regard to these experiments, we will discuss the feasibility, conditions of observation, and limitations of ^{17}O NMR as a tool for the study of peroxo groups, as compared to oxo groups.

We also illustrate one application of this technique in studies whose chemical implications are important to us, i.e., metal-catalyzed oxidations. The possibility of an exchange of oxo vs. peroxo oxygen:



has been proposed as a step in oxidation reactions based on early transition metal/hydroperoxide systems.[13] The results we report here exclude such an exchange in the case of compound **1**.

Experimental Section

Instrumentation. The ^{17}O and ^{95}Mo NMR spectra were obtained with a Bruker WM-400 spectrometer operating at 54.2 and 26.07 MHz, respectively.

The following operating conditions were used for all measurements: sweep width of 100 000 (^{17}O) and 70 000 Hz (^{95}Mo); delay time of 150 μs prior to data accumulation to eliminate pulse breakthrough; 90° radiofrequency pulse at 40 (^{17}O) and 45 μs (^{95}Mo). The data were accumulated with 2K data points in the time domain and transformed with optimal exponential multiplication of the FID (^{17}O, 50–200 Hz; ^{95}Mo, 5–50 Hz). The number of accumulated scans never exceeded 4.10^5 (ca. 2 h time).

Positive chemical shifts are taken downfield from the reference: H_2O for ^{17}O; 2 M MoO_4^{2-} solution in D_2O for ^{95}Mo.

The IR spectra were recorded on Perkin-Elmer 577 and Nicolet MX-S spectrometers.

Synthesis. Reagents. Labeled water (^{17}O, 10%) and molecular oxygen (^{17}O, 10%) were obtained from the Bureau des Isotopes Stables of the Commissariat ã l'Energie Atomique.

Preparation of Compounds for the NMR Study. Bis(triphenylphosphine)nitrogen(1+) oxo((^{17}O)peroxo)tetracyanomolybdate(VI) (**1**) was prepared in a manner analogous to the previously prepared ^{18}O isomer[14,15] using thoroughly degassed solvents and gaseous oxygen containing 11.36 atom % ^{17}O and 20.16 atom % ^{18}O. Oxodiperoxomolybdenum(VI) derivatives MoO_5·L were prepared by the method of ref 16.

Results

We synthesized compound **1**, which contains both an *oxo* and a *peroxo* ligand, in its peroxo-only ^{17}O-labeled form (10% $^{17}O)_2$. Its ^{17}O spectrum measured at 273 K on a 8 × 10^{-2} M solution in CH_2Cl_2 is shown in Figure 2. After only ca. 15 min of recording time a broad signal ($\Delta\nu_{1/2}$ = 1800 Hz) is already well detected in the spectrum at 487 ppm from H_2O (Figure 1a; 45 000 scans); we assign this to the two equivalent ^{17}O-enriched *peroxidic* oxygen atoms.

Subsequently, the addition of 2 molar equiv of 10% ^{17}O-enriched water, which is known to yield immediate labeling of the oxo group,[17] caused a second signal to appear in the ^{17}O spectrum as a sharp line ($\Delta\nu_{1/2}$ = 80 Hz) at 705 ppm (Figure 2b). This latter value is well within the range of chemical shifts usually observed for terminal oxomolybdenum (VI) groups.[4,5,8]

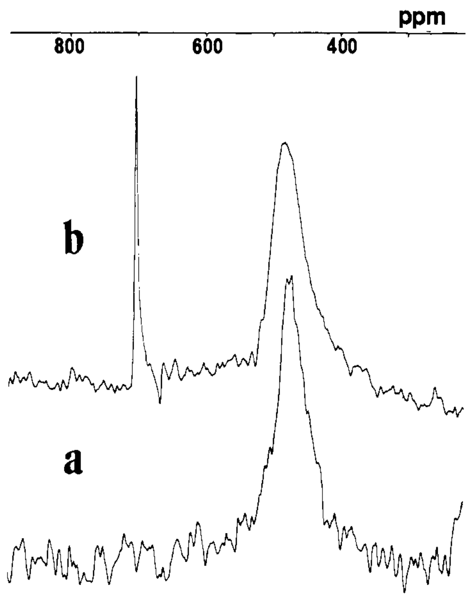
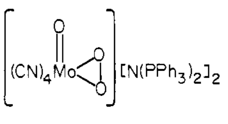


Figure 2. ^{17}O NMR spectra measured on a 80 × 10^{-2} M CH_2Cl_2 solution of



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(a) when the peroxydic oxygen has been enriched (10% $^{17}O_2$); (b) on the same solution after addition of 10% ^{17}O enriched water.

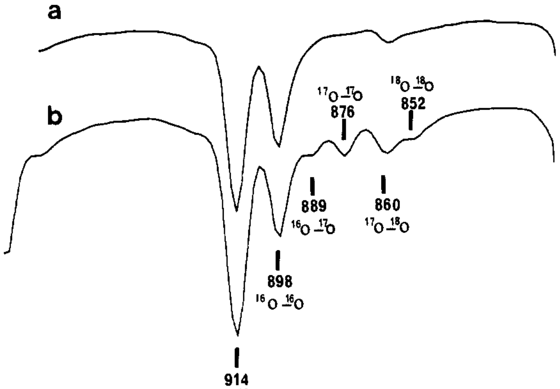
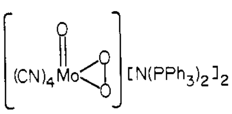


Figure 3. IR spectra measured in the 1000–800 cm^{-1} for (a)



and (b) **1**, i.e., the same compounds with peroxidic oxygen atoms enriched (10% $^{17}O_2$).

The assignment of the ^{17}O NMR spectra measured on **1** is further confirmed by the following results: The ^{95}Mo NMR spectra of **1**, recorded at 273 °K just before and after the ^{17}O experiments, exhibited the same single line at –610 ppm from the reference, hence establishing that compound **1** remained intact

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throughout the experiment.[18] The areas of the two ^{17}O signals measured for **1** are in an 1/6 oxo/peroxo ratio (Figure 2b), which shows that the ^{17}O-enrichment is different for these two types of oxygen atoms.

The latter observation is of importance as it established that there occurs *no exchange* of ^{17}O between the oxo and peroxo groups. The IR spectra measured in the 1000–800 cm^{-1} region for **1** (KBr pellets) are presented in Figure 3 for the nonenriched compound (Figure 3a), and for the peroxidic-enriched compound **1** (Figure 3b). The assignments, which were made through comparison with published spectra on comparable $Mo(O)_2$ derivatives,[5,15] are tentative, but likely. The IR spectrum measured on oxo- and peroxo-enriched **1** does not allow the precise determination of the relative level of enrichment of the oxo group as compared to that of the peroxo group, due to overlapping of the vibrations; it nevertheless confirms that the oxo group is less enriched than the peroxo oxygen atoms.

^{17}O NMR measurements of the M–O_2 pattern had previously been attempted, though without success, on group 8 transition-metal O_2 derivatives. In order to support our results further, we measured ^{17}O spectra on the alkyl peroxo platinum compound **2**. All oxygen atoms around platinum were detected, even on an *unlabeled* sample, in the spectrum after one night's accumulation (2.5×10^6 scans). The two oxygen atoms of the CF_3CO_2 groups are distinguished, each giving two signals: $C{=}\mathit{O}$ at 353 and 360 ppm; $C{-}\mathit{O}{-}Pt$ at 132 and 140 ppm. This indicates the presence of monodentate trifluoroacetates in nonequivalent environments. The peroxidic oxygen atoms of the "Pt-O-O-*t*-Bu" group appear as broad, shallow but reproducible signals at 1250 ($\Delta\nu_{1/2} = 1400$ Hz) for the Pt-bound oxygen and 230 ppm ($\Delta\nu_{1/2} = 1000$ Hz) for the other. The assignment of the latter signal was established through comparison with that measured on *t*-Bu–O–O–*t*-Bu (δ 269) and on $(CCl_3CO_2Pd{-}O{-}\mathit{O}{-}t{-}Bu)_4$ (δ 245).[19]

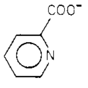
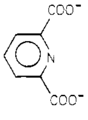
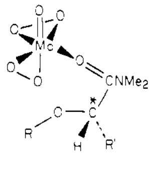
These results clearly establish that the tumbling correlation time for **2** in solution is short enough to allow the detection of the ^{17}O signal of the peroxidic oxygens. We interpret this to mean that it is not slow molecular motion in solution, i.e., too-large values for τ_c, that is responsible for the nondetection of the M–O_2 resonances in ^{17}O NMR spectra of small-to medium-sized molecules.

^{17}O NMR as a Tool for Studying Oxygenated Derivatives of Transition Metals: An Evaluation. ^{17}O NMR is rapidly becoming a routine tool for the characterization of oxo transition-metal derivatives. The labeling of an $M{=}O$ group is easy and immediate through addition of very small amounts of enriched water.[8,17] This allows the recording of ^{17}O spectra within minutes. Furthermore, the existing data are now sufficient to permit interpretation of $M{=}\mathit{O}$ chemical shifts in terms of the $M{=}O$ bond.[6] The lines measured for these terminal oxo groups show reasonably small widths, ca. 100 Hz, and ^{17}O spectra can be obtained even for nonenriched samples. During the last few years we have recorded *natural abundance* ^{17}O spectra for a series of $MoO(O_2)_2{\cdot}L$ compounds (see Table I). The terminal oxo group was always detected and gave reasonably good signals (signal/noise = 6) after ca. 10^6 scans (6 h) for ca. 5×10^{-2} M solutions.

Detection of the *peroxidic* ^{17}O resonance is less straightforward and deserves some comments.

(i) Its line width of ca. 2000 Hz (1800 Hz measured for **1**) is about 20 times wider than that usually found for terminal oxo groups where the electric field around the oxygen atom is obviously more symmetrical. This means that, for a given signal over noise ratio in the ^{17}O spectrum and for the same concentration, the detection of a peroxo group should require about 200 times as many scans as for the detection of an oxo group. From our measurements on nonenriched $MoO(O_2)_2{\cdot}L$ compounds (vide supra, Table I) where only the oxo groups were detected after ca. 10^6 scans, we can expect the *nonenriched* peroxo oxygen atoms to become detectable only after ca. 10^8 scans, which obviously is not very practicable.

Table I. ^{17}O NMR Chemical Shifts for the Oxo Resonance of Oxoperoxomolybdenum (VI) Derivatives

	compd	$\delta(^{17}O)$	$\Delta\nu_{1/2}$, Hz
HMPA = $OP[N(CH_3)_2]_3$	a, $MoO(O_2)_2{\cdot}HMPA$	863	120
	b, $MoO(O_2)_2{\cdot}py$	897	110
pic = 	c, $MoO(O_2)_2{\cdot}picH$	940	280
dipic = 	d, $MoO(O_2)dipic$	946	290
	e, $MoO(O_2)_2{\cdot}DMLA$ (R = H, R' = Me)	841, 875 (1:1)	260, 480
	f, $MoO(O_2)_2{\cdot}DMLA$ ester (R = Me, R' = Me)	872	300
	g, $MoO(O_2)_2{\cdot}DMCOLA$ (R = H, R' = COPh)	862, 885 (1:1)	340, 170

[a] In the case of compounds e and g (R = H), two lines of equal areas are measured, while a single line arises in f (R = Me). This was attributed to the existence in solution of an intramolecular hydrogen bond between R = H and one of the two peroxo groups, which causes the molybdenum to become chiral: the two diastereoisomers thus formed in solution are distinguished in the ^{17}O NMR.[9]

(ii) The line width of the ^{17}O signal for peroxidic oxygen atoms in small to medium sized molecules can be estimated from the formula

$$\Delta\nu_{1/2} = \frac{3\pi(2I + 3)}{10I^2(2I - 1)}\chi^2(1 + \tfrac{1}{3}\eta^2)\tau_c$$

where I is the spin of the observed nucleus (^{17}O, $I = {}^5/_2$), χ its quadrupolar constant, η the asymmetry parameter, and τ_c the isotropic tumbling correlation time of the compound.[20]

A ^{17}O nuclear quadrupolar resonance study on Vaska's iridium compound $Ir(O_2)Cl(CO)(PPh_3)_2$, **3**, led to the detection of two sets of quadrupolar coupling constants and asymmetry parameters,[12] i.e., one for each oxygen atom of the peroxo moiety. This definitely establishes a nonsymmetrical charge distribution around the oxygen atoms which should in principle be reflected by the presence of two resonances in ^{17}O NMR spectra. That these two lines could not be resolved in our spectra of compound **1** is assigned to the broadness of these resonance lines and vice-versa (and is expected to add to it). Nevertheless, if we take for χ and η the average values (χ = 16.2 MHz; η = 0.78) found for **3** and for τ_c a realistic value of 10 ps,[20] we obtain a rough estimation of the expected line width, the value of $\Delta\nu_{1/2}$ = 1900Hz. This value is very close to the 1800Hz experimental value measured for **1**.

All these results strongly suggest that it is neither a slow molecular tumbling rate nor a too-large quadrupolar coupling constant for peroxidic oxygen atoms bonded to transition elements that is responsible for the nondetection, up to now, of the $M(^{17}O_2)$ resonance. In the case of group 8 metals, which reversibly bind dioxygen, it is most likely the exchange with paramagnetic molecular dioxygen that causes line broadening to such an extent that the $M(^{17}O_2)$ line becomes undetectable even with high-resolution NMR equipment: its detection, if possible, will require special experimental conditions.

On the other hand, we can envisage that ^{17}O NMR measurements will become common practice on *labeled* peroxo derivatives of the early transition metals; they will also yield information on the ^{17}O-enriched alkylperoxo moiety bonded to a transition ele-

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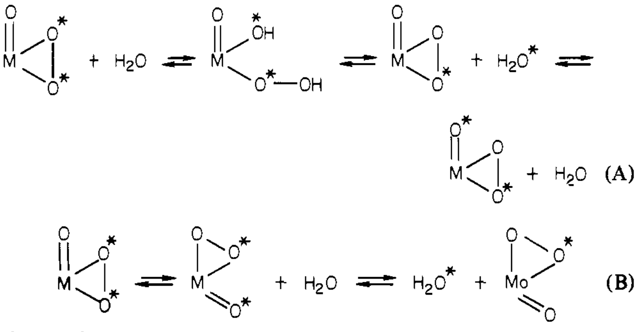
[18] Compound **1** decomposes slowly in CH_2Cl_2 solution at room temperature (decomposition products become detectable in ^{95}Mo spectrum after ca. 3 h) and faster in CH_3NO_2 or $CHCl_3$ solutions to yield what is probably a dioxomolybdenum species which then shows in the ^{95}Mo (δ −10) and ^{17}O (δ 720) spectra.

[19] Bregeault, J. M.; Mimoun, H. *Nouv. J. Chim.* **1981**, *5*, 287.

[20] Harris, R. K.; Mann, B. E. "NMR and the Periodic Table"; Academic Press: London, 1978.

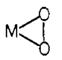
ment. We therefore expect ^{17}O NMR to play an important role in the better understanding of oxidation processes where the source of oxygen is hydrogen peroxide or alkyl hydroperoxides.

Evidence against an Exchange of Oxygen between Oxo and Peroxo Groups in Mo(VI) Derivatives. Peroxo species appear to play a determinant role in vanadium(V)- or molybdenum(VI)-catalyzed oxidations by hydrogen peroxide;[21] however, the structure of the peroxo moeity, i.e., identification of the actual oxidizing species, is still uncertain. Modena et al. recently proposed that, in the presence of water, one of the following exchange reactions takes place:[13]


(A)

(B)

If one of these exchanges were taking place, it would result for compound **1** in a random scrambling of the labeled oxygen atoms between $H_2{}^{17}O$ and the Mo=O and



groups: the areas of the two ^{17}O signals for **1** would then be in a 1/2 ratio and not 1/6 as we measured (Figure 2b).

Definite evidence against the occurrence of the oxo–peroxo exchange was obtained by comparing the ^{17}O NMR spectra of **1** measured in CH_2Cl_2 solutions (8×10^{-2} M) to which a tenfold amount (8×10^{-1} M) of either $H_2{}^{16}O$ or $H_2{}^{17}O$ (10%) was added. After 1 h, only one signal was detected in the ^{17}O NMR of the $H_2{}^{16}O$-containing sample, which corresponded to the peroxo group, instead of the two signals observed when $H_2{}^{17}O$ was present (vide supra). Taking into account the fact that the line width of the (^{17}O)peroxo signal is ca. 20 times wider than that of a terminal oxo group, the nondetection of a Mo=^{17}O signal means that the rate of exchange, if any, is too slow to be of any significance in a catalytic process.

Conversely when we measured the ^{17}O NMR spectra for the series of $MoO_5{\cdot}L$ compounds listed in Table I after addition of 10% ^{17}O-enriched water, i.e., after labeling of the oxo group specifically, we could not detect any peroxo signal, even after a 48 h contact with $H_2{}^{17}O$.

We interpret these results to mean that intra- or intermolecular oxygen exchange between the oxo and the peroxo groups in these Mo(VI) oxo peroxo derivatives does not take place to a measurable extent, and therefore is unlikely to be involved as a key step in Mo(VI)-catalyzed oxidations by hydrogen peroxide.

In conclusion, peroxidic oxygen atoms can be observed through ^{17}O NMR on Mo(VI) and Pt(II) compounds. Not only structural but also mechanistic information can be gained through this spectroscopy. As an example the absence of significant detectable oxo vs. peroxo oxygen exchange in Mo(VI) derivatives was established.

Our results clearly indicate that ^{17}O NMR should be an efficient tool in the study of peroxidic transition-metal derivatives provided there is no exchange with molecular dioxygen. However, ^{17}O-enriched samples will generally be necessary in order to record the ^{17}O spectra in reasonable conditions.

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Registry No. 1, 82281-65-0; **2**, 79359-93-6; $MoO(O_2)_2{\cdot}HMPA$, 25377-12-2; $MoO(O_2)_2{\cdot}py$, 67228-13-1; $MoO(O_2)_2{\cdot}picH$, 67584-06-9; $MoO(O_2)dipic$, 69594-30-5; $MoO(O_2)_2{\cdot}DMLA$ (R = H; R^1 = Me), 70355-53-2; $MoO(O_2)_2{\cdot}DMLA$ (R = Me, R^1 = Me), 85735-46-2; $MoO(O_2)_2{\cdot}DMCOLA$ (R = H; R^1 = COPh), 85748-26-1; ^{17}O, 13968-48-4.

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(21) Sheldon, R. A. "Aspects of Homogeneous Catalysts"; Ugo, R., Ed.; D. Reidel: London, 1981, Vol. IV.

EPR Evidence on the Structure of the Copper(II)–Bacitracin A Complex

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Abstract: Bacitracin is an antibiotic that is effective only in the presence of divalent metal cations. In this paper, the possible sites for the binding of divalent transition metal ions to bacitracin A are investigated by electron paramagnetic resonance. Manganese(II) shows only the characteristics of the aqueous ion. High-spin cobalt, suggesting distorted octahedral coordination, is indicated from the cobalt(II) EPR spectra. The copper(II) complex yields a rich spectrum and detailed structural information. The electronic Zeeman, hyperfine, and nuclear quadrupole coupling parameters show that copper is most probably square planar, coordinated to the glutamate γ-carboxyl, the histidine imidazole, the aspartate β-carboxyl, and the thiazoline nitrogen. This is the first reported case of a significant influence of quadrupole coupling on the EPR spectra of solutions of metal compounds of such complexity or of biological significance.

Bacitracin A (see Figure 1) is the major component of a group of closely related polypeptide antibiotics produced by *Bacillus licheniformis*. Bacitracin A is a dodecapeptide that acts against Gram-positive bacteria, apparently by blocking a critical step in cell wall synthesis.[1] This step is the dephosphorylation of the lipid carrier intermediate C_{55}-bactoprenyl pyrophosphate.[2] Strominger et al. have shown that bacitracin A forms a stoi-

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(1) Robinson, F. A. "Antibiotics"; Pitman and Sons, Ltd.: London, 1953, pp 107–111.

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