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Carbon-13 Nuclear Magnetic Resonance Studies of 8-Quinolinol and 4-Methyl-8-quinolinol and of Their Complexes with Zinc(II) and Molybdenum(VI) Ions

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The ^{13}C NMR spectra of 8-quinolinol (HQ) and 4-methyl-8-quinolinol (4MQH) have been recorded in Me_2SO-d_6 solution. In the case of 4MQH, spectra also have been obtained for its acidic ($4MQH_2^+$) and basic ($4MQ^-$) forms as well as for the zinc(II) and molybdenum(VI) complexes that are formed with $4MQ^-$ ($Zn(4MQ)_2$ and $Mo^{VI}O_2(4MQ)_2$). Assignment of the resonances for these ligands, their salts, and their complexes has been achieved by the use of chemical shift additivity relationships and continuous-wave off-resonance decoupling. The assignments are a self-consistent set and provide new insights to the solution structures and bonding for the metal complexes. The T_1 values for the carbons of 8-quinolinol also have been evaluated in Me_2SO-d_6.

The utility of 8-quinolinol (HQ), which has been used extensively as a ligand in analytical chemistry,[1,2] as a stereochemical probe,[3] and as a model compound for bioinorganic systems[4-6] is well-known. This has prompted several groups to determine the solid-phase structures for several metal 8-quinolinate complexes.[7] In addition, proton NMR has been used to study the solution stereochemistry and the nature of the metal–ligand bonds for the 8-quinolinate complexes of molybdenum(VI) and -(V), thorium(IV), and uranium(VI) in dimethyl sulfoxide (Me_2SO) solution.[5,8] In contrast, ^{13}C NMR has not been employed previously to characterize metal quinolinate complexes, presumably because the ^{13}C spectra for 8-quinolinol and for its 4-methyl derivative have not been assigned. The limited solubility of 8-quinolinate complexes also has been a deterrent to ^{13}C NMR studies. The present investigation includes the ^{13}C spectra of HQ and of several of its derivatives in Me_2SO-d_6 solution. The spectral resonances have been assigned by the use of chemical shift additivity relationships and by continuous-wave off-resonance decoupling. The solubility problem of the metal complexes has been at least partially overcome by the use of 4-methyl-8-quinolinol (4MHQ) rather than HQ as the ligand. Spectra for the $4MQ^-$ complexes of Zn(II) and $Mo^{VI}O_2$ have been recorded and assigned on the basis of the assignments for the free ligand.

Experimetal Section

Reagents. Methanol (Mallinckrodt), perdeuteriodimethyl sulfoxide (Me_2SO-d_6) (Aldrich), zinc acetate (Mallinckrodt), $Na_2MoO_4 \cdot 2H_2O$ (Matheson Coleman and Bell), 8-quinolinol (Matheson Coleman and Bell), and 2-methyl-8-quinolinol (Aldrich) were reagent grade and were used without further purification. The 4-methyl-8-quinolinol (4MQH) ligand was prepared by the method of Phillips and coworkers.[9] Solutions of its anion ($4MQ^-$) and cation ($4MQH_2^+$) were prepared in situ in 50% Me_2SO-d_6/H_2O solution by addition of a stoichiometric amount of tetramethylammonium hydroxide in methanol (Eastman) and perchloric acid in water (Mallinckrodt), respectively. Both salts percipitate from Me_2SO-d_6 solution unless water is present.

The $Zn(4MQ)_2$ complex was prepared by a procedure analogous to that for the preparation of $MnQ_2 \cdot 2H_2O$.[10] Likewise, the $MoO_2(4MQ)_2$ complex was prepared by an analogous procedure to that for the preparation of MoO_2Q_2.[4]

Recording Spectra. The ^{13}C NMR spectra were recorded on a Bruker WH-90 pulsed Fourier transform multinuclear NMR spectrometer, which was internally locked on the deuterium resonance of the solvent (Me_2SO-d_6). Chemical shifts are reported relative to tetramethylsilane.

T_1 measurements were obtained by using a 180–90° pulse sequence. The 90° pulse duration of 13.4 μs was determined by accurately measuring the 360° pulse (53.6 μs) and dividing by 4.

Results

The normal approach to the unequivocal assignment of ^{13}C resonances is to prepare a series of specifically substituted deuterium derivatives. However, this approach is fraught with synthetic problems and has prompted us to use chemical-shift additivity relationships for the ^{13}C assignments of these fused-ring heterocycles. Thus, on the basis of the chemical-shift assignments for naphthalene (N), quinoline (Q), and 1-naphthol (H1N), the ^{13}C chemical shifts for 8-quinolinol (HQ) can be estimated. The perturbation of naphthalene caused by the insertion of a nitrogen atom into the ring system is simply the difference in chemical shift ($\Delta\nu$) for each carbon in quinoline and naphthalene. Similarly, the chemical-shift differences for each carbon in 1-naphthol and naphthalene indicate the effect of the addition of a hydroxyl group to naphthalene. If these perturbations are assumed to be additive, the chemical shift differences ($\Delta\nu$) for the carbons of 8-quinolinol relative to those for naphthalene can be calculated directly by the relation

$$(\nu_{Q_i} - \nu_{N_i}) + (\nu_{H1N_i} - \nu_{N_i}) = \Delta\nu_{HQ_i} \tag{1}$$

where i represents carbons 1 and 10. This expression can be adjusted to provide a relation for the calculation of the individual ^{13}C resonances of 8-quinolinol:

$$\Delta\nu_{Q_i} + \Delta\nu_{H1N_i} + \nu_{N_i} = \nu_{HQ_i} \tag{2}$$

Although the ^{13}C spectral assignments for naphthalene[11] and quinoline[12] are available, the spectrum of 1-naphthol has not been reported. Its spectrum in Me_2SO-d_6 has been recorded and assigned by a procedure similar to that outlined for 8-quinolinol. For example, the perturbations that are caused by the addition of a hydroxyl group to benzene are known[13]

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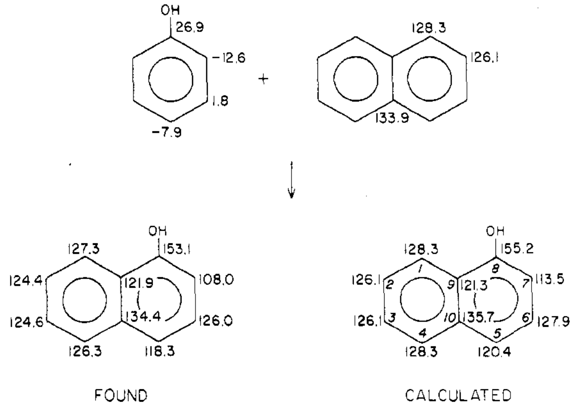

Figure 1. Calculated and observed assigned chemical shifts for 1-naphthol (numbered as 8-naphthol). Perturbations for phenol are relative to benzene.

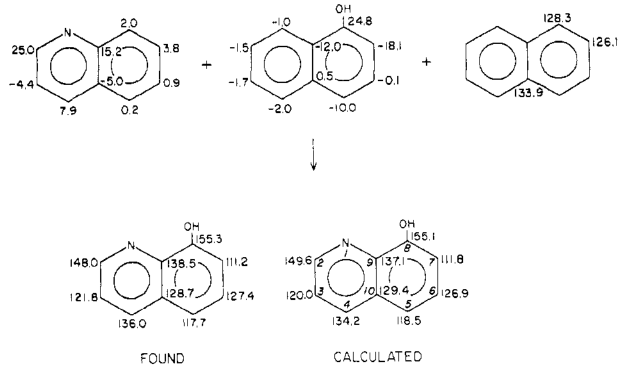

Figure 2. Calculated and observed assigned chemical shifts for HQ. Perturbations for quinoline and 1-naphthol are relative to naphthalene.

and can be added to the naphthalene chemical shifts. This calculation is shown schematically in Figure 1 with the experimental chemical shifts presented for comparison. Because there is good agreement between the calculated and observed chemical shifts, the observed shifts have been assigned on this basis. The resonances assigned to carbons 1, 9, and 10 remain singlets in off-resonance decoupling experiments which is consistent with the assignments.

The 1-naphthol chemical shift assignments of Figure 1 have been used in conjunction with those for naphthalene and quinoline to calculate the chemical shifts for the carbons of 8-quinolinol (see eq 1 and 2). The results of this calculation and the experimental data for HQ are illustrated by Figure 2. The good agreement indicates that the assignments are self-consistent and probably correct. Again, the results of off-resonance decoupling experiments are in accord with the assignments for carbons 8, 9, and 10.

The assignments of the C9 resonance (138.5 ppm) and the C10 resonance (128.7 ppm) for 8-quinolinol are confirmed by the results of the T_1 relaxation time study for HQ in Me_2SO-d_6 (Table I). The T_1 of 33.9 s for the 138.5-ppm resonance is significantly longer than the value of 24.7 s for the 128.7-ppm resonance. Carbon 9 is one bond further removed than carbon 10 from any carbon with a bond to a hydrogen atom and, thus, receives less of a T_1 contribution from proton–carbon relaxation processes.

The chemical shifts for the carbons of 2-methyl-8-quinolinol (2MQH) and 4-methyl-8-quinolinol have been calculated by adding the chemical shift differences for the individual carbons of 2- and 4-methylpyridine relative to pyridine[14] to the experimentally determined chemical shifts for HQ. The results of such a procedure are illustrated by Figure 3. Off-resonance decoupling results are consistent with the assignments for carbons 2, 8, 9, and 10 of 2MQH and 4, 8, 9, and 10 of 4MQH. The agreement between observed and calculated chemical shifts for 2MQH and 4MQH is good with the exception of carbons 4 and 5 in the latter compound.

Table I. T_1 Values for 8-Quinolinol from a 180–90° Pulse Sequence

assignt	T_1 (height)	T_1 (area)	shift
8	15.38 ± 0.44	12.85 ± 0.93	153.3
2	1.41 ± 0.01	1.47 ± 0.04	148.0
9	33.94 ± 1.17	32.22 ± 2.05	138.5
4	1.32 ± 0.05	1.32 ± 0.09	136.0
10	24.74 ± 0.51	22.16 ± 0.98	128.7
6	1.31 ± 0.02	1.39 ± 0.04	127.4
3	1.22 ± 0.01	1.35 ± 0.03	121.8
5	1.46 ± 0.01	1.40 ± 0.04	117.7
7	1.27 ± 0.01	1.22 ± 0.06	111.2

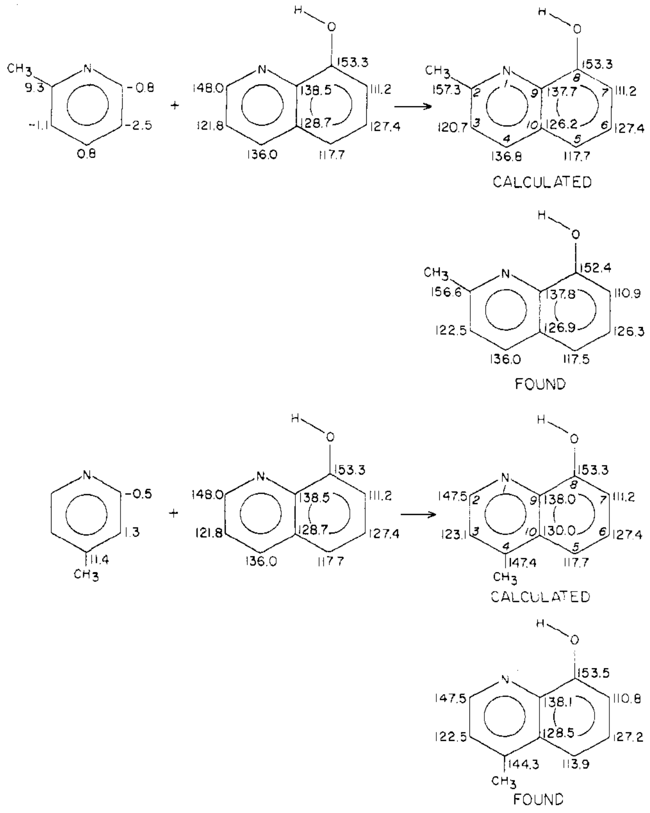

Figure 3. Calculated and observed assigned chemical shifts for 2MQH and 4MQH. Perturbations for 2-methyl- and 4-methylpyridine are relative to pyridine.

The chemical shifts for $4MQH_2^+$ and $4MQ^-$ have been calculated by adding the individual chemical-shift differences for the carbons in the pyridinium ion relative to pyridine[15] and in the phenolate ion relative to phenol[16] to the observed 4MQH and chemical shifts. The results of the calculation as well as the assignment of observed shifts are illustrated in Figure 4. Although the agreement between the calculated and observed shifts for $4MQ^-$ is good, the protonation of the nitrogen in $4MQH_2^+$ causes significant changes in chemical shifts for the carbons of the hydroxy-substituted ring that are beyond those predicted by the calculations.

The results of these assignments, along with the assignments for the 4MQH complexes of molybdenum(VI) and zinc(II), are summarized in Table II.

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Table II. ^{13}C NMR Chemical Shifts for 8-Quinolinol, Its Methylated Derivatives, and Their Salts and Complexes in Me_2SO-d_6[a]

	HQ	2MQH	H1N	$4MQH_2^+$	4MQH	$4MQ^-$	$Zn(4MQ)_2$	$MoO_2(4MQ)_2$
C2	148.0	156.6	124.4	143.2	147.5	146.6	144.3	145.9
C3	121.8	122.5	124.6	123.6	122.5	122.6	121.7	123.4
C4	136.0	136.0	126.3	158.5	144.3	145.7	147.5	159.5
C5	117.7	117.5	118.3	116.4	113.9	107.4	106.4	115.2
C6	127.4	126.3	126.0	131.1	127.2	129.9	129.2	129.0
C7	111.2	110.9	108.0	116.2	110.8	115.5	112.4	113.8
C8	155.3	152.4	153.1	149.0	153.5	166.4	161.4	148.6
C9	138.5	137.8	121.9	129.9	138.1	144.2	139.1	138.1
C10	128.7	126.9	134.4	129.4	128.5	131.5	128.8	128.8
Me		24.6		20.7	18.4	20.0	18.5	18.2
			(C1) 127.3					

[a] Abbreviations: HQ, 8-quinolinol; 2MQH, 2-methyl-8-quinolinol; H1N, 1-naphthol (numbered as 8-naphthol); $4MQH_2^+$, acid salt of 4-methyl-8-quinolinol; 4MQH, 4-methyl-8-quinolinol; and $4MQ^-$, its anion. Chemical shifts are in ppm vs. Me_4Si.

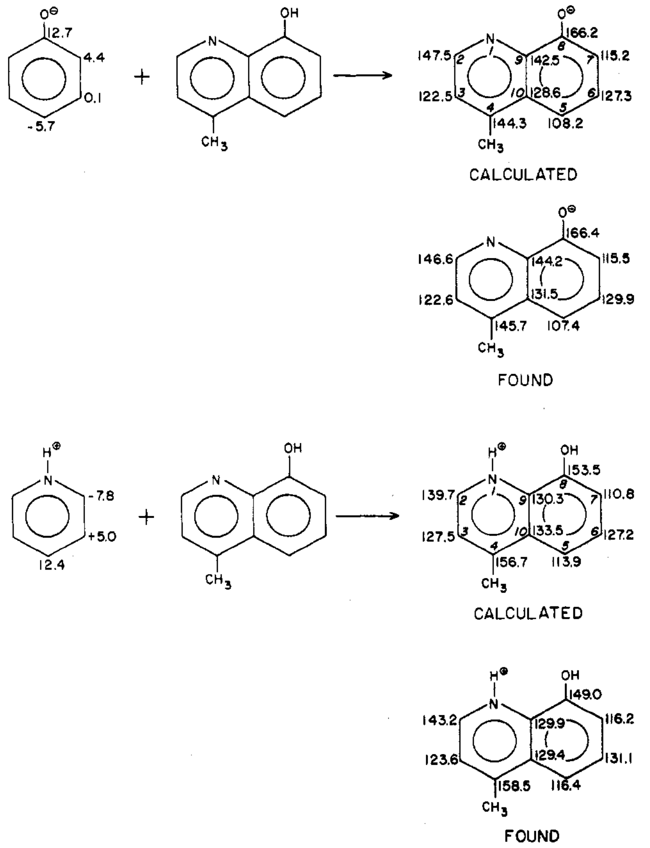

Figure 4. Calculated and observed assigned chemical shifts for $4MQH_2^+$ and $4MQ^-$. Perturbations for the pyridinium ion and the phenolate ion are relative to pyridine and phenol, respectively.

Discussion and Conclusions

The dependence of the chemical shifts for the carbons of 8-quinolinol and its methylated derivatives on the degree of protonation is instructive in several respects. Unlike the corresponding ^1H chemical shifts which are progressively deshielded and shifted downfield in a predictable fashion as the degree of protonation is increased,[8] the ^{13}C resonances move both upfield and downfield and may shift in one direction for the first protonation and the opposite for the second (see Table II). This is consistent with the protonation effects for the phenolate anion[16] and pyridine.[15] In the series $4MQ^- \rightarrow 4MQH \rightarrow 4MQH_2^+$ the carbon atoms whose resonances are shifted most include C4, C5, C7, C8, and C9 (-12.8, -9.0, -0.7, 17.4, 14.3 ppm, respectively). C7 is included in this list because the first protonation causes an upfield shift of 4.7 ppm and the second protonation causes a downfield shift of 5.4 ppm. The C8 and C9 resonances move monotonically upfield, and the C5 resonance moves monotonically downfield as the molecule is protonated. The C8 and C5 resonances are indicative of the extent to which protonation is localized at the oxygen of the ligand. The chemical shift of C4 is hardly affected by protonation of the oxygen (+1.4 ppm), but it is sensitive to protonation of the nitrogen (-14.2 ppm).

Proton–ligand interactions are analogous to metal–ligand interactions in systems where metal–ligand π bonding or ligand–metal π back-bonding are not important. A comparison of the chemical shifts for the ligand in a metal complex with those for the free ligand at various degrees of protonation frequently can give information about the nature of the metal–ligand bond. In a previous study[8] the ^1H spectra of a variety of neutral metal 8-quinolinate chelates have been analyzed in this way. Five types of metal–ligand interactions were used as limiting cases, and the chelates were classified according to the ^1H chemical shifts. In the present study the ^{13}C NMR spectra for $Zn(4MQ)_2$ and $Mo^{VI}O_2(4MQ)_2$ have been recorded with the expectation that the chemical shifts will be subject to analogous interpretation and provide insight to the metal–ligand bonding. Because of the poor solubility of the 8-quinolinol complexes of zinc(II) and molybdenum(VI), the 4-methyl derivative has been used.

The chemical shifts for $Zn(4MQ)_2$ are closely similar to those for the free ligand anion ($4MQ^-$), especially at C5, C6, and C8. However, the chemical shifts of C4 and C2 are indicative of weak bonding between the nitrogen and the metal. The C8 resonance for the complex is slightly upfield from that of the free anion, which implies that C8 is shielded weakly by the zinc ion. The chemical shift for C5 in the $Zn(2MQ)_2$ complex indicates that most of the negative charge remains localized at the ligand oxygen, however. Hence, the zinc–oxygen interaction appears to be weakly ionic. The C2 and C4 resonances indicate that the zinc–nitrogen interaction is not as strong as the proton–nitrogen bond of the $4MQH_2^+$ cation. However, the data provide a clear indication that zinc is bonded more strongly to the nitrogen than to the oxygen of the ligand.

In contrast to zinc(II), the $Mo^{VI}O_2(4MQ)_2$ spectrum closely resembles the fully protonated form of the ligand ($4MQH_2^+$). This is especially apparent for the C3, C4, C5, and C8 resonances. The C3 and C4 resonances indicate that the molybdenum–nitrogen bond is similar in strength to the proton–nitrogen bond of $4MQH_2^+$. Likewise, the C5 and C8 resonances indicate that molybdenum is as effective an acid toward the ligand oxygen as a proton. The chemical shift for the C5 carbon, which is para to the OH group of the ligand, is especially interesting. Previous work[17] has shown that electron-withdrawing groups tend to deshield para carbons. Because the C5 resonance for the $Mo^{VI}O_2(4MQ)_2$ complex is almost as deshielded as it is for the MQH_2^+ cation, the

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(17) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York and London, 1972; p 199.

$Mo^{VI}O_2^{2+}$ group is nearly as effective as a proton at electron withdrawing. Hence, the molybdenum–ligand oxygen interaction has significant covalent character, which is in accord with the interpretations of the proton NMR data for this complex.[5]

Reference to Table II indicates that the chemical shift differences between $Zn(4MQ)_2$ and $Mo^{VI}O_2(4MQ)_2$ for C4, C5, and C8 (12.0, 8.8, and –11.8 ppm, respectively) provide a sensitive measure of the nature of the metal–ligand bonding relative to that for the zinc 4-methyl-8-quinolinate complex. These three resonances should be useful diagnostic probes for the bonding of other metal–4MQ complexes, especially with respect to the degree of covalent character of the metal–ligand oxygen bond.

Because only a single set of ligand resonances is observed for each of the $Zn(4MQ)_2$ and $Mo^{VI}O_2(4MQ)_2$ complexes, the two ligands of each complex must be equivalent. Although this is in accord with the proton NMR results,[5,8] the much greater sensitivity of ^{13}C NMR to shielding effects adds convincing support for the conclusion that the ligands are symmetrical to each other in the $Zn(4MQ)_2$ and $Mo^{VI}O_2(4MQ)_2$ complexes.

Acknowledgment. This project was initiated several years ago through the use of a locally fabricated ^{13}C NMR spectrometer. Although the instrument's sensitivity proved inadequate, the efforts and contributions of J. L. Sudmeier, L. J. DeHayes, and P. C. Curb are gratefully acknowledged. The work was supported by the National Science Foundation under Grants CHE 76-24555 and CHE 79-22040.

Registry No. HQ, 148-24-3; 2MQH, 826-81-3; H1N, 90-15-3; $4MQH_2^+$, 73940-74-6; 4MQH, 3846-73-9; $4MQ^-$, 35489-22-6; $Zn(4MQ)_2$, 14406-95-2; $MoO_2(4MQ)_2$, 73953-19-2.

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Mass Spectra of Organometallic Compounds. 8.[1] Electron-Impact Study of the Cyclopentadienylmanganese Derivatives $RC_5H_4Mn(CS)(NO)I$ (R = H, CH_3)

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The mass spectra of the related cyclopentadienylmanganese complexes $RC_5H_4Mn(CS)(NO)I$ (R = H, CH_3) have been examined, and the appearance potentials of manganese-containing ions with intact ligands determined. Primary fragmentations in the mass spectra of these complexes have been assigned and compared. The strength of the manganese-to-ligand bonds in the fragment ions was shown to follow the order I > RC_5H_4 > CS ≫ NO.

Introduction

Appearance potentials of ions produced under electron-impact conditions provide valuable information concerning fragmentation processes. In general, metal-containing ions with all ligands account for most of the ion current in the majority of the spectra of organometallic compounds. This feature indicates that under electron-impact conditions the cleavage of metal-to-ligand bonds is greatly favored over fragmentations involving the decay of coordinated ligands. Most metal-containing ions in the mass spectra of organometallic compounds exhibit one detectable appearance potential, and this probably suggests the existence of a single primary precursor for each of the ions. In a fragmentation sequence proceeding via primary precursors, subsequent ions are expected to exhibit higher appearance potentials due to the endothermicity of the bond-breaking processes involved. Except for the detailed study of fragmentation sequences, appearance potentials also furnish valuable information concerning the energetics of such processes.

The behavior of coordinated ligands under electron-impact conditions is of considerable importance in the understanding of the mass spectra of organometallic compounds. A detailed comparison between the behavior of several ligands has been investigated in the mass spectral study of $RC_5H_4Mn(CO)(CS)L$ [L = CO, Ph_3P, Ph_3As, Ph_3Sb; R = H, CH_3].[2,3] A recently reported mass spectral study of the novel binuclear complexes $[RC_5H_4Mn(CS)(NO)]_2$ (R = H, CH_3) and $[C_5H_5Fe(CS)(CO)]_2$ brought into focus the behavior of carbon-bridging thiocarbonyl as compared with those of the terminal nitrosyl and carbonyl ligands, respectively. A detailed analysis of the mass spectra of $RC_5H_4Mn(CS)(NO)I$ (R = H, CH_3), described in the current paper, was undertaken in order to obtain a meaningful comparison between the behavior of the terminal thiocarbonyl and nitrosyl ligands under electron-impact conditions.

Experimental Section

The complexes $RC_5H_4Mn(CS)(NO)I$ (R = H, CH_3) were prepared according to a reported procedure.[4] The mass spectra of the complexes under consideration were measured at 80 eV on a Hitachi RMU-7E mass spectrometer which has been modified with a Keithley 427 current amplifier and a ITT Model F 4074, 16-stage electron multiplier. The samples were introduced directly into the ionization chamber of the mass spectrometer under a low pressure of $\sim 10^{-6}$ torr. The conditions [sample heater temperature (SHT) and ionization chamber temperature (ICT)] utilized in obtaining the spectra are specified in Table I. Intensities (*I*) of the ions (Table I), those containing the most abundant isotopes of the elements involved, are given relative to an arbitrary value of 100 chosen for the base peak, that of the most intense peak in each spectrum. Ions having high *m*/*z* values were determined with the aid of perfluorokerosene (PFK) standard. Metastable transitions observed in the spectra of the manganese complexes are listed in Table I.

The ionization and appearance potentials, reported in Table I, were determined by a modified Honig method[5] according to the procedure[6]

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