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Magnetic Resonance Spectra of Some Mixed-Metal Paramagnetic Dinuclear Complexes with 2-Pyridyl Methyl Ketazine

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Received June 26, 1978

2-Pyridyl methyl ketazine (PMK) is known to form dinuclear octahedral complexes of formula $M_2(PMK)_3Y_4 \cdot nH_2O$ (M = Co, Ni, Cu, Zn; Y = ClO_4, I, BF_4). The exchange coupling between the two metal ions appears to be small. We have prepared also solid compounds containing metal complexes of formula $MM'(PMK)_3(NO_3)_4 \cdot 3H_2O$ and have recorded the proton magnetic resonance spectra of all the complexes. The isotropic shifts of the ligand protons have been discussed in terms of a simple additive model according to which they are the result of two independent contributions, one from the closer and the other from the farther metal ion. This model allowed us also to assign all the observed signals in the mixed-metal species. Dipolar contributions to the isotropic shifts have been discussed using ESR data. The effect of the two neighboring paramagnetic centers on the signal widths is discussed.

Introduction

Although the published papers regarding dinuclear transition-metal complexes are extremely numerous,[1-6] there are few reports on compounds which contain two different metal ions.[7-11] An investigation of this type of compound should in principle provide new experimental data which help in working out an exhaustive theory of magnetic interactions in polynuclear metal complexes. Further they can be used as models for understanding the mechanism of action of naturally occurring substances which contain couples of different metal ions.[12]

Magnetic resonance spectroscopy is in principle a powerful tool in investigating the nature of metal–metal interactions, since it can provide information on the effect of a metal ion on both the energetics and the relaxation properties of the neighboring metal ion. In particular nuclear magnetic resonance can provide information on the role of the ligands in the superexchange pathway as well as on the electronic states of the coupled metal centers,[13,14] while electron spin resonance can yield information on the spin state of the complex and provide parameters which help in the interpretation of the NMR experiments.

The simplest dinuclear systems to study were those where exchange interactions are small; therefore we considered the complexes formed by the tetradentate ligand 2-pyridyl methyl ketazine (PMK). This ligand is known[15] to form paramagnetic nickel(II) and cobalt(II) complexes of general formula $M_2(PMK)_3Y_4 \cdot nH_2O$ (Y = I, ClO_4, BF_4; n = 2, 3), which have been postulated to contain dinuclear $M_2(PMK)_3^{4+}$ cations, where each metal ion is in a pseudooctahedral environment. We have also synthesized the copper(II) and zinc(II) homologue derivatives and solid compounds containing the mixed metal complexes $MM'(PMK)_3^{4+}$. We wish to report here their magnetic resonance spectra.

Experimental Section

Synthesis of the Complexes. The ligand 2-pyridyl methyl ketazine (PMK) was synthesized and purified according to the reported procedure.[15] Cobalt(II), copper(II), and zinc(II) nitrate derivatives of general formula $M_2(PMK)_3(NO_3)_4 \cdot 3H_2O$ were prepared by mixing methanolic solutions containing stoichiometric amounts of the metal salt and of the ligand at room temperature. Crystals began to appear after a few minutes; they were filtered, washed with methanol, and dried in vacuo. The nickel(II) homologue was prepared by addition of a stoichiometric amount of the nickel(II) salt to a stirred suspension of the ligand in water. After 30 min the unreacted ligand was removed by filtration and acetone was added until crystallization occurred. The brown complex was filtered, washed with acetone, and dried in vacuo.

The compounds of analytical formula $M_{2-x}M'_x(PMK)_3(NO_3)_4 \cdot 3H_2O$, which are believed to contain the heteronuclear "mixed" species $MM'(PMK)_3^{4+}$, in addition to the homonuclear species $M_2(PMK)_3^{4+}$ or $M'_2(PMK)_3^{4+}$, were prepared using the procedure followed for the nickel(II) derivatives, i.e., by addition of aqueous solutions containing two metal salts in various molar ratios to suspensions of the stoichiometric amount of the ligand in water. Crystals were formed by addition of acetone. All these complexes are very soluble in water and therefore can be conveniently used for ^1H NMR studies. The perchlorate and iodide derivatives (those of copper(II) and zinc(II)

0020-1669/79/1318-0089$01.00/0

Table I. Analytical and Physical Data for the Complexes

compound	% found C	% found H	% found N	% found M	% calcd C	% calcd H	% calcd N	% calcd M	μ, μ_B 293 K	μ, μ_B 85 K	absorption max, cm^{-1} × 10^3 (ϵ_{molar} for soln)^a	($\Lambda_0 - \Lambda_e$)/$c^{1/2}$ ^{b}
$Co_2(PMK)_3(NO_3)_4 \cdot 3H_2O$	44.3	4.3	19.8	10.2	44.45	4.26	19.75	10.39	4.78	4.42	R 11.1, 20 sh W 11 (37), 20 sh	430
$Ni_2(PMK)_3(NO_3)_4 \cdot 3H_2O$	44.3	4.5	19.6	10.1	44.47	4.26	19.76	10.35	3.08	2.85	R 12.8, 18.5 W 12.5 (72), 18.8	410
$Cu_2(PMK)_3(NO_3)_4 \cdot 3H_2O$	43 8	4.0	19.3	11.0	44.09	4.23	19.59	11.14	1.99	1.95	R 8, 14.3 W 8.5 (47), 14 (202)	460
$Zn_2(PMK)_3(NO_3)_4 \cdot 3H_2O$	44.0	4.1	19.3	11.4	43.95	4.22	19.53	11.39				440

[a] Key: R = diffuse reflectance, W = water. [b] In water at 20 °C; for reference values see R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

Table II. Isotropic Shift Data (ppm)^a and Spectral Assignments for the $MM'(PMK)_3{}^{4+}$ Complexes in D_2O at 34 °C

compd M	compd M′	CH_3(M)	3-H(M)	4-H(M)	5-H(M)	6-H(M)	CH_3(M′)	3-H(M′)	4-H(M′)	5-H(M′)	6-H(M′)
Co	Co	−50.5	−54.6	−4.7	−30.7	−133	−50.5	−54.6	−4.7	−30.7	−133
Co	Zn	−43.1	−64.3	−2.6	−40.5	−132	−7.8 (−7.4)^b	9.6 (9.7)^b	−2.2 (−2.1)^b	9.6 (9.8)^b	−1.2 (−1)^b
Ni	Ni	−26.5	−49.2	−10.3	−28.9	*c*	−26.5	−49.2	−10.3	−28.9	*c*
Ni	Zn	−35.5	−59	−8.3	−37	*c*	9.8 (10.0)^b	8.9 (9.8)^b	−2.0 (−2.0)^b	7.8 (8.1)^b	−2.3
Co	Ni	−32.7 (−33.3)^d	−54.9 (−55.4)^d	−4.5 (−4.6)^d	−33.0 (−32.7)^d	−137 (−134)^d	−43.1 (−43.3)^e	−49.1 (−49.4)^e	−10.5 (−10.6)^e	−27.8 (−27.4)^e	*c*
Co	Cu	−39.8	−60.2	−3.3	−36.4	−135	−24.2	−26.5	−7.8	−11.8	−82
Cu	Zn	−17 (−16.4)^f	−36 (−36.1)^f	−7 (−5.6)^f	−21 (−21.4)^f	*c* (−81)^f	3.6 (3.3)^g	*h* (4.1)^g	−1 (−0.7)^g	*h* (4.1)^g	−2.5 (−3.0)^g
Cu	Cu	−13 (−13)^i	−33 (−32)^i	−8 (−8)^i	−18 (−17)^i	*c* (−84)^i	−13 (−13)^i	−33 (−32)^i	−8 (−8)^i	−18 (−17)^i	*c* (−84)^i
Ni	Cu	−32 (−31.9)^d	−55 (−55)^d	−9 (−9.3)^d	−33 (−33)^d	*c*	−6 (−7)^e	*c* (−27)^e	−8 (−9)^e	−13 (−13)^e	*c*

[a] The isotropic shifts are determined relative to the shifts of the diamagnetic Zn-Zn complex: $CH_3 = -2.1$, 3-H = −8.4, 4-H = −8.5, 5-H = −8.0, 6-H = −8.75 (ppm from DSS). Estimated errors in isotropic shifts data: shifts > −100 ppm, 1.5 ppm; shifts < −100 ppm, 1 ppm. [b] Calculated by the difference of the corresponding $\Delta H_i/H$(M) of the M-M and M-Zn complexes. [c] Not detected because of its broadness. [d] Calculated by the sum of the corresponding $\Delta H_i/H$(M) in the M-Zn complex and $\Delta H_i/H$ in the M-Zn complex. [e] Calculated by the sum of the corresponding $\Delta H_i/H$(M′) in the M′-Zn complex and $\Delta H_i/H$(Zn) in the M′-Zn complex. [f] Calculated by the difference of the corresponding $\Delta H_i/H$(Cu) in the Co-Cu complex and $\Delta H_i/H$(Zn) in the Co-Zn complex. [g] Calculated by the difference of the corresponding $\Delta H_i/H$(Co) in the Co-Cu and Co-Zn complexes. [h] Not detected because of the overlap with the HDO signal. [i] Calculated by the sum of the corresponding $\Delta H_i/H$(Cu) and $\Delta H_i/H$(Zn) in the Cu-Zn complex.

can be be prepared in the same way as the nickel(II) and cobalt(II) compounds previously reported) are sparingly soluble in any common solvent and therefore were not utilized.

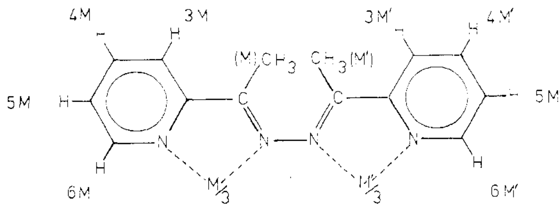
^{1}H NMR Measurements. Proton magnetic resonance spectra were recorded with a Varian EM-390 spectrometer at 90 MHz. *tert*-Butyl alcohol was used as internal reference and chemical shifts were reported relative to DSS (4,4-dimethyl-4-silapentane-1-sulfonate) using a value of 1.23 ppm for t-C_4H_9OH. The spectra were recorded both in HR mode and in HA mode in internal lock. Deuterium oxide (Merck, 99.8%) was used as solvent.

EPR Measurements. Electron paramagnetic resonance spectra were obtained with a Varian E-9 spectrometer, operating at ~9 GHz, using diphenylpicrylhydrazone (DPPH) as external standard (g = 2.0037).

Other Physical Measurements. Spectrophotometric, magnetic, and conductometric measurements were carried out as described previously.[16]

Results and Discussion

According to Stratton,[15] all the complexes, whose analytical and physical data are shown in Table I, can be postulated to contain $M_2(PMK)_3{}^{4+}$ cations, with the two metal ions in pseudooctahedral environments according to the following structure.



Further supports to this conclusion are given by (i) conductometric dilution studies, the slopes $\Lambda_0 - \Lambda_e$ vs. $c^{1/2}$ plots being significantly greater than those of typical uni-divalent electrolytes, and (ii) the ^{1}H NMR spectra of the solutions of these compounds, as it will be discussed below. Magnetic susceptibility measurements of the paramagnetic complexes down to liquid-nitrogen temperature indicate that exchange interactions, if any, are small (Table I).

If the ligand PMK is allowed to react with aqueous solutions containing two different metal ions, M and M′, it is possible to isolate crystalline compounds containing both the metal ions. We postulate that in addition to the homonuclear species M_2(or M'_2)$(PMK)_3{}^{4+}$ (which will be labeled as M–M or M′–M′, respectively), the heteronuclear species $MM'(PMK)_3{}^{4+}$ (M–M′) are formed. The relative abundance of M–M, M′–M′, and M–M′ is mainly statistically determined so that using a large excess of, say, M on M′ will give essentially M–M plus some M–M′ species and negligible quantities of M′–M′. Whereas experimental evidence of the existence of heteronuclear species in the solid state cannot be easily drawn, they can be detected by the ^{1}H NMR spectra of solutions containing the paramagnetic complexes, since the homonuclear and heteronuclear species give rise to different patterns of isotropic shifts. In Figure 1 are shown the ^{1}H NMR traces of solutions containing (a) the pure cobalt (Co–Co), (b) the pure copper (Cu–Cu), and (c) the mixed cobalt–copper (Co–Cu) complexes. It is apparent that beyond the signals of Co–Co other signals are present in (c) which do not correspond to those observed for the Cu–Cu species.

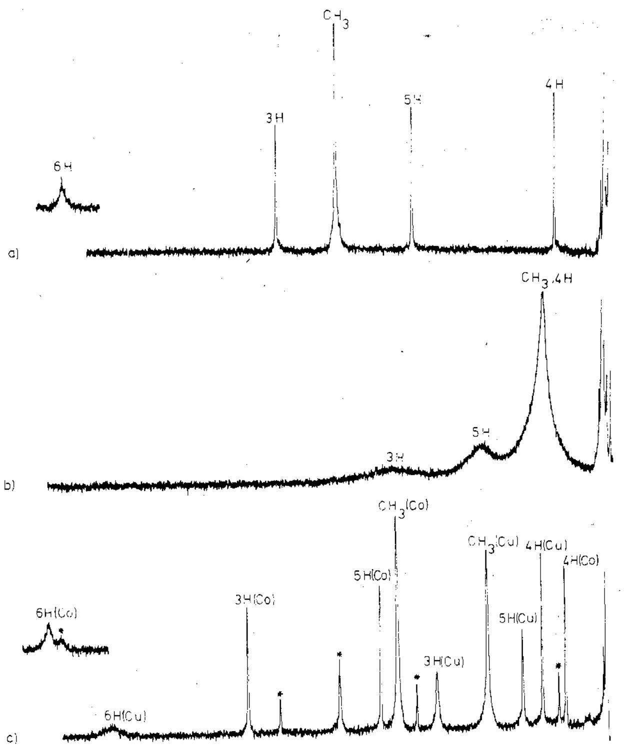


Figure 1. Proton magnetic resonance spectra at 34 °C of D_2O solutions of (a) $Co_2(PMK)_3(NO_3)_4$, (b) $Cu_2(PMK)_3(No_3)_4$, and (c) $CoCu(PMK)_3(NO_3)_4$. In the last spectrum the signals labeled with * are due to $Co_2(PMK)_3^{4+}$ species.

It must be concluded, therefore, that heteronuclear species are formed.

The isotropic shifts at 34 °C of D_2O solutions of the homonuclear and heteronuclear complexes derived from the nine paramagnetic combinations of the four metal ions considered are shown in Table II. The isotropic shifts were calculated as referenced against the diamagnetic Zn–Zn complex. The assignment of the signals of complexes labeled as Co–Co and Ni–Ni has been performed on the basis of their intensities and by comparison with the reported spectra of mononuclear complexes formed by bipyridine and Schiff-base ligands derived from 2-pyridinecarboxaldehyde.[17,18] The observed number of signals supports the postulated symmetrical arrangement of the ligand molecules around the two metal ions. The 6-H proton resonance could not be detected for the Ni–Ni species, probably because of its broadness. For the Cu–Cu complex only three signals can be safely detected (Figure 1); however, their broadness and the lack of data for reference does not allow us to suggest any assignment at this stage.

The ^1H NMR spectra of the Co–Zn and Ni–Zn species are similar, although not identical, to those of the corresponding Co–Co and Ni–Ni species in the region concerning the protons of the pyridine ring which is closer to the paramagnetic metal ion (in the following we will indicate as M proton a proton which is closer to M in the mixed metal species). The spectrum of the Cu–Zn species cannot be unambiguously assigned.

The signals of the protons of the pyridine ring which is farther from the paramagnetic center, i.e., the zinc protons are easily recognized since they show smaller shifts and are narrower (see Table III). Two signals of these protons are shifted upfield and two are downfield with respect to their diamagnetic positions. The zinc methyl in these complexes is seen upfield in the Ni–Zn complex, while it is downfield in the Co–Zn species.

The assignment of these peaks is not straightforward, in the absence of variously substituted derivatives. However, we succeeded in assigning them by resorting to a simple model.

Table III. Signal Half-Widths (Hz) of $MM'(PMK)_3^{4+}$ Complexes in D_2O at 34 °C[a,b]

compd											
M	M′	CH_3 (M)	3-H (M)	4-H (M)	5-H (M)	6-H (M)	CH_3 (M′)	3-H (M′)	5-H (M′)	5-H (M′)	6-H (M′)
Co	Co	23	17	14	15	120	23	17	14	15	120
Co	Zn	18	16	15	16	120	11	6	4	6	4
Ni	Ni	900	700	150	550		900	700	150	550	
Ni	Zn	600	1100	130	750		380	70	30	35	35
Co	Ni	60	20	15	16	140	85	60	15	45	
Co	Cu	33	28	17	21	120	38	42	18	26	280

[a] For the Cu-Zn, Cu-Cu, and Cu-Ni derivatives no values are reported because of the broadness and the overlap of the signals. [b] Estimated error ±10%.

In the hypothesis of small interactions between the two metal ions the isotropic shift of a given proton i in the M–M species ($\Delta H_i/H$(M–M)) can be considered as given by the sum of two contributions, one from the metal which is closer ($\Delta H_i/H$(M)), the other from the metal which is farther from the proton ($\Delta H_i'/H$(M)), according to the relationship

$$\frac{\Delta H_i}{H}(\text{M–M}) = \frac{\Delta H_i}{H}(\text{M}) + \frac{\Delta H_i'}{H}(\text{M})$$

This simple model can be compared with that of supertransferred hyperfine field suggested by Kokoszka[7] in order to justify the observed differences in the copper hyperfine coupling constants in copper–copper and copper–zinc dinuclear complexes. $\Delta H_i/H$(M–M) is known from the spectra of the M–M species, $\Delta H_i/H$(M) is the isotropic shift of the M-protons in M–Zn, so that $\Delta H_i'$/H(M) can be calculated. According to the model this should be the isotropic shift of the zinc proton i in M–Zn. As a matter of fact the calculated values correspond quite closely to observed resonances, when they are calibrated from the diamagnetic positions (see Table II), thus allowing us to assign the signals of zinc protons in M–Zn and to confirm the validity of the model.

Also the isotropic shifts of the heteronuclear Co–Ni species, which contain two different paramagnetic metal ions, can be obtained by the sum of two contributions, which can be guessed from the Co–Zn and Ni–Zn derivatives. Also in this case the agreement between the observed and calculated isotropic shifts is quite good (Table II).

A relevant feature of the spectrum of the Co–Ni derivative is the substantial sharpening of the signals of the Ni–protons, as compared to those of the Ni–Zn complexes (Table III). A similar result is observed for the Co–Cu complex (Figure 1, Table III). The sharpening of the signals allowed us to detect all the expected signals of the Co–Cu species and using the above model it is possible to calculate the isotropic shifts of the protons in the other species containing the copper(II) ion, as assigned in Table II.

The observed pattern of the isotropic shifts of the protons of the pyridine ring closer to the paramagnetic ion indicates that the overall delocalization mechanism is essentially of the σ type.[19,20] This is in agreement with all the previous findings on nickel(II) and cobalt(II) complexes with similar ligands;[20–24] the copper(II) ion, whose complexes with similar ligands to our knowledge were never detected previously, is not an exception and behaves analogously to the other two paramagnetic metal ions.

The protons of the pyridine ring farther from the paramagnetic ion show a different delocalization pattern, as well evidenced in the M–Zn complexes, where the alternating behavior is characteristic of a π-delocalization mechanism.[19] This can be explained taking into account that while for the pyridine ring closer to the paramagnetic center the delocalization is determined by the interaction with the σ lone pair of the nitrogen, which is orthogonal to the π system of the ring, for the farther pyridine the unpaired spin density is delocalized through the N–N group, which is not orthogonal to the π orbitals.[25,26] Of interest is also the behavior of the zinc methyl group in these complexes. It is shifted upfield in both Ni–Zn and Cu–Zn, while it is shifted downfield in Co–Zn. Dipolar effects, to be discussed below, can be responsible for this different behavior.

It is well-known that for octahedral cobalt(II) complexes dipolar effects can give large contributions to the isotropic shifts. Powder ESR spectra of Co–Zn at 4.2 K, which is magnetically diluted by Zn–Zn, can be interpreted using an effective spin Hamiltonian with $S = {}^1/_2$, yielding $g_{\parallel} = 2.10$ and $g_{\perp} = 4.10$. These values compare well with those found for other elongated octahedra.[27,28] Although anisotropic magnetic susceptibilities would be required for the calculation of the dipolar shifts,[29] the g values can be used to make some guesses of the relative dipolar shifts. It is apparent that $\chi_{\parallel} - \chi_{\perp}$ must be negative, as was found by Horrocks for the complex $Co(bpy)_3Br_2$.[30] Therefore the pattern of dipolar contributions for the cobalt protons must be similar to that of $Co(bpy)_3Br_2$. No structural data are available for the present compounds, but using the reported bond distances and angles and molecular models negative shifts are calculated for the 3-, 4-, and CH_3 cobalt protons and positive shifts for the 5- and 6-protons. The ratios of the geometric factors of the above protons referred to that of the 3-proton are the following: 1:0.3:0.9:–0.3:–2.9. The geometric factor of the 3-proton is calculated as -8.7×10^{-3} Å^3. For the zinc methyl group a large negative contribution can be anticipated. Since the observed upfield shifts for the resonance of the same groups in the Ni–Zn and Cu–Zn species are small it is possible that the large negative dipolar shift of the cobalt(II) derivative is sufficient to reverse the sign of the hyperfine coupling constant. No values are available for the magnetic anisotropy of Ni–Zn but it is expected to be small. Powder ESR spectra of Cu–Cu yielded $g_{\parallel} = 2.28$, $g_{\perp} = 2.04$, and $|A_{\parallel}| = 140 \times 10^{-4}$ cm^{-1}, in accord with an unpaired electron in a $d(x^2 - y^2)$ orbital.[31] It is worth noting that also frozen solution spectra of Cu–Cu yielded the same spin Hamiltonian parameters, indicating that the environment around the metal atom remains the same in both complexes and that the influence of one metal atom on the relaxation of the other is small. No signal could be detected in the $\Delta M = 2$ region, confirming that exchange interactions, if any, are very small. The fluid solution spectra of Cu–Cu yielded $g_{iso} = 2.13$ and $|A_{iso}| = 60 \times 10^{-4}$ cm^{-1}. Finally it must be mentioned that also the Co–Cu species diluted in Co–Co at room temperature yielded ESR spectra typical of copper(II) with the same parameters above, showing the copper(II) hyperfine structure. Apparently the presence of a cobalt(II) ion near copper(II) does not interfere too severely on the relaxation mechanism of the copper(II) ion.

As observed above, the ^{1}H NMR spectra of the Co–M species (M = Ni, Cu) show a neat decrease in the line width of the signals of the protons closer to M as compared to that of the signals of the M–M and M–Zn species (Table III). Since the isotropic shift of a given proton can be considered as due to the sum of the two contributions of the closer and of the farther metal ions, it can be reasonably suggested that its relaxation behavior is also determined by the weighed influence of both the paramagnetic metal ions. It is well-known that the main factors which affect the nuclear spin relaxation in a paramagnetic complex are the electronic spin–lattice relaxation time of the metal ion, the distance between the paramagnetic center and the resonating nucleus, and the value of the contact coupling constant. High-spin octahedral cobalt(II) are known to have electronic spin lattice relaxation times significantly shorter than octahedral nickel(II) and copper(II) ions (10^{-12} vs. $10^{-10}/10^{-9}$ s).[32] The observed sharpening of the signals of the M–protons in the Co–M complexes as compared to M–M forces us to consider that electronic spin relaxation time of the cobalt(II) ion, although its effect is weighed (attenuated) by the large distance and by the small contact interactions, largely determines the relaxation properties of these protons. On the other hand the line width of the signals of the Co protons are broader than those found for the Co–Co and Co–Zn derivative, as a result of the less favorable electronic relaxation time of the M paramagnetic metal ion. However, the observed increase of the line width is small, as both contact and dipolar contributions due to the cobalt(II) ion dominated in this case.

Conclusions

The results of the previous section show that the ^{1}H NMR spectra of dinuclear complexes containing different metal atoms can be interpreted on the basis of a simple additive model, in the case of vanishing exchange interactions between the two metal ions. Further it was shown that the presence of a paramagnetic metal ion characterized by a very short electronic relaxation time can reduce significantly the line widths of the signals of protons closer to a different paramagnetic metal ion characterized by a longer relaxation time. This effect can be important in order to characterize through ^{1}H NMR spectroscopy dinuclear metal complexes containing two different paramagnetic metal ions.

Acknowledgment. Thanks are expressed to Professor Luigi Sacconi for constant encouragement and to Professor Ivano Bertini for helpful discussions. We are indebted to Mr. G. C. Vignozzi for microanalyses and to Mr. D. Masi and F. Cecconi for technical assistance.

Registry No. $Co_2(PMK)_3(NO_3)_4$, 68200-87-3; $Ni_2(PMK)_3(NO_3)_4$, 68200-88-4; $Cu_2(PMK)_3(NO_3)_4$, 68200-90-8; $Zn_2(PMK)_3(NO_3)_4$, 68200-92-0; $CoZn(PMK)_3{}^{4+}$, 68200-93-1; $NiZn(PMK)_3{}^{4+}$, 68200-94-2; $CoNi(PMK)_3{}^{4+}$, 68200-95-3; $CoCu(PMK)_3{}^{4+}$, 68200-96-4; $CuZn(PMK)_3{}^{4+}$, 68200-97-5; $NiCu(PMK)_3{}^{4+}$, 68200-98-6.

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^{17}O Nuclear Magnetic Resonance Spectroscopy of Polyoxometalates. 1. Sensitivity and Resolution

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Received August 23, 1978

Over 100 ^{17}O NMR chemical shifts are reported for 27 diamagnetic polyoxoanions of the early transition metals. Efficient procedures for obtaining ^{17}O-enriched compounds are described, and the factors which control sensitivity and spectral resolution are examined and discussed in detail. Comparisons of chemical shift values with structural data show that chemical shifts are determined largely by metal–oxygen bond strengths.

Introduction

The early transition metals vanadium, niobium, tantalum, molybdenum, and tungsten in their highest oxidation states are known to form a wide variety of polynuclear metal–oxygen complexes.[2] X-ray crystallographic studies have yielded solid-state structures for several of these species, but solution structures have in many cases remained ambiguous due to the rapid and complex structural equilibria which often prevail in solution. The ^{17}O NMR technique was first successfully applied to polyoxoanion chemistry in 1965 by two groups in independent investigations of the aqueous $Cr_2O_7^{2-}$ anion.[3] Due to sensitivity problems, however, little progress was possible until the advent of Fourier transform NMR (FT NMR) spectroscopy. Since 1975, this technique has enabled ^{17}O NMR spectra of polyvanadates, -niobates, -tantalates, -molybdates, and -tungstates to be obtained.[4–16]

In this paper, we attempt to delineate the scope and limitations of the ^{17}O NMR technique as a structural and dynamic probe in polyoxoanion chemistry. First, the factors which influence spectral resolution and sensitivity are discussed, and experimental procedures for optimizing spectral quality are outlined. Next, the 13.5-MHz ^{17}O NMR spectra of a variety of diamagnetic polyoxometalates measured in solution under various conditions are presented and compared. Finally, these results are briefly summarized and areas for future investigation defined.

Experimental Section

A. Spectral Measurements. ^{17}O NMR spectra were recorded at 13.51 MHz using the pulse FT NMR technique on a Jeol PFT/PS-100 NMR spectrometer interfaced with a Nicolet 1080 data system. All spectra were digitized using 4096 data points such that digital spectrometer resolution varied between 3.7 and 4.9 Hz/data point, depending on the spectral bandwidth employed. The spectrometer was locked on the ^{1}H resonance of an external H_2O sample. Spectra were obtained using cylindrical 10-mm o.d. sample tubes (1.1-mL sample volume) and referenced externally to pure H_2O at 25 °C by the sample replacement method. Chemical shifts were calculated in parts per million, with positive values in the low field direction relative to H_2O. The error associated with chemical shift values is ±3 ppm for line widths <200 Hz, ±5 ppm for line widths >200 Hz and <400 Hz, and ±7 ppm for line widths >400 Hz. All line widths reported below in hertz have been corrected for exponential line broadening. The error associated with line-width values is ±20 Hz for line widths <100 Hz, ±40 Hz for line widths >100 Hz and <400 Hz, and ±60 Hz for line widths >400 Hz. Unless otherwise indicated, samples were neither rotated nor degassed since such precautions were found to have no measurable effect on line widths.

B. Spectral Parameters. In this section, spectra are numbered as indicated in column one of Tables II and III. The following abbreviations are used: cpd for compound, sol for solvent, $|X|$ for molar concentration of X, T for temperature in °C, enr for ^{17}O content in atom percent ^{17}O, np for number of pulses, pr for pulse repetition frequency in hertz, bdw for spectral bandwidth in hertz, and exp for exponential line broadening in hertz. All pH measurements were made at 25 °C.

1: cpd = $[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$, sol = $(CH_3)_2NCHO$, $|Mo| = 1.4$, $T = 25$, enr = 0.9, np = 5729, pr = 2.4, bdw = 15152, exp = 9.

2: cpd = $[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$, sol = CH_3CN, $|Mo| = 0.1$, $T = 80$, enr = 20, np = 4096, pr = 7.1, bdw = 15152, exp = 2.

3: cpd = $[(n\text{-}C_4H_9)_4N]_2W_6O_{19}$, sol = $(CH_3)_2NCHO$, $|W| = 0.52$, $T = 25$, enr = 2, np = 9926, pr = 1.5, bdw = 15152, exp = 24.

4: cpd = $K_7HNb_6O_{19}\cdot 13H_2O$, sol = H_2O (pH 14), $|Nb| = 5$, $T = 100$, enr = 3, np = 1046, pr = 5.0, bdw = 15152, exp = 24.

5: cpd = $K_8Ta_6O_{19}\cdot 17H_2O$, sol = H_2O (pH 14), $|Ta| = 1.2$, $T = 25$, enr = 3, np = 7000, pr = 2.2, bdw = 15152, exp = 24.

6: cpd = $[(n\text{-}C_4H_9)_4N]_3VMo_5O_{19}$, sol = CH_3CN, $|Mo| = 0.4$, $T = 80$, enr = 10, np = 16 384, pr = 6.7, bdw = 20 000, exp = 11.

7: cpd = $[(n\text{-}C_4H_9)_4N]_3VW_5O_{19}$, sol = CH_3CN, $|W| = 0.3$, $T = 30$, enr = 18, np = 14 926, pr = 8.3, bdw = 20 000, exp = 8.

8: cpd = $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_4SiMo_{12}O_{40}$, sol = CH_3CN, $|Mo| = 0.4$, $T = 85$, enr = 9, np = 32 768, pr = 8.3, bdw = 20 000, exp = 31.

9: cpd = $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_4SiW_{12}O_{40}$, sol = CH_3CN, $|W| = 0.4$, $T = 90$, enr = 10, np = 18 204, pr = 6.7, bdw = 20 000, exp = 31.

10: cpd = $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_4SiMoW_{11}O_{40}$, sol = CH_3CN, $|W| = 0.3$, $T = 90$, enr = 25, np = 65 536, pr = 3.1, bdw = 20 000, exp = 31.

11: cpd = $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_3PMo_{12}O_{40}$, sol = CH_3CN, $|Mo| = 0.5$, $T = 80$, enr = 30 (phosphate oxygens), enr = 3 (remaining oxygens), np = 184 978, pr = 3.2, bdw = 20 000, exp = 31.

12: cpd = $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_3PW_{12}O_{40}$, sol = CH_3CN, $|W| = 0.6$, $T = 80$, enr = 2, np = 32 768, pr = 7.7, bdw = 15 152, exp = 24.

13: cpd = $\alpha\text{-}[(C_4H_9)_4N]_{11}H(P_2W_{18}O_{62})_2$, sol = CH_3CN, $|W| = 0.5$, $T = 85$, enr = 4, np = 131 072, pr = 7.7, bdw = 15 152, exp = 24.

14: cpd = $\beta\text{-}[(n\text{-}C_4H_9)_4N]_{11}H(P_2W_{18}O_{62})_2$, sol = CH_3CN, $|W| = 0.4$, $T = 90$, enr = 4, np = 262 000, pr = 7.7, bdw = 15 152, exp = 24.

15: cpd = $[(n\text{-}C_4H_9)_4N]_4(C_6H_5As)_4Mo_{12}O_{46}\cdot H_2O$, sol = CH_3CN, $|Mo| = 0.5$, $T = 94$, enr = 25, np = 9915, pr = 3.1, bdw = 20 000, exp = 47.

16: cpd = $[(n\text{-}C_4H_9)_4N]_4H_4As_4Mo_{12}O_{50}\cdot 5H_2O$, sol = CH_3CN, $|Mo| = 0.6$, $T = 80$, enr = 25, np = 1119, pr = 3.1, bdw = 20 000, exp = 31.

17: cpd = $[(n\text{-}C_4H_9)_4N]_2(CH_3)_2AsMo_4O_{15}H$, sol = CH_3CN, $|Mo| = 0.9$, $T = 80$, enr = 25, np = 4734, pr = 3.2, bdw = 20 000, exp = 47.

18: cpd = $[(n\text{-}C_4H_9)_4N]_2(C_6H_5)_2AsMo_4O_{15}H$, sol = CH_3CN, $|Mo| = 0.9$, $T = 80$, enr = 25, np = 16 000, pr = 3.2, bdw = 20 000, exp = 31.

19: cpd = $[(n\text{-}C_4H_9)_4N]_4W_{10}O_{32}$, sol = CH_3CN, $|W| = 2.5$, $T = 25$, enr = 2, np = 16 384, pr = 2.9, bdw = 15 152, exp = 12.

20: cpd = $\beta\text{-}[(n\text{-}C_4H_9)_4N]_3KMo_8O_{26}\cdot 2H_2O$, sol = CH_3CN, $|Mo| = 0.05$, $T = 25$, enr = 34, np = 131 072, pr = 3.2, bdw = 20 000, exp = 23.