nitrogen family are also known[8a,d,21,26] to function simultaneously as π-bonders and heteroatom σ-donors, but always each bonding mode is to two different metal centers. Such an interaction in our pyrrolyl systems requires the metal center be situated relatively close to the N atom. This is difficult for III, because the $Mn(CO)_3$ moiety would experience a large steric repulsion from the methyl groups ortho to the N atom.

Acknowledgment. We thank the National Science Foundation for the support of this research. D.L.K. thanks the graduate school at Northwestern University for a fellowship. We thank A. V Satish for measuring the pK_a's of the dimethylpyrrole molecules.

Registry No. I, 32761-36-7; II, 105899-94-3; III, 94280-88-3; IV, 110825-42-8; V, 68229-11-8; (η^5-3,4-$C_4(CH_3)_2H_2N)Mn(CO)_2P(n\text{-}Bu)_3$, 110825-43-9; ($\eta^5$-3,4-$C_4(CH_3)_2H_2N)Mn(CO)_2P(OEt)_3$, 110825-44-0; ($\eta^5$-3,4-$C_4(CH_3)_2H_2N)Mn(CO)_2PPh_3$, 110825-45-1; ($\eta^5$-2,5-$C_4(CH_3)_2H_2N)Mn(CO)_2P(Bu)_3$, 110825-46-2; ($\eta^5$-2,5-$C_4(CH_3)_2H_2N)Mn(CO)_2P(OEt)_3$, 110825-47-3; ($\eta^5$-2,5-$C_4(CH_3)_2H_2N)Mn(CO)_2PPh_3$, 110825-48-4; ($\eta^5$-2,5-$C_4(CH_3)_2H_2N)Mn(CO)_2P(OPh)_3$, 110825-49-5; ($\eta^5$-2,5-$C_4(CH_3)_2H_2N)Mn(CO)_2PMe_3$, 110825-50-8; ($\eta^5$-2,5-$C_4(CH_3)_2H_2P)Mn(CO)_2PPh_3$, 110825-51-9; ($\eta^5$-2,5-$C_4(CH_3)_2H_2As)Mn(CO)_2PPh_3$, 110825-52-0.

Supplementary Material Available: Table of observed rate constants, k_{obsd}, for reactions of (η^5-pyrrolyl)$Mn(CO)_3$ complexes with different concentrations of $P(n\text{-}Bu)_3$ or $P(OEt)_3$ at different temperatures in Decalin solution (1 page). Ordering information is given on any current masthead page.

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(26) Abel, E. W.; Clark, N.; Towers, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1552–1556.

Effects of Paramagnetic and Diamagnetic Transition-Metal Monosubstitutions on ^{183}W and ^{31}P NMR Spectra for Keggin and Wells–Dawson Heteropolytungstate Derivatives. Correlations and Corrections. ^{183}W NMR Two-Dimensional INADEQUATE Studies of α-$[(D_2O)ZnO_5X^{n+}W_{11}O_{34}]^{(10-n)-}$ Wherein X^{n+} = Si^{4+} and P^{5+}

Thomas L. Jorris,[†] Mariusz Kozik,[†] Nieves Casan-Pastor,[†] Peter J. Domaille,[‡] Richard G. Finke,[§] Warren K. Miller,[§] and Louis C. W. Baker*[†]

Contribution from the Department of Chemistry, Georgetown University, Washington, D.C. 20057, Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898, and Department of Chemistry, University of Oregon, Eugene, Oregon 97403.

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Abstract: ^{31}P NMR spectra are reported for α_1 and α_2 isomers of $[(H_2O)M^{n+}O_5P_2W_{17}O_{56}]^{(10-n)-}$ complexes wherein M^{n+} = Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, and Mn^{3+} and for α-$[(D_2O)M^{2+}O_5PW_{11}O_{34}]^{5-}$ complexes wherein M^{2+} = Zn^{2+}, Ni^{2+}, and Co^{2+}. ^{183}W NMR spectra are reported for the α_2 isomers of $[(D_2O)M^{2+}O_5P_2W_{17}O_{56}]^{8-}$ wherein M^{2+} = Co^{2+}, Ni^{2+}, and Zn^{2+}; for α_1-$[(D_2O)Zn^{2+}O_5P_2W_{17}O_{56}]^{8-}$; and for α-$[(D_2O)M^{2+}O_5X^{m+}W_{11}O_{34}]^{(10-m)-}$ wherein M^{2+} = Co^{2+}, Ni^{2+}, and Zn^{2+} and X^{m+} = P^{5+} and Si^{4+}. Those spectra show that when either α_1 or α_2 isomers of the Wells–Dawson 17-tungsto derivatives are prepared and purified by standard methods, there is always a significant proportion of the other isomer present as impurity. The spectra provide the first direct proofs of the structures of these α_1 and α_2 substitution isomers. The degrees of ^{31}P NMR line broadenings caused by the paramagnetic atoms are explained in terms of the orbital degeneracy or nondegeneracy of the electronic states of the paramagnetic ions. The extents of the NMR chemical shifts for P atoms nearest the substitution sites may be explained in terms of contact shifts modified by some dipolar contribution and/or second-order effects. Effects of possible partial delocalization of unpaired electron spins are discussed. Errors in previous reports of the ^{31}P NMR spectra of some of these complexes are explained. In the ^{183}W NMR spectra, signals are not observed from those W atoms which are structurally adjacent to the paramagnetic atoms. ^{183}W NMR 2D INADEQUATE studies of $[(D_2O)ZnO_5X^{n+}W_{11}O_{34}]^{(10-n)-}$ wherein X^{n+} = Si^{4+} and P^{5+} are presented. Differences and similarities relative to 2D studies of other substituted Keggin 11-tungsto derivatives are noted.

This paper reports ^{183}W NMR spectra for α_2-$[(D_2O)M^{n+}O_5P_2W_{17}O_{56}]^{(10-n)-}$ complexes wherein M^{n+} = Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, and Mn^{3+}. These spectra prove[1] that the preparative procedures usually used in the past[2] yield primarily α_2 isomers (cap-substituted α Wells–Dawson structures[6]) but that, in each case, a significant proportion of the complexes in the recrystallized product is the belt-substituted α_1 isomer.[3a] See Figure 1. This conclusion is confirmed by ^{31}P NMR, which also shows that standard preparations[3b] for α_1 species (via the α_1-lacunary 17-tungstodiphosphate made in the presence of Li^+) lead to 2–11% of the product complexes present being α_2. Although

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[†] Georgetown University.

[‡] E. I. du Pont de Nemours and Co. Contribution No. 4344.

[§] University of Oregon.

(1) While the common assumption is that the complexes prepared according to Weakley and Malik[2] are α_2 isomers when produced in the absence of Li^+ ions,[3b] because it was shown[4] by ^{183}W NMR that it is the α_2-lacunary species that forms under such conditions, there has not heretofore been unambiguous evidence for the isomer assignment for these substituted species. Indirect evidence, based on electrochemical and ESR studies[4,5] for the V^{4+}-substituted complex, is confirmed herein.

(2) (a) Malik, S. A.; Weakley, T. J. R. *J. Chem. Soc., Chem. Commun.* **1967**, 1094. (b) Malik, S. A.; Weakley, T. J. R. *J. Chem. Soc. A* **1968**, 2647. (c) Tourné, C. M.; Tourné, G. F.; Malik, S. A.; Weakley, T. J. R. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3875.

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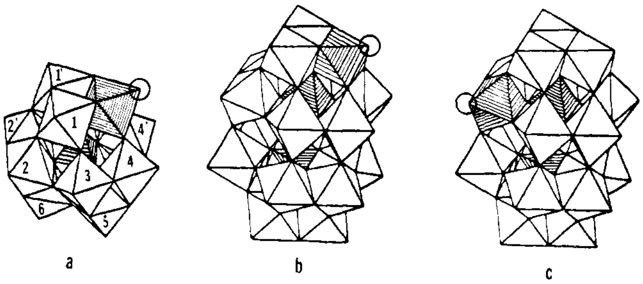

Figure 1. Structures of complexes. Each vertex of a polyhedron locates the center of an oxygen atom. A W atom is within each white octahedron, displaced off-center toward its unshared O atom. Each (hatched) tetrahedron contains a P atom (or a Si atom in the cases of the 11-tungstosilicate complexes). Each hatched octahedron contains the substituted transition-metal atom. The circled vertices locate the H_2O (or D_2O) molecules coordinated to that metal atom. (a) α-Monometallo-11-tungstate structure. The W-containing octahedra are numbered in accordance with the 2D NMR INADEQUATE studies of α-$[(D_2O)ZnO_5SiW_{11}O_{34}]^{6-}$ and α-$[(D_2O)ZnO_5PW_{11}O_{34}]^{5-}$. Octahedra 3′ and 5′ are out of sight behind the complex. (b) α_2-Monometallo-17-tungstodiphosphate structure. (c) α_1-Monometallo-17-tungstodiphosphate structure.

it appears, therefore, that obtaining pure α_1 or pure α_2 isomer is not common,[3a] this situation, provided it is known, should cause relatively little difficulty with respect to NMR spectra, where lines from α_1 and α_2 species are distinguishable, being of different chemical shifts and patterns, and where the signals from a minor component are much less intense than the signals from the major component.

The ^{31}P NMR spectra for the above complexes and for their α_1 isomers are also reported. Broadened signals from both P atoms are observed for each paramagnetic Wells–Dawson derivative, but shifts and broadenings are less dramatic for the α_2 cases than for the α_1. As expected, these effects are less pronounced on that P atom which is more distant from the M^{n+} ion in each paramagnetic complex.

The ^{31}P and ^{183}W NMR spectra are also reported for α-$[(D_2O)M^{2+}O_5PW_{11}O_{34}]^{5-}$ complexes wherein $M^{2+} = Zn^{2+}, Co^{2+}$, and Ni^{2+}. The ^{183}W spectra are reported for α-$[(D_2O)M^{2+}O_5SiW_{11}O_{34}]^{6-}$ wherein $M^{2+} = Co^{2+}, Ni^{2+}$, and Zn^{2+}. See Figure 1.

For isomorphous complexes (substituted α_1 Wells–Dawson, substituted α_2 Wells–Dawson, or substituted Keggin) of *different* paramagnetic metal ions, the relative ^{31}P signal broadenings are explained in terms of the optical spectroscopic states of the substituted transition-metal ions. For the various complexes (α_1, α_2, and substituted Keggin) of a *given* paramagnetic ion, increased line broadening accompanies increased change of chemical shift (relative to that for the corresponding diamagnetic Zn isomorph) for the P atoms near the substitution sites. This may be interpreted as indicating that these shifts are primarily of a contact shift character. However, lack of quantitative fit of the ratios of $\Delta\nu_{1/2}$'s to the ratios of the squares of the chemical shift differences indicates some contribution from a dipolar mechanism and/or second-order effects. Effects of possible partial delocalization of unpaired electron spins are discussed.

The origins of substantial errors in previously reported[7] ^{31}P NMR spectra and interpretations are elucidated.

Connectivities determined for α-$[(D_2O)ZnO_5SiW_{11}O_{34}]^{6-}$ and α-$[(D_2O)ZnO_5PW_{11}O_{34}]^{5-}$ by the 2D INADEQUATE sequence[8] fix all the ^{183}W line assignments for these two complexes.

Background

Since the first report,[9] in 1956, of preparations of heteropoly complexes having exposed second-heteroatom paramagnetic octahedrally coordinated transition-metal atoms in exterior sites of the complexes, it has been evident that such species, being soluble in nonaqueous as well as aqueous media, are potentially important as catalysts in both homogeneous and heterogeneous situations. The very unusual fact that M^{n+} in α_1-$[(L)M^{n+}O_5P_2W_{17}O_{56}]^{m-}$ (L = ligand) is a center of chirality which virtually certainly does not racemize while, at the same time, the L–M attachment is often labile[10,11] may prove to be of considerable catalytic interest.

The first heteropoly complex containing two different elements as heteroatoms, one being a transition metal, was reported[12,13] in 1962. By 1966 it was fully established,[14,15] on the basis of structural elucidation of five species, that such complexes are members of a large class of 11-heteropoly anions, in each of which an octahedrally coordinated transition-metal atom has replaced one W (or Mo) of a Keggin structure. Subsequently, others[16,17] reported many other examples.[18]

Malik and Weakley[2] extended the idea of transition-metal substitution for a W (or Mo) atom to derivatives of the 18-tungsto Wells–Dawson structure,[6] without distinguishing cap from belt substitution, and those authors noted from analytical results that each substituted derivative appeared to contain two H atoms. Baker and Figgis[20] then demonstrated that both those H atoms reside on the O atom at the unshared vertex of the $M^{n+}O_6$ octahedron and that that water molecule can be replaced by any of a variety of monodentate ligands coordinating to M^{n+} or the H_2O molecule can be stripped away leaving[21] a reactive 5-coordinate M^{n+}. The structural and electronic analogy to metalloporphyrins, with the substituted metal atom coordinated about its equator into an electron-conducting structure, was emphasized.[22] Simmons[13] discussed the ligand field spectrum of the $(H_2O)Co^{2+}O_5$ group in the subject complexes. Malik and Weakley[2] extended such spectroscopic interpretations to the substituted $(H_2O)Co^{3+}O_5$, $(H_2O)Ni^{2+}O_5$, and $(H_2O)Mn^{3+}O_5$ octahedra, while Figgis[21] interpreted the spectra for several $(L)M^{n+}O_5$ chromophores. Contant and Ciabrini[3] proposed the difference between α_1 and α_2 lacunary isomers of the Wells–Dawson derivatives and discovered how to make α_1 derivatives. After introduction of ^{183}W NMR,[23a,b] various structures were

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(3) (a) Recently, α_2-$[(H_2O)M^{n+}O_5P_2W_{17}O_{56}]^{(10-n)-}$ species ($M^{n+} = Co^{2+}, Fe^{2+}, Mn^{3+}$) have been made in pure form. These results, as well as catalytic applications of those α_2 complexes, will be reported in due course. Finke, R. G.; Miller, W. K.; Lyon, D. K.; Mansuy, D., unpublished results. (b) Contant, R.; Ciabrini, J.-P. *J. Chem. Res. Synop.* **1977**, 222; *J. Chem. Res. Miniprint* **1977**, 2601.

(4) Acerete, R.; Harmalker, S. P.; Hammer, C. F.; Pope, M. T.; Baker, L. C. W. *J. Chem. Soc., Chem. Commun.* **1979**, 777.

(5) (a) Kazanskii, L. P. *Koord. Khim.* **1976**, *5*, 719. (b) Harmalker, S. P. Doctoral Dissertation, Georgetown University, 1982. (c) Harmalker, S. P.; Pope, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 7381.

(6) (a) Wells, A. F. *Structural Inorganic Chemistry*, 1st ed.; Oxford University: Oxford, 1945; p 344. (b) Dawson, B. *Acta Crystallogr.* **1953**, *6*, 113. (c) D'Amour, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 729.

(7) (a) Spitsyn, V. I.; Kazanskii, L. P.; Torchenkova, E. A. *Sov. Sci. Rev., Sect. B* **1981**, *3*, 111. (b) Feist, M. Thesis, Moscow University, 1980.

(8) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677.

(9) Baker, L. C. W.; McCutcheon, T. P. *J. Am. Chem. Soc.* **1956**, *78*, 4503.

(10) Landis, A. M. Doctoral Dissertation, Georgetown University, 1973.

(11) Bezas, C. E. Doctoral Dissertation, University of Athens, 1972 (based on research with L.C.W.B. at Georgetown University).

(12) Simmons, V. E.; Baker, L. C. W. *Proc. Int. Conf. Coord. Chem., 7th* **1962**, 195.

(13) Simmons, V. E. Doctoral Dissertation, Boston University, 1963.

(14) Baker, L. C. W.; et al. *Proc. Int. Conf. Coord. Chem., 9th* **1966**, 421.

(15) Baker, L. C. W.; et al. *J. Am. Chem. Soc.* **1966**, *88*, 2329.

(16) (a) Weakley, T. J. R.; Malik, S. A. *J. Inorg. Nucl. Chem.* **1967**, *29*, 2935. (b) Ripan, R.; Puscasu, M. *Z. Anorg. Allg. Chem.* **1968**, *83*, 358.

(17) (a) Tourné, C. M. *C. R. Seances Acad. Sci., Ser. C* **1968**, *266*, 702. (b) Tourné, C. M.; Tourné, G. F. *C. R. Seances Acad. Sci., Ser. C* **1968**, *266*, 1363; *Bull. Soc. Chim. Fr.* **1969**, 1124. (c) Zonnevijlle, F.; Tourné, C. M.; Tourné, G. F. *Inorg. Chem.* **1982**, *21*, 2742; **1982**, *21*, 2751; **1983**, *22*, 1198.

(18) It is interesting to note that, until the application of ^{183}W NMR to polytungstate structures[19] in 1979, the only unambiguous proof[15] that these complexes are 11-tungstates was based on crystallographic unit cell volumes and densities, with the distinction between 11-tungsto and 12-tungsto formulations being within the error of all other analytical techniques and thwarted by crystallographic disorder.

(19) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, *101*, 267.

(20) Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794.

(21) Figgis, J. S. Doctoral Dissertation, Georgetown University, 1970.

(22) Baker, L. C. W. *Plenary Lecture, Int. Conf. Coord. Chem., 15th* **1973**.

Table I. ^{31}P NMR Chemical Shifts (from 85% H_3PO_4) and Line Widths ($\Delta\nu_{1/2}$'s) for α_1- and α_2-Monometallo-17-tungstodiphosphates and α-Monometallo-11-tungstophosphates at 297 K (0.01 M Solutions of K^+ Salts in 20% D_2O)

	P(1) (close to M)		P(2) (far from M)		
heteropolyanion	δ	$\Delta\nu_{1/2}$, Hz	δ	$\Delta\nu_{1/2}$, Hz	comments
α_2-$[(H_2O)Zn^{2+}P_2W_{17}O_{61}]^{8-}$	-8.0	<1.0[a]	-13.5	<1.0[a]	diamagnetic; 17% α_1 impurity present (Figure 3)
α_1-$[(H_2O)Zn^{2+}P_2W_{17}O_{61}]^{8-}$	-7.9	<1.0[a]	-12.8	<1.0[a]	diamagnetic; 8% α_2 impurity present (Figure 3)
α_2-$[(H_2O)Co^{2+}P_2W_{17}O_{61}]^{8-}$	+250	25	-23.7	5	30% α_1 impurity present (Figure 2)
α_1-$[(H_2O)Co^{2+}P_2W_{17}O_{61}]^{8-}$	+1135	103	-34.5	4.9	11% α_2 impurity present (Figure 3)
α_2-$[(H_2O)Ni^{2+}P_2W_{17}O_{61}]^{8-}$	+228	825	-14.0	12	20% α_1 impurity present
α_1-$[(H_2O)Ni^{2+}P_2W_{17}O_{61}]^{8-}$	+895	5700	-16.6	60	10% α_2 impurity present
α_2-$[(H_2O)Mn^{3+}P_2W_{17}O_{61}]^{7-}$	+575	~9000	-12.5	60	20% α_1 impurity present
α_1-$[(H_2O)Mn^{3+}P_2W_{17}O_{61}]^{7-}$	~700 probably	>30000	+8.0	450	10% α_2 impurity present
α_2-$[(H_2O)Mn^{2+}P_2W_{17}O_{61}]^{8-}$	~600	~40000	-13.4	200	15% α_2 impurity present
α_1-$[(H_2O)Mn^{2+}P_2W_{17}O_{61}]^{8-}$	very broad[b]		-4.0	650	10% α_1 impurity present
α-$[(D_2O)Zn^{2+}PW_{11}O_{39}]^{5-}$	-11.5	<0.4			diamagnetic; resolved $^2J_{P-O-W}$ = 1.30 Hz; Li^+ salt in pure D_2O
α-$[(D_2O)Co^{2+}PW_{11}O_{39}]^{5-}$	+458	28			Li^+ salt soln in pure D_2O
α-$[(D_2O)Ni^{2+}PW_{11}O_{39}]^{5-}$	+472	~1650			Li^+ salt soln in pure D_2O

[a] Line widths not determined more accurately owing to incompletely resolved P–O–W couplings. [b] Observation questionable.

substantiated or corrected.[8,23-28]

Experimental Section

The complexes were prepared by standard methods[2,3,13,23-29] and recrystallized as potassium salts. Owing to low NMR sensitivity of ^{183}W and relatively low solubility of the K^+ salts, the latter were converted to more soluble solid Li^+ salts, for use in ^{183}W NMR experiments, by ion exchange[30] (Dowex 50W-X8) and subsequent crystallization. To ensure that the observed presence of α_1 isomers in the α_2 preparations had not been caused by the presence of Li^+ in this treatment, ^{31}P NMR spectra were obtained for the solutions of the α_2 Li^+ salt of the Co complex and for its parent, the α_2 K^+ salt, which had been prepared in the complete absence of Li^+. The percentages of α_1 impurity (30%) were identical for the Li^+ and K^+ salts.

NMR spectra were taken on either a Bruker AM300WB or a Nicolet NT360WB spectrometer. NMR chemical shifts for ^{31}P and ^{183}W were referenced to 85% H_3PO_4 and 2 M Na_2WO_4 in D_2O, respectively, by the sample replacement method. Since relaxation rates of ^{31}P are known to be very slow in diamagnetic heteropoly species, correct relaxation delays were determined by increasing the delay for the $[(H_2O)M^{n+}O_5P_2W_{17}O_{56}]^{(10-n)-}$ species until the integration ratios for the two P atoms were equal. Owing to the large chemical shift separations involved, it was often necessary, for observation of the equal intensities, to set the transmitter frequency midway between the signals. The ^{31}P chemical shifts do not have large concentration or ionic strength dependences. The ^1H NMR spectrum was taken of a solution of α-$[(D_2O)Co^{2+}O_5SiW_{11}O_{34}]^{6-}$ in D_2O with DSS[31] added as the chemical shift standard. The DSS signal moved only very slightly (±0.2 ppm) relative to its signal in the absence of paramagnetic species, allowing confidence in the external references in lieu of internal shift references.

Results and Discussion

For the paramagnetic 17-tungstodiphosphate species, signals from the two P atoms were assigned on the basis that the sharper line always had a chemical shift very near to all the closely similar shifts in all the diamagnetic species[32,33] (α-$P_2W_{18}O_{62}{}^{6-}$, β-$P_2W_{18}O_{62}{}^{6-}$, α_2-$P_2W_{17}O_{61}{}^{10-}$, α_1- and α_2-$(H_2O)ZnP_2W_{17}O_{61}{}^{8-}$, α_1-

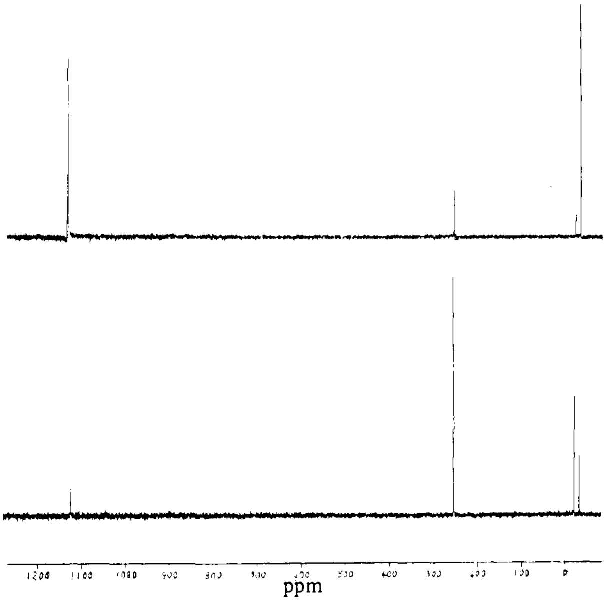

Figure 2. ^{31}P NMR spectra. The line heights in this figure do not reflect the true integrations owing to differences in line widths, very different relaxation times, and unsymmetrical locations of the widely separated peaks with respect to the irradiating frequency. The integrations represented in Table I by percents of impurities are correct, having been made on the respective P(2) narrow peaks with very long relaxation delays (>20 s). Upper spectrum: ^{31}P NMR spectrum of 0.01 M solution, in 20% D_2O, of K^+ salt of α_1-$[(H_2O)Co^{2+}O_5P_2W_{17}O_{56}]^{8-}$, showing 11% impurity of the α_2 isomer. Lower spectrum: ^{31}P NMR spectrum of 0.01 M solution, in 20% D_2O, of K^+ salt of α_2-$[(H_2O)Co^{2+}O_5P_2W_{17}O_{56}]^{8-}$, showing 30% impurity of the α_1 isomer.

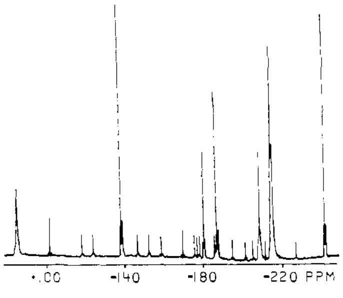

Figure 3. ^{183}W NMR spectrum of 0.2 M solution, in pure D_2O, of Li^+ salt of diamagnetic α_2-$[(D_2O)ZnO_5P_2W_{17}O_{56}]^{8-}$. The large peaks are from the α_2 isomer, and the small peaks coincide exactly, with expected overlaps, to a ~17% impurity of the α_1 isomer. See summaries of chemical shifts in Table II.

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(23) (a) Acerete, R. Doctoral Dissertation, Georgetown University, 1981. (b) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, *101*, 267. (c) Acerete, R.; Harmalker, S.; Hammer, C. F.; Pope, M. T.; Baker, L. C. W. *J. Chem. Soc., Chem. Commun.* **1979**, 777. (d) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1982**, *104*, 5384. (e) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *Inorg. Chem.* **1984**, *23*, 1478. (f) Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 2748.

(24) Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 244.

(25) Brevard, C.; Schimpf, R.; Tourné, G. F.; Tourné, C. M. *J. Am. Chem. Soc.* **1983**, *105*, 7059.

(26) Domaille, P. J.; Knoth, W. H. *Inorg. Chem.* **1983**, *22*, 818.

(27) (a) Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *22*, 1006. (b) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947.

(28) (a) Lefebvre, J. E.; Chauveau, F.; Doppelt, P.; Brevard, C. *J. Am. Chem. Soc.* **1981**, *103*, 4589. (b) Jeannin, Y.; Martin-Frère, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 1664.

(29) North, E. O.; Haney, W. *Inorg. Synth.* **1939**, *1*, 127.

(30) Baker, L. C. W.; Loev, B.; McCutcheon, T. P. *J. Am. Chem. Soc.* **1950**, *72*, 2374.

(31) DSS = sodium 3-(trimethylsilyl)-1-propane-d_6-sulfonate.

Table II. ^{183}W NMR Chemical Shifts (from 2 M Na_2WO_4) and Line Widths ($\Delta\nu_{1/2}$'s) for α_1- and α_2-Monometallo-17-tungstodiphosphates, α-Monometallo-11-tungstophosphates, and α-Monometallo-11-tungstosilicates at 303 K (~0.2 M Solutions of Li^+ Salts in D_2O)

heteropolyanion	δ and $\Delta\nu_{1/2}$ (Hz)	comments
α_2-$[(D_2O)Zn^{2+}P_2W_{17}O_{61}]^{8-}$	-84.4 (2 W), -138.7 (2 W), -180 (1 W), -186.7 (2 W), -208.6 (2 W), -214.8 (6 W), -242.7 (2 W)	P-O-W couplings make each 1 W and 2 W line a narrow doublet; diamagnetic; α_1 impurity present (Table I; Figure 3)
α_1-$[(D_2O)Zn^{2+}P_2W_{17}O_{61}]^{8-}$	all 1 W lines: -99.4, -117.4, -123.0, -146.1, -151.9, -157.7, -167.6, -174.2, -175.7, -177.3, -193.3, -200.1, -203.7, -210.3, -214.1, -214.6, -225.5	P-O-W couplings make each line (except first) a narrow doublet; diamagnetic; α_2 impurity present (Table I; Figure 3)
α_2-$[(D_2O)Co^{2+}P_2W_{17}O_{61}]^{8-}$	+533.7 (60 Hz) (2 W), +475.7 (60) (2 W), -146 and -153 (3 W-overlap), -200 (45) (2 W), -232 and -236 (~40 each) (4 W overlap)	line widths for the 3 W overlap uncertain; α_1 impurity present (Table I; Figure 2)
α_2-$[(D_2O)Ni^{2+}P_2W_{17}O_{61}]^{8-}$	+468.3 (82) (2 W), +338.7 (55) (2 W), -142 and -146 (~30 each) (4 W overlap), -200 and -202 (~25 each) (3 W overlap), -230.5 (27) (2 W)	α_1 impurity present (Table I)
α-$[(D_2O)Zn^{2+}PW_{11}O_{39}]^{5-}$	-73.0 (2 W), -106.5 (2 W), -130.1 (1 W), -130.6 (2 W), -140.4 (2 W), -157.1 (2 W)	P-O-W couplings make each 1 W and 2 W line a narrow doublet; diamagnetic
α-$[(D_2O)Co^{2+}PW_{11}O_{39}]^{5-}$	+817.8 (145) (2 W), +725.0 (104) (2 W), -192.4 (104) (2 W), -256.0 (134) (1 W)	
α-$[(D_2O)Ni^{2+}PW_{11}O_{39}]^{5-}$	+642.3 (67) (2 W), +592.9 (57) (2 W), -120.6 (27) (2 W), -197.0 (25) (1 W)	
α-$[(D_2O)Zn^{2+}SiW_{11}O_{39}]^{6-}$	-71.6 (2 W), -115.1 (2 W), -139.9 (1 W), -146.4 (2 W), -166.3 (2 W), -182.9 (2 W)	all lines narrow (Figures 4 and 5)
α-$[(D_2O)Co^{2+}SiW_{11}O_{39}]^{6-}$	+437.6 (171) (2 W), +390.2 (168) (2 W), -222.2 (167) (2 W), -280.2 (169) (1 W)	
α-$[(D_2O)Ni^{2+}SiW_{11}O_{39}]^{6-}$	+327.7 (84) (2 W), +307.9 (72) (2 W), -133.9 (53) (2 W), -224.5 (55) (1 W)	

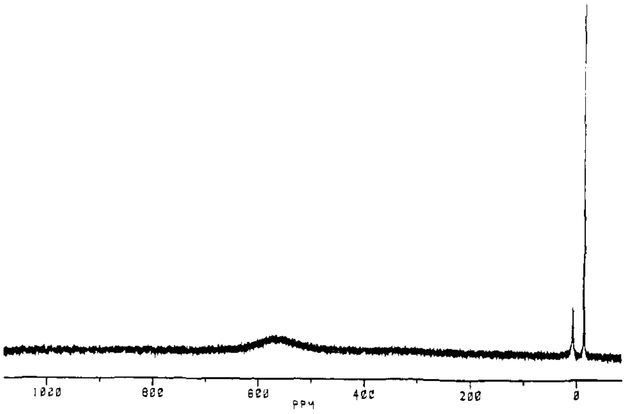

Figure 4. ^{31}P NMR spectrum of α_2-$[(D_2O)Mn^{3+}O_5P_2W_{17}O_{56}]^{7-}$. The P(1) peak is the very broadened downfield signal. The minor peak just downfield from the major P(2) signal is the P(2) line for the impurity of α_1 isomer.

and α_2-$MoP_2W_{17}O_{62}{}^{6-}$, α-$(H_2O)ZnPW_{11}O_{39}{}^{5-}$, α_2-$P_2W_{17}VO_{62}{}^{7-}$). That line was assigned to "P(2)", the P atom farthest from the substitution site. No line having close to that δ was observed for any of the paramagnetic 11-tungstomonophosphates. Instead, each paramagnetic 17-tungstodiphosphate exhibited one line considerably shifted in a manner similar to that observed for the single line of the 11-tungstophosphate containing the same paramagnetic atom. For the 17-tungstodiphosphates, that line was assigned to the P atom nearest the substitution site, designated "P(1)". For the α_1 Mn^{2+} and Mn^{3+} derivatives, broadening of the P(1) signal was so severe that lines were difficult to discern accurately from base-line artifacts.

The NMR results, for the lines from the major isomer present in each case, are listed in Tables I and II. Figures 2–4 reproduce representative spectra showing typical presence of the isomeric impurities. Figure 5 presents a graphical representation of comparative ^{183}W NMR chemical shifts.

A recent review[7] reports ^{31}P NMR chemical shifts for several heteropoly complexes containing substituted paramagnetic atoms. Because the researchers were not aware that standard preparations of α_2-substituted 17-tungsto Wells–Dawson derivatives contain substantial amounts of the α_1 isomer, the two ^{31}P NMR peaks in their spectrum of α_2-$[(H_2O)Co^{2+}O_5P_2W_{17}O_{56}]^{8-}$, for example, were attributed to the two P atoms in the α_2 isomer. However, those peaks coincide almost exactly with those reported in the present paper for the P(2) of the α_2 isomer and the P(2) of the α_1 isomer. The significantly shifted signals from both (α_1 and α_2) P(1) atoms were missing from their spectrum, so the P(2) line from the α_1 isomer was incorrectly identified as the P(1) peak of the α_2. Hence, the direction and magnitude of the chemical shift for the P atom near the paramagnetic Co atom were incorrectly interpreted.

Another source of difficulty with their data and interpretation[7] is attributable to use of insufficiently large sweep widths for

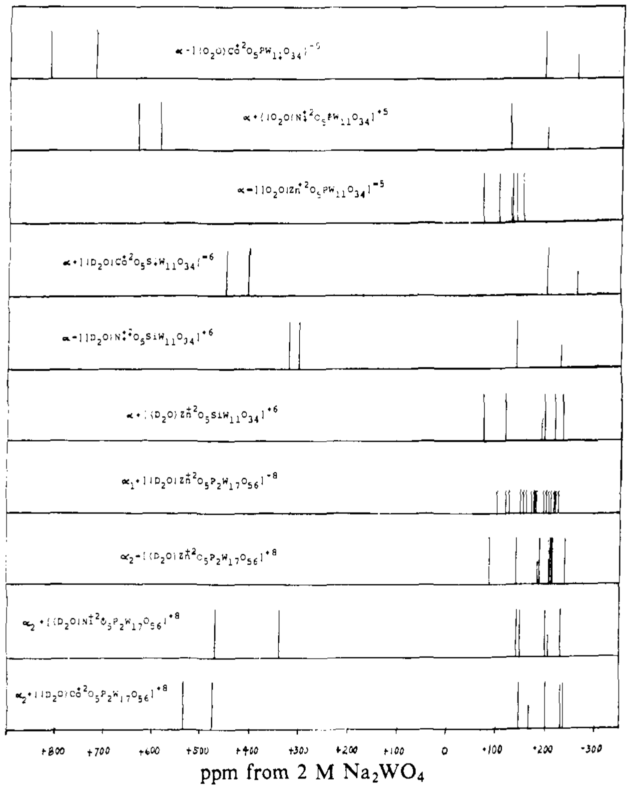

Figure 5. Graphical summary of ^{183}W NMR spectra.

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(32) Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 7627.

(33) Massart, R.; Contant, R.; Fruchart, J. M.; Ciabrini, J. P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916.

obtaining the spectra. This evidently resulted in fold-over of signals from outside the spectral window. Thus, for example, they report ^{31}P shifts of −115 and −88 ppm for Co^{2+}- and Ni^{2+}-substituted 11-tungstophosphates, respectively, and −14 and −100 ppm for the two P atoms in α_2-$[(H_2O)Ni^{2+}O_5P_2W_{17}O_{56}]^{8-}$. The present work finds shifts of +458 and +472 ppm, respectively, for these 11-tungstophosphates and −14 and +228 ppm for this 17-tungstodiphosphate. The spectra reported in the present paper do not suffer from such fold-over difficulties because neither change of irradiation frequency nor increase of sweep width resulted in changes in chemical shifts.

^{31}P NMR Line Widths. For each series of complexes (α_2 isomers, substituted Keggin species, and α_1 isomers), the order of line broadenings is the same, for corresponding P atoms. The data are presented in Table I. For example, the $\Delta\nu_{1/2}$'s for the P(1)'s in the Wells–Dawson derivatives are as follows: Zn^{2+} complexes (diamagnetic), signals very narrow (<1 Hz); Co^{2+} complexes, signals relatively narrow (25 and 103 Hz); Ni^{2+} complexes, signals intermediate (825 and 5700 Hz); Mn^{3+} complexes, signals very broad (9000 and >30 000 Hz); and Mn^{2+} complexes, signals extremely broad (over 40 000 Hz).

This is consistent with the electronic ground states[2] of the respective paramagnetic ions, when octahedral: Mn^{2+}, $^6A_{1g}$; Mn^{3+}, ^5E_g (but after Jahn–Teller distortion $^5B_1$); Ni^{2+}, $^3A_{2g}$; Co^{2+}, $^4T_{1g}$. Although there is some distortion of the octahedral geometry about the Mn, Co, and Ni ions, as revealed by greatly enhanced extinction coefficients of ligand field spectral lines,[13,20] that distortion is insufficient to change fundamentally the ground states cited above.

The complexes containing paramagnetic ions with orbitally nondegenerate ground states are those giving very broad ^{31}P signals. As expected,[34] the orbitally nondegenerate states have slow relaxation times for electrons and hence fast nuclear relaxations, and vice versa. The P(1) signals from the Mn^{3+} and especially the Mn^{2+} (nondegenerate) complexes are much broader than those from the Co^{2+} (degenerate) complex. Although Ni^{2+} has $^3A_{2g}$ orbitally nondegenerate ground state, its magnetic susceptibility and UV-vis spectrum in these compounds[2] show sizable configurational interaction of the singlet ground state and a triply degenerate excited state. The excited state of Ni^{2+} exhibits appreciable spin–orbit coupling.[35] This consideration puts the Ni^{2+} complexes in an intermediate category, closer to the Co^{2+} species, with respect to line broadenings.

Comparisons between the ^{31}P line widths for the three kinds of structures, α_1 isomers, α_2 isomers, and substituted Keggin species, present difficulties for which present data are insufficient. These include various correlation times about different axes and different distortions of the polyhedra resulting from decidedly different structural features of the site of the substituted metal ions in the α_1 versus the α_2 species.

^{31}P NMR Chemical Shifts. The data are presented in Table I. A basic question is the fundamental origins of the chemical shifts for a given type of P atom. Possibilities include contact or dipolar shift mechanisms or some mixture of these with one another and/or with second-order effects such as admixture of excited states. While it is not possible, on the basis of the present data, to decide with certainty on the basic shift mechanism and the roles of the various factors that could modify it, the following observations are pertinent.

For complexes of a *given* paramagnetic atom, *each* series of species (α_2, substituted Keggin, and α_1, in that order) involves sizably increasing changes of ^{31}P chemical shifts (relative to those for the diamagnetic Zn isomorphs) accompanied by markedly increasing line broadenings, for the P's in the Keggin derivatives and for the P(1)'s in both sorts of Wells–Dawson species. This argues rather strongly that the chemical shift mechanism is primarily contact in character[36] for those P atoms. If magnetic anisotropy factors are taken to be equal for the paramagnetic atoms, in the α_2 and Keggin cases, a pure dipolar shift mechanism for localized spins would keep both the broadenings and the changes of chemical shifts constant for a given paramagnetic metal ion.[36] Structural considerations lead to the supposition that the M^{n+} ion's magnetic anisotropy in the substituted Keggin structure must be at least very close to that in the α_2 Wells–Dawson complex. The localization of the spins may not be such a sure assumption, however, as explained below. On the other hand (again presuming the rotationally averaged electronic g's are essentially equal, for α_2 and Keggin cases), a pure contact shift mechanism would see that the ratios of the changes in line widths (for P_1 in the α_2 vs P in the Keggin derivative) equal the square of the ratios of the corresponding changes of chemical shifts.[36] This criterion is moderately far from being fulfilled in each series. The fit is much worse for the α_1 P(2)'s vs the α_2 P(2)'s. This leads to the conclusion that while the chemical shift mechanism for P(1)'s and Keggin derivative P's is probably primarily of a contact shift character, there is probably a significant contribution of other effects. The shift mechanism for the P(2)'s is even further from being of a purely contact nature.

It is interesting to consider the fact that the three Co^{2+} complexes (α_2, substituted Keggin, and α_1) exhibit markedly different *changes* of chemical shifts (relative to the corresponding Zn^{2+} complexes) for the P atoms adjacent to the substitution sites (+258, +470, and +1143 ppm, respectively). The same order is found for the Ni^{2+} complexes (+236, +484, and +903 ppm, respectively). In all these cases, the substitution sites are equidistant from these P atoms and each M^{2+} is connected to P by a M^{2+}–O–P linkage as well as by M^{2+}–O–W–O–P routes.

For the complexes of a given substituted paramagnetic M^{2+}, it is not surprising to find the P(1) chemical shift for the α_1 species to be very different from those of the P(1) in the α_2 or the P in the Keggin derivative. The total symmetry of the substitution site in α_1 is decidedly different from that in the α_2 or Keggin derivative, which would affect the couplings. See Figure 1. The α_2 and substituted Keggin structures, however, have virtually identical substitution-site symmetries and M^{2+}–O–P angles. It is probably instructive, then, to consider why their P chemical shifts might be so different, and different in a consistent order.

The unusually small Racah *B′* parameters for M^{2+} ions in the substitution sites[13,21] indicate rather considerable nephelauxetic effects for the d electrons, spreading their density and influence into or perhaps throughout the tungsten–oxygen frameworks of the heteropoly structures. This is consistent (a) with the rapidity of redox reactions of metal ions in the centers of Keggin heteropoly species, (b) with the rapidity of exchanges of delocalized electrons between heteropoly blue species,[32] and (c) especially with the complete diamagnetic pairing, via multiroute superexchange, of the added electrons when α_1- or α_2-$[P_2MoW_{17}O_{62}]^{6-}$ is reduced by addition of two electrons (one of which ends up anchored on the more easily reduced Mo atom while the other one is delocalized by rapid hopping among other, sometimes distant, W atoms).[37] The extensive pairing of the spins of d electrons from paramagnetic atoms in the tetrahedral centers of Keggin derivatives with d electrons from paramagnetic atoms substituted for W atoms[38] is also pertinent.

Any spread of the unpaired d electron density in a substituted Wells–Dawson case might possibly be expected to be preferentially concentrated in the belts of the structure,[23f] while such a spread would involve all the atoms in a Keggin derivative,[23f] thus even reaching around to the far side of the P atom in the substituted Keggin cases but much less so in the Wells–Dawson derivatives.

In any case, the consistent differences in α_2 P(1) versus substituted Keggin P chemical shifts emphasize that the effect of the

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[34] Swift, T. J. In *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, W. DeW., Jr., Holm, R. H., Eds.; Academic: New York, 1973; pp 53–85.

[35] Drago, R. S. *Physical Methods in Chemistry*; Saunders: Philadelphia, 1977; p 426.

[36] Horrocks, W. DeW., Jr. In *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, W. DeW., Jr., Holm, R. H., Eds.; Academic: New York, 1973; pp 127–177.

[37] Kozik, M. Doctoral Dissertation, Georgetown University, 1987.

[38] (a) Baker, L. C. W.; Baker, V. E. S.; Wasfi, S. H.; Candela, G. A.; Kahn, A. H. *J. Am. Chem. Soc.* **1972**, *94*, 5499; *J. Chem. Phys.* **1972**, *56*, 4917. (b) Wasfi, S. H. Doctoral Dissertation, Georgetown University, 1971.

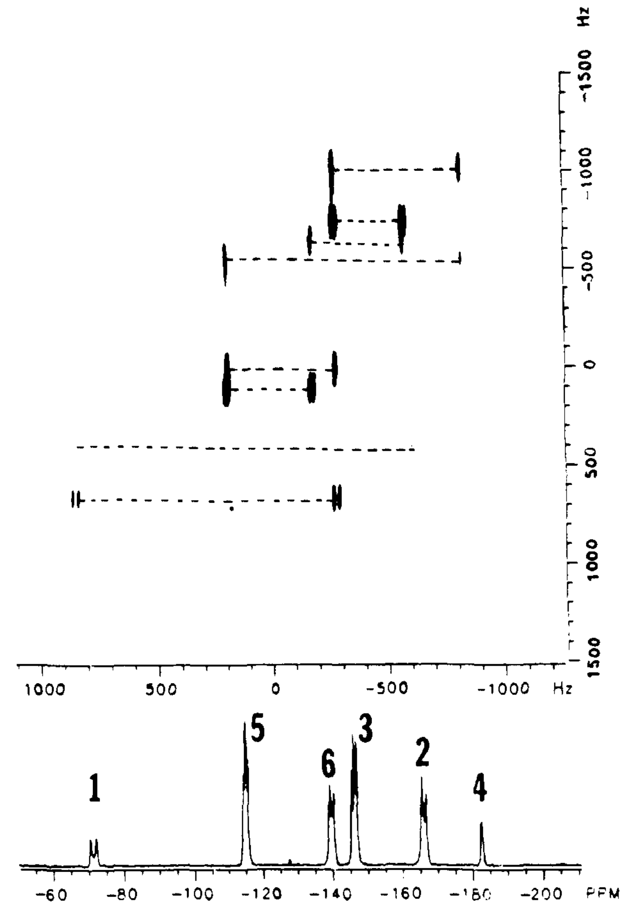

Figure 6. Contour plot of the ^{183}W NMR 2D INADEQUATE spectrum for α-$[(D_2O)ZnO_5SiW_{11}O_{34}]^{6-}$ at 303 K. A 20-mm sideways-spinning probe was used. At the bottom is the 1D ^{183}W NMR spectrum with band assignments numbered in accordance with Figure 1a. Connectivities between ^{183}W resonances are indicated by dashed lines. Corner couplings appear as "dumbbells", while edge couplings appear as "single ovals". The connectivity between W(1) and W(2) is not seen on this contour plot, but it is clearly visible on the plot of the appropriate matrix row in the double-quantum dimension.

electronic influence of the unpaired d electrons must be considered for the whole structure, and not just as acting through the M^{n+}–O–P attachment or the local site symmetry.

^{183}W NMR Spectra. The ^{183}W NMR spectrum reported for the α_1-aquozinc-17-tungstodiphosphate complex, with its 17 equal-intensity lines, provides the first direct structure proof for a monosubstituted α_1 isomer. See Table II and Figures 3 and 5.

For all the Co and Ni complexes, signals from the four W atoms closest to the paramagnetic atoms were not observed, presumably owing to their signals having been broadened into nonobservability. All the other ^{183}W signals were substantially broadened (by 50–170 Hz).

Further discussion of the ^{183}W NMR line broadenings and chemical shifts, although tempting, is not warranted at this time because assignments of the W signals from the paramagnetic species would have to be very speculative. This is emphasized by the inconsistency of relative placements and even of directions of changes of chemical shifts (from the δ's in the corresponding Zn complexes) for the one assignable W line in each α_2 or substituted Keggin spectrum (the line for the single structurally unique W), even though that W atom is the one farthest away from the substitution sites.

For the Zn, Co, and Ni complexes, the ^{183}W spectra of the 17-tungsto complexes proved which ^{31}P signals belong to α_1 isomers and which to α_2 by confirming that each preparation resulted primarily in the species intended.

Preliminary investigation of the ^{183}W NMR spectra of the α_2 Mn complexes indicated patterns substantially different from those observed for the other α_2 complexes. Fewer lines were discernible, possibly owing to great broadening of signals from next-to-nearest W neighbors of the Mn's or because of more extreme shifts. The pattern of chemical shifts for the Mn^{3+} derivative was quite different from that seen for the other α_2 complexes.

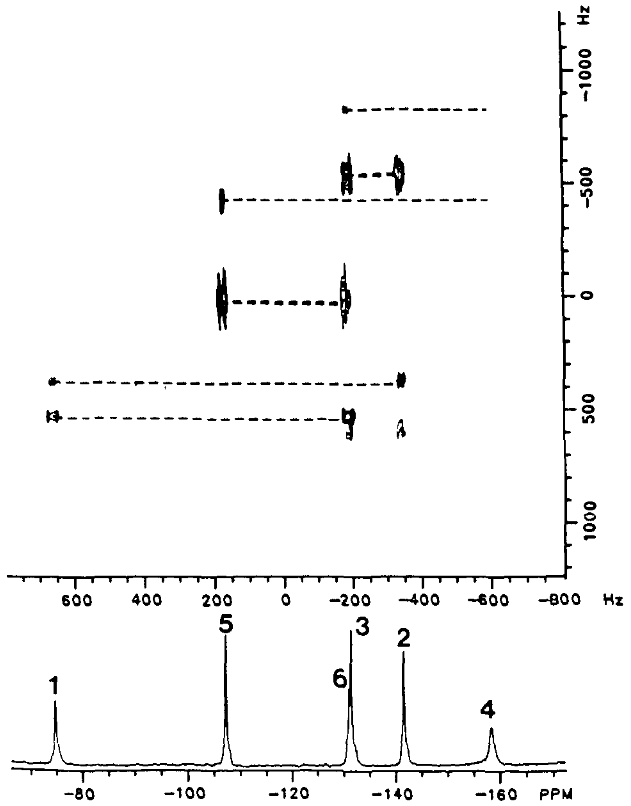

Figure 7. Contour plot of the ^{183}W NMR 2D INADEQUATE spectrum for α-$[(D_2O)ZnO_5PW_{11}O_{34}]^{5-}$ at 303 K. The 1D ^{183}W NMR spectrum is shown with band assignments numbered in accordance with Figure 1a.

2D NMR INADEQUATE Connectivity Studies. The two-dimensional ^{183}W NMR spectrum of α-$[(D_2O)ZnO_5SiW_{11}O_{34}]^{6-}$ is shown in Figure 6, wherein horizontal lines connect coupled sites. The magnitudes of the $^2J_{W-O-W}$ values are clear from the contour map because the edge couplings (J = 5–12 Hz) appear as unresolved "ovals" owing to their large line widths, whereas the stronger corner couplings (J = 15–30 Hz) produce "dumbbells" for all four resolved components of the AX spin systems.[26,28a] The numbering of W octahedra is shown in Figure 1a. The structure has five nonequivalent pairs of structurally identical W atoms plus a single structurally unique W. Its 11 W atoms therefore produce 5 signals of equal intensity plus 1 signal having half that intensity. See Figure 6.

The signal from the unique W (W(6)) at −139.9 ppm is easily assigned on the basis of intensity. Its corner connection to W(5) (−115.1 ppm) is clearly distinguishable from the W(6) edge-sharing connection to W(2) (−166.3 ppm). W(5) shows edge connections to both W(3) and W(4). W(2) shows corner connections to W(3) and W(1). Thus, W(3) is unambiguously identified (−146.4 ppm), and consequently W(1) (−71.6 ppm) and W(4) (−182.9 ppm) are also identified. The assignment is further confirmed by the remaining two connectivities, of which one is observed (edge sharing between W(3) and W(4)), while the other (corner sharing between W(1) and W(3)) can be seen clearly on the plot of the appropriate matrix row.

An analogous 2D ^{183}W NMR INADEQUATE connectivity study was made on α-$[(D_2O)ZnO_5PW_{11}O_{34}]^{5-}$. The chemical shifts are listed in Table II. The connectivities and the order of the line assignments came out to be identical with those of the Si complex described immediately above. See Figure 7.

There is only one previous 2D connectivity study of a complex wherein a metal atom in +2 oxidation state has been substituted into one of the 12 identical sites occupied by W atoms in the

Keggin structure. The previous studies involved V^{5+} substitution when the central heteroatom was Si, P, or B[8] and Pb^{2+} and Ti^{4+} substitution when the central atom was P.[25,39] The Pb^{2+} complex was atypical,[40] involving a temperature-dependent shift of the signal from W(4) far downfield from its position in the other complexes, owing presumably to some rapid exchange, possibly with the lacunary species, and to unusual steric placement of the Pb atom.[25] All the other complexes, including the present ones, show some remarkably similar, although not identical, features with respect to orders of chemical shifts. In all of the spectra, the most downfield line (most deshielded W's) is for W(1) (the pair of W's sharing edges with the substituted metal), while the most shielded or second most shielded W's are W(4), those sharing corners with the substituted metal. The order of line assignments for the present study of the Zn^{2+} complexes is most similar to that for the V^{5+} derivative of 11-tungstosilicate.

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(39) Knoth, W. H.; Domaille, P. J.; Roe, D. C. *Inorg. Chem.* **1983**, *22*, 198.

(40) Tourné, G. F.; Tourné, C. M.; Schouten, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1414.

Complexes of (Arylimido)vanadium(V). Synthetic, Structural, Spectroscopic, and Theoretical Studies of V(Ntol)Cl$_3$ and Derivatives

David D. Devore,[†] Joseph D. Lichtenhan,[†] Fusao Takusagawa,[‡] and Eric A. Maatta*[†]

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, and Department of Chemistry, University of Kansas, Lawrence, Kansas 66045. *Received March 23, 1987*

Abstract: The reactions of VOCl$_3$ with various para-substituted aryl isocyanates, p-XC$_6$H$_4$NCO (X = CH$_3$, CF$_3$, OCH$_3$, F, Cl, Br), afford the corresponding (arylimido)vanadium(V) trichloride species, V(NC$_6$H$_4$X)Cl$_3$. The p-tolylimido complex, V(Ntol)Cl$_3$, **1**, displays an extensive derivative chemistry. The reaction of **1** with Lewis bases affords monoaddition products such as V(Ntol)Cl$_3$(THF) and V(Ntol)Cl$_3$(PPh$_3$). The chloride ligands of **1** readily participate in nucleophilic substitution reactions, affording a range of alkoxide (V(Ntol)Cl$_{3-n}$(O-t-Bu)$_n$: n = 1, **2**; n = 2, **3**; n = 3, **4**), aryloxide (V(Ntol)Cl$_{3-n}$(OAr)$_n$: n = 1, **5**; n = 2, **6**; n = 3, **7**; Ar = 2,6-C$_6$H$_3$(CH$_3$)$_2$), and organometallic (V(Ntol)Cl$_{3-n}$(CH$_2$SiMe$_3$)$_n$: n = 1, **8**; n = 2, **9**; n = 3, **10**; (η^5-C$_5$H$_5$)V(Ntol)Cl$_2$, **11**) derivatives. The electronic spectra of complexes **1-10** each display an absorption in the near-IR region at ca. 1000 nm. Complexes **1-7** also display a second absorption in the visible region of the spectrum, and the energy of this absorption increases with increasing electronegativity of the basal ligand donor atoms. The ^{51}V NMR spectra of these (arylimido)vanadium(V) complexes have been determined; ^{51}V chemical shifts in this series span a range of 1700 ppm. The ^{51}V chemical shifts also correlate with the electronegativity of the basal ligand donor atoms. The lowest field position is observed for **10** ($\delta(^{51}$V) = +1048), and a regular progression of $\delta(^{51}$V) to higher field occurs as the purely σ-donating alkyl groups are replaced by ligands of increased electronegativity and increased π-donating ability. The observed correlations of the electronic and ^{51}V NMR spectra with the chemical constitutions of complexes **1-10** are explained in terms of a dominating paramagnetic shielding contribution. Extended Hückel calculations on several model complexes are used to provide an explanation of the electronic factors underlying the disparate ^{51}V chemical shifts observed for complexes **1-10** and related vanadium(V) complexes bearing oxo and alkylimido ligands. An X-ray crystal structure determination reveals that complex **6** possesses a dimeric structure in the solid state. Each vanadium atom in the centrosymmetric dimer is coordinated in a trigonal-bipyramidal geometry, with a terminal tolylimido ligand and a bridging aryloxide group occupying the apical sites. There is a decided asymmetry in the V-O-V bridge bonding. Crystal data for **6**: monoclinic, $I2/c$; a = 24.937 (5), b = 10.790 (2), c = 16.662 (3) Å; β = 97.18 (2)°; Z = 8.

Although a number of vanadium(V) organoimido complexes are now known,[1] these species are generally insular and lack a systematic derivative chemistry. We now report that trichloro(p-tolylimido)vanadium(V), V(Ntol)Cl$_3$,[2] can be readily functionalized to afford a variety of alkoxide, aryloxide, and organometallic derivatives of (p-tolylimido)vanadium(V). The wide range of compounds accessible in this series has allowed us to begin to delineate the influence of various coordination environments on the ^{51}V NMR characteristics of (organoimido)vanadium(V) complexes. Correlations between the ^{51}V NMR results and the electronic spectra of these species are examined with the aid of extended Hückel calculations and provide an illustrative comparison to related vanadium(V) complexes of oxo and alkylimido ligands. We also report the molecular structure of a dimeric (2,6-dimethylphenoxide) species, [V(Ntol)(OAr)$_2$Cl]$_2$. A subsequent paper will describe various chelate derivatives of V(Ntol)Cl$_3$ and the preparations of (p-tolylimido)vanadium(IV) species.[3]

[†] Kansas State University.

[‡] University of Kansas.

(1) (a) Burger, H.; Smrekar, O.; Wannagat, U. *Monatsh. Chem.* **1964**, *95*, 292. (b) Slawisch, A. *Z. Anorg. Allg. Chem.* **1970**, *374*, 291. (c) Shihada, A. F. *Z. Anorg. Allg. Chem.* **1974**, *408*, 9. (d) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1979**, 342. (e) Preuss, F.; Towae, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1130. (f) Bradley, D. C.; Hursthouse, M. B.; Jelfs, A. N. M.; Short, R. L. *Polyhedron* **1983**, *2*, 849. (g) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965. (h) Preuss, F.; Towae, W.; Kruppa, V.; Fuchslocher, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1510. (i) Schweda, E.; Scherfise, K. D.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, 117. (j) Preuss, F.; Becker, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 185. (k) Preuss, F.; Noichl, H.; Kaub, J. *Ibid.* **1986**, *41B*, 1085.

(2) Maatta, E. A. *Inorg. Chem.* **1984**, *23*, 2560.

(3) Wheeler, D. E.; Maatta, E. A., to be submitted for publication.

0002-7863/87/1509-7408$01.50/0