1.0/1.0). These facts will be considered later.

If the relative concentrations of free BR_3 and HBR_3^- could be obtained directly from ^{11}B NMR data, it would be possible to obtain a value for the equilibrium constants at −80 and −23 °C and from these constants a ΔH value for the process of cation formation. Unfortunately the ^{11}B NMR data completed up to the present time have not been particularly helpful in establishing BR_3/HBR_3^- concentration ratios. The ^{11}B NMR showed that because an excess of L-Selectride had been used in the original reduction, the major boron containing species in solution at −23 °C was represented by a peak for L-Selectride ($LiHBR_3$) at −7.3 ppm vs. $F_3D{\cdot}OEt_2$. Free BR_3 in solution at −23 °C was seen as a small, broad peak near 84 ppm. At −80 °C no peak for free R_3B could be detected.

Synthesis of $[(CO)_3Ni\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+[PF_6]^-$ by Halide Extraction. To verify the identity of the cationic nickel complex, it was prepared by a more conventional halide abstraction process by adding equimolar amounts of the fluoride reagents in CH_2Cl_2 rather than in THF.

$$(CO)_3Ni\overline{P(F)N(CH_3)CH_2CH_2N}(CH_3) + PF_5 \xrightarrow[-40\text{ to }+25\ °C]{CH_2Cl_2} [(CO)_3Ni\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+ + [PF_6]^- \quad (8)$$

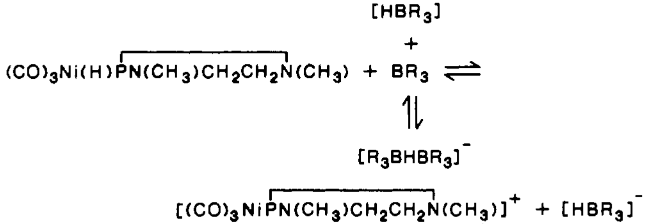
The solution changed from colorless to yellow. The ^{31}P NMR spectrum of the product solution resulting from fluoride extraction showed a chemical shift value of 276 ppm for the complex phosphorus cation. The difference of 2 ppm (274 vs. 276 ppm) in the ^{31}P NMR chemical shift value would be expected when the solvent is changed and possible hydride exchange equilibrium are considered in the THF solution. The data leave little doubt about the validity of the original hydride-transfer process for the formation of the tricarbonyl(phosphenium)nickel cation.

Reaction of $(CO)_3Ni(H_3C\overline{NCH_2CH_2N(CH_3)P}H)$ and $(C_6H_5)_3C^+PF_6^-$. Another Attempt at Hydride Extraction. The "trityl" cation, $[(C_6H_5)_3C]^+$, is widely used as a hydride-extracting reagent in a number of organic systems. It was thus of interest to see if the trityl cation could remove a hydride ion from $(CO)_3Ni(H_3C\overline{NCH_2CH_2N(CH_3)P}H)$ to give the complex cation. When reagents were mixed at −80 °C, all dissolved in CH_2Cl_2 and the color of the system changed from yellow to very dark red, but the ^{31}P NMR gave no evidence for the expected $[-P^+-][PF_6]^-$ compound. Decomposition products plus the signal for $(CO)_3Ni(H_3CNCH_2CH_2N(CH_3)PF)$ were seen as the system was warmed from −80 °C. The system went very dark brown. In our hands, up to the present time, the use of the trityl cation as a hydride acceptor did not give a satisfactory route to the desired nickel cation complex, but further work seems justified.

Comparisons of the Cation System in the Presence of the PF_6^- and HBR_3^- Anions. While the ^{31}P NMR spectrum indicates clearly that cation **2**, $[(CO)_3N\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+$, is present in solutions containing both the HBR_3^- and the PF_6^- anions, a number of significant differences exist that deserve comment. One of the most obvious contrasts is the color of the cation in the presence of different anions. When cation **2** was made by fluoride extraction, the solution color was a clear yellow; when it was made by hydride extraction, the solution color was red-brown, suggesting possible perturbation of the color center or the presence of impurities. At the present time we believe color differences are a result of decomposition since such yellow to red-brown color development is seen during the decomposition of the cyclic and acyclic $(R_2N)_2PH$ species and their metal carbonyl adducts.

Color changes can also result from interaction of a borane acid with a phosphine substituted metal carbonyl. Recently Paine, Nöth, and their co-workers[9] reported that purple (Cp)Mo(CO)$_2$[P(Ph){N[Si(CH$_3$)$_3$]$_2$}] will add BH_3 to give green (Cp)Mo(CO)$_2$[P(BH$_3$)(Ph){N[Si(CH$_3$)$_3$]$_2$}], which contains the Mo–H–B–P linkage. Such a reaction is accompanied by large shifts in the ^{31}P resonance (about 266 ppm). Since NMR shifts in this study did not correlate with color changes (^{31}P shift was that expected for the cation), decomposition products remain the preferred explanation for the red-brown color.

The ^{11}B NMR showed that BR_3 was not present at −80 °C and the compound $(CO)_3Ni\overline{P(H)N(CH_3)CH_2CH_2N}(CH_3)$ was the dominant nickel species. The following equilibrium is suggested:



$$\begin{array}{c} (CO)_3Ni(H)\overline{PN(CH_3)CH_2CH_2N}(CH_3) + \begin{array}{c}[HBR_3]^- \\ + \\ BR_3\end{array} \rightleftharpoons \\ \upharpoonleft\downharpoonright \\ [R_3BHBR_3]^- \\ [(CO)_3Ni\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+ + [HBR_3]^- \end{array}$$

Since the solution contained an excess of HBR_3^- from the original reduction operation, this anion could interact with BR_3 at lower temperature to give the double ion of the type reported by Brown and co-workers.[10] Such an equilibrium would explain the ^{11}B NMR observations and existence of the nonionic B–H species as the preferred compound at low temperature.

Experimental Section

Synthesis of $[(CO)_3Ni\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+[HB(\textit{sec}\text{-}Bu)_3]^-$. The literature synthesis[8] of $(CO)_3Ni(H)PN(CH_3)CH_2CH_2N(CH_3)$ by reduction of the fluorocomplex with L-Selectride (Aldrich) was used. The solution from the above reduction stood for 12 days at −19 °C in an NMR tube. A dark red-brown color developed. The cation was identified by NMR.

Synthesis of $[(CO)_3Ni\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+[PF_6]^-$. A 9-mm-o.d. NMR tube equipped with a 100-mL gas expansion bulb, a stopcock, and ground-glass joint was the reaction vessel. On top of about a 1.0-mmol sample of $(CO)_3Ni(F)PN(CH_3)CH_2CH_2N(CH_3)$ dissolved in 1 mL of CH_2Cl_2, an equimolar quantity of PF_5 was frozen. The system was monitored by ^{31}P NMR. At −40 °C and up to +25 °C, NMR showed the signal for $[(CO)_3NiPN(CH_3)CH_2CH_2N(CH_3)]^+[PF_6]^-$. Data are given in Table I.

Reaction of $(CO)_3Ni(H)\overline{PN(CH_3)CH_2CH_2N}CH_3$ with Trityl Hexafluorophosphate, $[(C_6H_5)_3C]^+[PF_6]^-$. A 1.4-mmol sample of $(CO)_3Ni(H)PN(CH_3)CH_2CH_2NCH_3$ was dissolved in 1 mL of dry CH_2Cl_2 and then a 1.0-mm sample of $[(C_6H_5)_3C]^+[PF_6]^-$ in 1.0 mL of CH_2Cl_2 was added at −80 °C. The reaction system was warmed to −40 °C where reaction took place. The system did not change appreciably as the temperature was raised to 23 °C.

Acknowledgment. Major support of this work by the National Science Foundation through Grant No. CHE 7920313 is gratefully acknowledged.

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(9) McNamara, W. F.; Duesler, E. N.; Paine, R. T.; Ortiz, J. V.; Kolle, P.; Nöth, H. *Organometallics*, **1986**, *5*, 380–383.

(10) (a) Brown, H. C.; Khuri, A.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1977**, *99*, 6237. (b) Brown, H. C.; Krishnamurthy, S.; Hubbard, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3343.

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Dinitrogen Pentoxide. New Synthesis and Laser Raman Spectrum

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Dinitrogen pentoxide, the anhydride of nitric acid, was first prepared in 1849 from the reaction of Cl_2 with dry $AgNO_3$ at 60 °C.[1] Subsequent methods involve either the dehydration of concentrated nitric acid by phosphorous pentoxide[2-7] or the oxidation of N_2O_4 with ozone.[8,9] Since N_2O_5 is unstable at ambient temperature and decomposes to N_2O_4 and O_2, the above methods require the use of an efficient ozone generator to suppress the formation of N_2O_4. Dinitrogen pentoxide is also formed when a mixture of oxygen and nitrogen is passed through an electric arc at high voltages[10] and in the reactions of $POCl_3$ or NO_2Cl with $AgNO_3$.[1,11]

The gas-phase structure of N_2O_5 has been established by electron diffraction and consists of two NO_2 groups joined by an oxygen atom. The N–O–N bond angle is 111.8°, and the $-NO_2$ groups undergo large amplitude torsional motions about a point of minimum energy corresponding to C_2 symmetry.[12] In the solid phase, N_2O_5 has the ionic structure $NO_2^+NO_3^-$, which was supported by vibrational spectroscopy[13-15] and was subsequently confirmed by an X-ray diffraction study.[16] The latter indicated linear symmetric NO_2^+ cations with an N–O bond length of 1.154 ± 0.01 Å.

In a recent study[17] we have shown that BrF_5 interacts with an excess of $LiNO_3$ to give $BrONO_2$ and FNO_2 (eq 1). However,

$$BrF_5 + 3LiNO_3 \rightarrow 3LiF + BrONO_2 + O_2 + 2FNO_2 \quad (1)$$

when the ratio of $LiNO_3$:BrF_5 was significantly higher than 3, N_2O_5 was produced instead of FNO_2, implying (2) as a secondary reaction.

$$FNO_2 + LiNO_3 \rightarrow LiF + N_2O_5 \quad (2)$$

Since the methods generally used for the synthesis of N_2O_5 require an efficient ozone generator and, particularly when HNO_3 is the starting material, involve cumbersome purification steps, we examined reaction 2 for its potential as a simple, new synthesis of pure N_2O_5.

During the characterization of N_2O_5, its laser Raman spectrum was also recorded. Although the observed spectrum confirms the ionic $NO_2^+NO_3^-$ structure of solid N_2O_5, previously unreported bands were observed that are incompatible with a completely linear NO_2^+ cation.

Experimental Section

Materials and Apparatus. FNO_2 was prepared from BrF_5 and alkali-metal nitrates, as previously described.[18] $LiNO_3$ (J. T. Baker, 99.7%) was dried in vacuo at 120 °C for 12 h before use. Volatile materials were handled in a well-passivated (with $ClONO_2$) stainless-steel Teflon–FEP vacuum line.[19] Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Raman spectra were obtained on a Spex Model 1403 spectrophotometer by using the 647.1-nm exciting line of a Kr ion laser and a previously described[20] device for recording the low-temperature spectra. Sealed glass tubes were used as sample containers in the transverse-viewing–transverse-excitation mode.

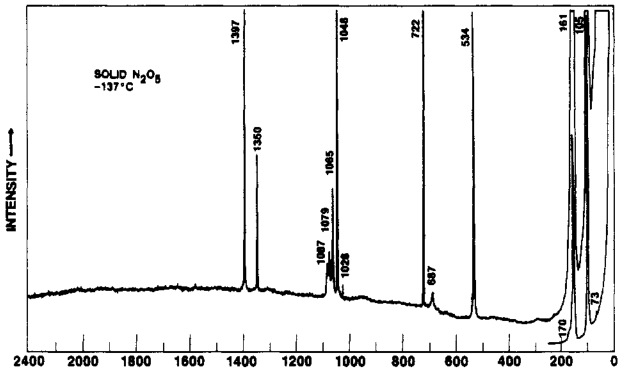

Figure 1. Low-temperature laser Raman spectrum of solid N_2O_5.

Table I. Vibrational Spectra of Solid N_2O_5

obsd freq, cm^{-1} (rel intens)		assignt (point group)[a]	
Raman	IR[b]	NO_2^+ ($D_{\infty h}$)	NO_3^- (D_{3h})
	2375 s	ν_{as}, $\nu_3(\Sigma_u^+)$	
	2365 s		
1397 (72)		ν_s, $\nu_1(\Sigma_g^+)$	
1350 (4)	1350–1450 vs, br		ν_{as}, $\nu_3(E')$
1087 (1)		$2\nu_2$	
1079 (1)	1078 w		
1065 (3)			
1048 (84)			ν_s, $\nu_1(A_1')$
1028 (0+)			?
	824 m		$\delta_{\text{out of plane}}$, $\nu_2(A_2'')$
722 (10)	722 w		$\delta_{\text{in plane}}$, $\nu_4(E')$
687 (0+)		(534 + 161)	
534 (28)	538 s	δ, $\nu_2(\Pi_u)$	
170 sh		lattice vibrations	
161 (61)			
156 sh			
105 (100)			
73 (1)			

[a] In view of the uncertainty about the actual symmetry of the ions, the idealized $D_{\infty h}$ and D_{3h} symmetries were used for NO_2^+ and NO_3^-, respectively. [b] Values from ref 15.

Preparation of N_2O_5. A prepassivated 30-mL stainless-steel cylinder was loaded in the drybox with $LiNO_3$ (2.85 mmol). The cylinder was connected to the vacuum line, and FNO_2 (1.34 mmol) was condensed in at −196 °C. The cylinder was slowly warmed from −196 to 0 °C and kept at this temperature for 24 h. It was then cooled back to −196 °C and checked for noncondensible material (O_2), but none was observed. The material volatile at 20 °C was then separated by fractional condensation in a dynamic vacuum through traps kept at −142 and −196 °C while the cylinder was allowed to warm up from −196 to +20 °C. The −142 °C trap contained a white solid (146 mg; weight calculated for 1.34 mmol of N_2O_5 is 145 mg), which was shown by low-temperature Raman spectroscopy to be pure N_2O_5. The −196 °C trap contained nothing. The nonvolatile residue in the cylinder consisted of a white solid (140 mg; weight calculated for 1.51 mmol of $LiNO_3$ and 1.34 mmol of LiF is 139 mg), which was spectroscopically identified as a mixture of $LiNO_3$ and LiF.

Results and Discussion

Synthesis of N_2O_5. Nitryl fluoride reacts with an excess of $LiNO_3$ to provide pure N_2O_5 in quantitative yield. If the reaction temperature is limited to 0 °C and well-passivated equipment is used, decomposition or hydrolysis of N_2O_5 is avoided and the need for an ozone generator is eliminated. Furthermore, the product separation is extremely simple because N_2O_5 is the only volatile material.

Raman Spectrum and Structure of N_2O_5. During the characterization of the N_2O_5 prepared by the above method from FNO_2 and $LiNO_3$, its low-temperature laser Raman spectrum was also

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(1) Sainte-Claire Deville, H. *C. R. Hebd. Seances Acad. Sci.* **1849**, *28*, 257.
(2) Weber, R. *Pogg. Ann.* **1872**, *147*, 113.
(3) Berthelot, M. *Bull. Soc. Chim. Fr.* **1874**, *21*, 53.
(4) Russ, F.; Pokorny, E. *Monatsh. Chem.* **1913**, *34*, 1051.
(5) Daniels, F.; Bright, A. C. *J. Am. Chem. Soc.* **1920**, *42*, 1131.
(6) Berl, E.; Saenger, H. H. *Monatsh. Chem.* **1929**, *53-54*, 1036.
(7) Gruenhut, N. S.; Goldfrank, M.; Cushing, M. L.; Caesar, G. V. *Inorg. Synth.* **1950**, *3*, 78.
(8) Helbig, D. *Atti. Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1902**, *2*, 311.
(9) Yost, D. M.; Russell, H. *Systematic Inorganic Chemistry*; Prentice-Hall: New York, 1944.
(10) Ehrlich, V.; Russ, F. *Monatsh. Chem.* **1911**, *32*, 917.
(11) Odet, M.; Vignon, L. *C. R. Hebd. Seances Acad. Sci.* **1869**, *69*, 1142; **1870**, *70*, 96.
(12) McClelland, B. W.; Hedberg, L.; Hedberg, K.; Hagen, K. *J. Am. Chem. Soc.* **1983**, *105*, 3789.
(13) Chédin, J. Thesis, Paris, 1937; *C. R. Hebd. Seances Acad. Sci.* **1935**, *200*, 1397.
(14) Millen, D. J. *J. Chem. Soc.* **1950**, 2606.
(15) Teranishi, R.; Decius, J. C. *J. Chem. Phys.* **1954**, *22*, 896.
(16) Grison, E.; Eriks, K.; DeVries, J. L. *Acta Crystallogr.* **1950**, *3*, 290.
(17) Wilson, W. W.; Christe, K. O. *Inorg. Chem.*, companion article in this issue.
(18) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1987**, *26*, 916.
(19) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.
(20) Miller, F. A.; Harney, B. M. *Appl. Spectrosc.* **1969**, *23*, 8.

Table II. Correlation for the Intramolecular Vibrations of NO_2^+ and NO_3^- in the $NO_2^+NO_3^-$ Crystal between Their Point Groups, Site Groups, and Factor Groups and Their Infrared and Raman Activities

	approx descripn of mode	point group	site group	factor group
NO_3^-		D_{3h}	D_{3h}	D_{6h}
	symm str	A_1' (R)	A_1' (R)	A_{1g} (R) B_{1u}
	out-of-plane def	A_2'' (IR)	A_2'' (IR)	A_{2u} (IR) B_{2g}
	antisymm str	E' (R, IR)	E' (R, IR)	E_{1u} (IR) E_{2g} (R)
	in-plane def	E' (R, IR)	E' (R, IR)	E_{1u} (IR) E_{2g} (R)
NO_2^+		$D_{\infty h}$	D_{3d}	D_{6h}
	symm str	Σ_g^+ (R)	A_{1g} (R)	A_{1g} (R)
	antisymm str	Σ_u^+ (IR)	A_{2u} (IR)	A_{2u} (IR) B_{1u}
	def	Π_u (IR)	E_u (IR)	E_{1u} (IR) E_{2u}
	2× def (D_{6h})			
	$2E_{1u} = A_{1g} + A_{2g} + E_{2g}$ (R)			
	$2E_{2u} = A_{1g} + A_{2g} + E_{2g}$ (R)			
	$E_{1u} \cdot E_{2u} = B_{1g} + B_{2g} + E_{1g}$ (R)			

recorded. The observed spectrum (see Figure 1 and Table I) exhibited more bands than previously reported[13,14] and predicted from the known crystal structure[16] and a factor group analysis (see Table II). To verify that these additional Raman bands belonged indeed to N_2O_5, a sample of N_2O_5 was also prepared from N_2O_4 and ozone and its Raman spectrum was recorded. The observed spectrum was identical with that of Figure 1.

According to the previous X-ray crystal study.[16] N_2O_5 crystallizes in the space group D_{6h}^4 ($C6/mmc$) with $Z = 2$ and trigonal-planar NO_3^- anions in D_{3h} sites and linear symmetric NO_2^+ cations in D_{3d} sites. The structure was based on 64 nonzero reflections with a final R value of 0.120. The refinement of this structure was subsequently confirmed by Cruickshank and coworkers but raised a question concerning the bond lengths of the NO_2^+ cations in $NO_2^+NO_3^-$ and $NO_2^+ClO_4^-$. Although the symmetric NO_2^+ stretching modes are practically identical in both compounds, the bond lengths differed by 0.049 Å and rotational oscillation corrections were suggested as a possible explanation for this large discrepancy.[21]

If we return to the Raman spectrum of solid N_2O_5, the only two previous studies[13,14] were carried out with Toronto arc excitation. Only two Raman lines at about 1400 and 1050 cm^{-1} were observed and correctly attributed to the symmetric NO_2^+ and NO_3^- stretching modes, respectively. We have now also observed (see Figure 1 and Table I) the antisymmetric stretch and the in-plane deformation modes for NO_3^- at 1350 and 722 cm^{-1}, respectively, and the deformation mode for NO_2^+ at 534 cm^{-1}. Whereas the Raman activity of ν_{as} and $\delta_{in\ plane}$ of NO_3^- is in accord with the results of the factor group analysis (see Table II), the latter cannot explain the intense Raman band observed for the NO_2^+ deformation mode.

The Raman and infrared activities and relative intensities of the NO_2^+ modes in $NO_2^+NO_3^-$ closely resemble those in $NO_2^+ClO_4^-$,[22] which contains a slightly bent (∠ONO = 175.2 ± 1.4°) NO_2^+ cation.[21] Our data for $NO_2^+NO_3^-$, therefore, suggest that the NO_2^+ cation in solid N_2O_5 might be similarly bent. The failure of the X-ray crystal structure study to detect this nonlinearity of NO_2^+ for $NO_2^+NO_3^-$ might be attributed to facts such as the low precision of the X-ray study (64 reflections, $R = 0.12$)[16] or, more likely, rotational oscillation of the NO_2^+ cation,[21] which could result in an averaged linear structure for a slightly nonlinear ion. Such an averaging would not be observable on the vibrational spectroscopy time scale.

In addition to the above discussed fundamental vibrations, several very weak bands were observed in the Raman spectrum of solid $NO_2^+NO_3^-$. The three bands at 1087, 1079, and 1065 cm^{-1} can be attributed to the first overtone of the NO_2^+ deformation mode in Fermi resonance with the symmetric stretching mode. The splitting into three components can be explained by the assumption of an E_{2u} component for the deformation mode that is inactive in both the infrared and Raman spectra but whose overtone and combination bands are Raman active (see Table II). The weak band at 687 cm^{-1} is attributed to a combination band of the NO_2^+ deformation with the 161-cm^{-1} lattice mode. For the very weak band at 1028 cm^{-1} we do not have, at the present time, a plausible explanation.

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(21) Truter, M. R.; Cruickshank, D. W. J.; Jeffrey, G. A. *Acta Crystallogr.* **1960**, *13*, 855.

(22) Nebgen, J. W.; McElroy, A. D.; Klodowski, H. F. *Inorg. Chem.* **1965**, *4*, 1796.

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Preparation and Molecular Structure of $OMo^{IV}[S_2C_2(CN)_2](Ph_2PCH_2CH_2PPh_2) \cdot (CH_3)_2CO$ and Its Possible Relevance to the Active Site of Oxo-Transfer Molybdoenzymes

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The apparent role of oxo-type molybdenum centers in various enzymatic redox processes has stimulated exploration of the structural, spectroscopic, and reactivity features of higher oxidation state molybdenum compounds as well as efforts to construct models for these molybdoenzymes. A combination of EXAFS, EPR, electrochemical, chemical modeling, and microbiological studies on these oxidoreductases (e.g. sulfite, xanthine, and CO oxidases and nitrate reductase) has led to the widely held belief that these enzymes contain a common cofactor in which the Mo atom shuttles between the Mo(IV) and Mo(VI) states and has at least one oxo and two S-donor ligands (e.g. thiolate).[1]

On the basis of recent chemical degradation studies of the molybdenum cofactor (Mo(co)) from xanthine and sulfite oxidases,

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(1) Reviews: Burgmayer, S. J. N.; Stiefel, E. I. *J. Chem. Educ.* **1985**, *62*, 943. *Molybdenum and Molybdenum-Containing Enzymes*; Coughlan, M. P., Ed.; Pergamon: New York, 1980. *Molybdenum Chemistry of Biological Significance*; Newton, W. E., Otsuka, S., Eds.; Plenum: New York, 1980.

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