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Metal Chelates Containing Bicyclic Rings. I. Infrared Spectra and Oligomer Formation of Hydroxymethylenecamphorate Chelates

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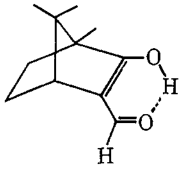
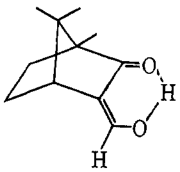
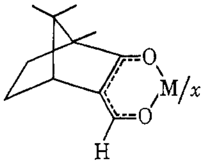
Thirteen chelates containing the ligand anion hydroxymethylenecamphorate (HMC^-) have been prepared. The series is made up of tris and bis chelates, as well as bis chelates containing the adduct ligands water and pyridine. Frequencies for the vibrations associated with the chelate rings in $M(HMC)_x$ are similar to those observed in the infrared spectra of 1,3-diketonate chelates. The most significant difference is the separation between the two strong bands assigned to carbon to oxygen stretches. The relatively large separation in the HMC^- chelates is attributed to different $C\overset{...}{-}O$ bond lengths in a distorted resonance tautomeric form. The distortion is believed to be due to the five-membered ring fused to the chelate ring. The infrared spectra of several of the bis chelates differ slightly from the spectra of all other chelates studied. The metal ions in these bis chelates have a tendency to achieve an idealized octahedral configuration by forming oligomers containing bridging oxygen bonds. Indeed, several of these bis(hydroxymethylenecamphorate) chelates are proven to be oligomers on the basis of molecular weight, magnetic, and analytical data. Thus, the infrared spectra can be used to detect oligomer formation in HMC^- chelates.

Introduction

Chelates containing bicyclic ring systems, such as hydroxymethylenecamphorate (HMC^-) chelates, are of special interest because of the optical properties of the ligand and because of the presence of a bridgehead group in metal chelates. Garbisch[1] has stated that the tautomeric form Ib of hydroxymethylenecamphor is energetically favored because of the strain introduced by an internal double bond in the five-membered ring of tautomer Ia. Such strain, Garbisch claims, forces an almost complete exclusion of Ia in favor of Ib. If this is true in the hydrogen-bonded ligand, it is of interest to determine whether similar restrictions operate in the metal chelate rings. The bonding situation when the enolic proton is replaced by a metal ion may be changed enough to make the more symmetric form, Ic, predominate in the metal chelates.


Ia


Ib


Ic

If Ic does predominate, the infrared spectra would be expected to be quite similar to the spectra of metal 1,3-diketonates. One phase of this work was undertaken to determine whether or not spectral evidence supports the view that the chelate ring exists in the hydroxymethylene form, similar to Ib, or in the form Ic (or a distorted version thereof).

During the course of the spectral investigation, it became apparent that the structures of the M(II) chelates were of particular interest. Several observations are explained by the fact that most of the M(II) chelates studied form oligomeric molecules. Thus, the bis(hydroxymethylenecamphorate) chelates form a new class of oligomers believed to be structurally similar to the oligomeric bis(acetylacetonates).[2-9] The second part of the work reported herein was undertaken to characterize these $M(HMC)_2$ chelates.

Experimental Section

Hyroxymethylenecamphor.—The general method employed was that of Claisen.[10] However, several modifications were made which are noted below.

A mixture of 9.3 g (0.4 g-atom) of sodium metal and 100 ml of dry analytical reagent grade ether was placed into a 1000-ml three-necked flask. The flask was fitted with a condenser and a dropping funnel. The mixture was stirred with a stirring motor. A solution containing 60.0 g (0.4 mol) of camphor in 225 ml of dry ether was added to the flask with vigorous stirring. Addition time was about 1 hr. A solution containing 60 ml (0.45 mol) of isopentyl formate in 100 ml of dry ether was added slowly (90 min) with vigorous stirring. In about 3 hr all of the sodium reacted and a brown-yellow reaction mass resulted. The reaction mass was dissolved by adding 300 ml of an ice-water mixture. The water and ether layers were separated and the water layer was washed with three 50-ml portions of ether. The ether layers were discarded and air was bubbled through the water solution to remove remaining ether. Glacial acetic acid (about 100 ml) was added to the solution until precipitation of the product was complete. This mixture was placed in a refrigerator until crystallization was complete. The product was filtered on a coarse sintered-glass filter, ground to a powder, and washed three times with 50-ml portions of cold petroleum ether (bp

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(1) E. W. Garbisch, *J. Am. Chem. Soc.*, **85**, 1696 (1963).

(2) G. J. Bullen, *Nature*, **177**, 537 (1956).

(3) G. J. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961).

(4) G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).

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(7) D. P. Graddon and G. M. Mockler, *Australian J. Chem.*, **17**, 1119 (1964).

(8) D. A. Buckingham, R. C. Gorges, and J. T. Henry, *ibid.*, **20**, 281 (1967).

(9) F. A. Cotton and R. Eiss, *J. Am. Chem. Soc.*, **90**, 38 (1968).

(10) L. Claisen, *Ann.*, **281**, 306, 314 (1894).

37–55°). The product was vacuum dried for several hours at room temperature and stored in a refrigerator. The white powder has a melting point of 71°. The yield was about 25 g.

The original preparation reported by Claisen gave a melting point of 81°. A mixture whose melting point is very near 81° is obtained if the product is recrystallized from boiling petroleum ether (bp 37–55°). This recrystallization always produces a yellow oil in addition to white HMC. Product recrystallized in this way converts to a sticky yellow material on standing at room temperature. Analyses of the white compound produced in this manner were very poor. On subsequent recrystallizations the entire batch would eventually be converted to the yellow oily material. For this reason recrystallization and heating were avoided.

$Cu(HMC)_2$.—A solution was prepared by adding ammonium hydroxide to a mixture of 3.0 g (0.017 mol) of HMC in 100 ml of distilled water with vigorous stirring. A second solution containing 2.0 g (0.0083 mol) of cupric nitrate trihydrate in 50 ml of distilled water was prepared in a separate beaker. The crude product was formed by adding the ligand solution to the metal ion solution. This mixture was refluxed for 1 hr, cooled, and filtered; the crude product was dried at 110°. The crude yield was 3.4 g. Purification was accomplished by recrystallization from *n*-heptane. The dark green product has a melting point of 176° and is very soluble in most organic solvents.

$Mg(HMC)_2 \cdot {}^2/_3H_2O$.—This chelate was prepared in the same manner as $Cu(HMC)_2$. The crude yield was 2.4 g or 74%. The product was recrystallized from ethanol (2.4 g is soluble in 50 ml of hot ethanol). The off-white powder turned bright yellow at about 250° but did not melt up to 325°. A broad absorption in the 3400-cm^{-1} region of the infrared spectrum substantiated a hydrated formulation.

$Zn(HMC)_2 \cdot 1.0H_2O$.—A ligand solution was prepared by dissolving 3.0 g (0.017 mol) of HMC in 25 ml of warm methanol. A zinc ion solution was prepared by dissolving an excess of zinc acetate in 200 ml of distilled water. This solution was heated to boiling and filtered. The two solutions were mixed and allowed to cool, and the product was filtered. The white precipitate was washed several times with water and then with acetone and allowed to air dry on the filter. The white powder sublimed at 200° (atmospheric pressure) and melted to a yellow liquid at 286°. A hydrated form was indicated by a broad absorption centered at 3450 cm^{-1} in the infrared spectrum.

$Zn(HMC)_2$.—The monohydrate was dehydrated by recrystallizing from pyridine followed by recrystallization from acetone. The anhydrous product has no infrared absorption in the 3400-cm^{-1} region. The white powder sublimed at 200° (atmospheric pressure) and melted at 286°.

$Co(HMC)_2$ and $Co(HMC)_2 \cdot {}^4/_3H_2O$.—The preparation of the cobalt(II) chelates was accomplished by the procedure used to prepare $Zn(HMC)_2 \cdot H_2O$. The product was isolated in essentially stoichiometric yields as the hydrate, $Co(HMC)_2 \cdot {}^4/_3H_2O$. The hydrate was quite insoluble in common organic solvents. It was dehydrated by repeated washing with dry acetone in a Soxhlet extractor. Analysis of the pink compound remaining in the thimble after 8 hr of washing proved the compound to be anhydrous. The infrared spectrum showed no absorption due to water at 3400 cm^{-1}. The pink compound did not melt up to 300°.

$Co(HMC)_2(py)_2$.—The pyridine adduct was prepared by dissolving $Co(HMC)_2$ in a small amount of pyridine. Concentration of the pyridine yielded yellow-orange crystals. The product was recrystallized twice from acetone. The compound turned red at 150–170°, sublimed (atmospheric pressure) readily at 220°, but did not melt up to 300°.

$Ni(HMC)_2 \cdot {}^2/_3H_2O$.—This chelate was prepared by the same method used for the preparation of $Cu(HMC)_2$. The crude product precipitated in high yields. Purification of the relatively insoluble compound was carried out by repeated washing with acetone in an extractor. Unlike $Co(HMC)_2 \cdot {}^4/_3H_2O$, the anhydrous chelate of Ni(II) was not formed. Its infrared spectrum and analysis proved that even after exhaustive washing with acetone the compound remained hydrated. Attempted dehydration by suspending the compound in triethyl *o*-formate for several days was unsuccessful, also. The light bluish green compound had no melting point up to 300°.

$Ni(HMC)_2(py)_2$.—The pyridine adduct was prepared by dissolving the hydrated nickel chelate in pyridine. Upon the addition of water the adduct precipitated. The product was purified chromatographically on an alumina column, using methanol as the eluent. The green compound had no melting point up to 300°.

$Cr(HMC)_3$.—A solution of the ammonium salt of HMC was prepared by adding ammonium hydroxide to a mixture of 3.0 g (0.017 mol) of HMC in 50 ml of water. A separate solution of the metal ion was prepared by dissolving 1.1 g (0.0041 mol) of chromium(III) chloride hexahydrate in 50 ml of water. These solutions were mixed and refluxed for 1 hr. The solution was cooled and the crude product was collected and dried at 110°. The crude yield of the light green compound was 2.3 g or 95%. Purification of this compound was not satisfactorily accomplished by recrystallization because of its very great solubility in all organic solvents used. For this reason, the product was purified chromatographically. An alumina column was prepared and the crude chelate was placed on the column in the form of a benzene solution. It was eluted with acetone. Two bands were observed. The first band, containing the bulk of the sample, was collected. The solvent was evaporated with a stream of air and the product was dried at 110° for several hours. The yellow-green product sublimed at about 204° and melted at 230–231°.

$Co(HMC)_3$.—The preparation of this compound is reported elsewhere.[11] The green compound turned blue at 150°, melted at 171°, and was a red liquid at 185–190°.

$Fe(HMC)_3$.—A solution containing 2.70 g (0.01 mol) of iron(III) chloride hexahydrate in 150 ml of water was added to a solution of 5.4 g (0.03 mol) of HMC in 50 ml of methanol. A dark blue solution and an oily precipitate resulted. The mixture was extracted with ether. The second extraction gave an almost clear ether solution; however, the water layer remained dark blue. The crude product was isolated by evaporating the ether layer. Recrystallization attempts from organic solvents yielded glasses. Successful recrystallization was accomplished by adding a measured amount of water to the crude product and then the same amount of methanol to make a 50:50 solution. The solution was heated until the product dissolved. The chelate crystallized on cooling. The purple product melted at 203°.

$Mn(HMC)_2$.—This chelate was prepared using the method of Charles.[12] The light tan compound did not melt up to 340°. The infrared spectrum indicated that the chelate was not hydrated. Purification of the acetone-insoluble compound by washing with acetone in a Soxhlet extractor apparently resulted in some decomposition as evidenced by a low carbon content after several hours of washing.

Nuclear Magnetic Resonance Spectra.—All spectra reported were recorded using a Varian A-60 nuclear magnetic spectrometer. The solvent used was carbon tetrachloride. All peaks were calibrated *vs.* TMS (chemical shift = 0). The solutions were all freshly prepared from HMC with a melting point of 71°. There was no significant difference between the spectra of 10 and 20% solutions. Marked changes in the spectra did occur if the samples were allowed to age.

Infrared Spectral Measurements.—All spectra were recorded on a Perkin-Elmer Model 621 infrared spectrophotometer. Solution, KBr pellet, and Nujol mull techniques were used. Generally, there were no significant differences in the solid or solution spectra of the chelates. The spectra were calibrated in the 2850, 1600, and 900-cm^{-1} regions using appropriate polystyrene absorptions. Reproducibility was ±2 cm^{-1}.

Molecular Weight Determination.—The molecular weights were determined cryoscopically in camphor. The camphor used was purified by sublimation (mp 176°). A solution of known

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(11) J. H. Dunlop, R. D. Gillard, and R. Ugo, *J. Chem. Soc., A*, 1540 (1966).

(12) R. G. Charles, *Inorg. Syn.*, **6**, 164 (1960).

TABLE I

ANALYSES OF COMPOUNDS

Compound	Theoretical, % C	Theoretical, % H	Theoretical, % Metal	Found, % C	Found, % H	Found, % Metal
HMC	73.3	8.9	...	72.8	9.0	...
$Cu(HMC)_2$	62.6	7.1		62.6	7.2	
$Mg(HMC)_2 \cdot {}^2/_3H_2O$	66.9	7.8	6.16	66.9	7.9	5.92
$Zn(HMC)_2 \cdot 1.0H_2O$	59.9	7.3	14.83	60.1	7.1	14.84
$Zn(HMC)_2$	62.4	7.1		62.2	7.0	
$Co(HMC)_2$	63.3	7.2		63.1	7.2	
$Co(HMC)_2(py)_2$	66.8	7.0		66.6	7.0	
$Ni(HMC)_2 \cdot {}^2/_3H_2O$	61.5	7.3		61.5	7.5	
$Ni(HMC)_2(py)_2$	66.8	7.0		66.4	7.1	
$Cr(HMC)_3$	67.2	7.6		67.4	7.7	
$Co(HMC)_3$	66.4	7.6		67.3	7.8	
$Fe(HMC)_3$	66.8	7.6		66.8	7.8	
$Co(HMC) \cdot {}^4/_3H_2O$	59.86	7.31	17.01 (CoO)	59.86	7.35	17.05 (CoO)
$Mn(HMC)_2$	63.92	7.26		64.53	7.87	

molality was prepared by dissolving the chelate in molten camphor. After cooling, the melting point of the solid mixture was observed. Typical melting point depressions for the mixtures used were 5–6° (K_f(camphor) = 39.7°).

Magnetic Susceptibility Measurements.—Magnetic moments were determined using standard Gouy method techniques. The complex $Hg[Co(CNS)_4]$ was used as a calibrant. The results have been corrected for the diamagnetic effect of the ligands.

Results

Nuclear Magnetic Resonance Spectra.—The low-field spectrum of HMC in carbon tetrachloride recorded in this study differs appreciably from that reported by Garbisch.[1] The fresh solution containing pure HMC shows low-field absorptions at 6.63, 9.53, and 9.78 ppm. The assignments and relative intensities follow. The aldehyde proton in the enolized form is 6.63 (1) ppm, 9.53 (0.3) ppm is the aldehyde proton in the keto form, and 9.78 (1) ppm (1) is the hydrogen-bonded O–H···O proton in the enol. Preliminary results with the compound benzoylcamphor, in which the aldehydic proton is replaced by phenyl, confirm the assignments. The peaks corresponding to the enol and keto aldehyde proton resonance are no longer present in benzoylcamphor. The hydrogen-bonded proton resonance is much broader and is shifted downfield to 12.56 ppm. The spectrum of HMC reported by Garbisch[1] was duplicated for a sample with a high melting point (82°) and of indefinite analysis. The spectrum reported herein differs from the one reported by Garbisch in that the peak at 7.39 ppm is not observed and the hydrogen-bonded proton resonance occurs at 9.78 ppm rather than 10.15 ppm. It is possible that the spectrum reported by Garbisch may have been of the high melting point (82°) material and that the peak at 7.39 ppm is due to impurity.

Infrared Spectra.—The infrared spectra of the ligand (HMC) and of camphor were recorded so that typically organic group absorptions could be detected and assigned in the chelates of HMC. These assignments are supported by the fact that absorptions not associated with the 1,3-diketone ring change very slightly or not at all upon chelation with several metals. Absorptions that occur in the spectrum of solid HMC and are absent in the spectrum of solid camphor, together with their tentative assignments, follow. A strong, broad band between 2800 and 3400 cm^{-1} is assigned to the hydrogen-bonded O—H stretch. Aldehydic C—H stretching and deformation frequencies occur at 2810, 2750, and 945 cm^{-1}. A strong peak at 1628 cm^{-1} is assigned to the C=C stretching frequency of the hydroxymethylene group. A relatively strong band at 1172 cm^{-1} is assigned to the O—H···O bend. The strong C=O stretch in camphor (1746 cm^{-1}) is shifted to 1711 cm^{-1} in solid HMC.

The 3500–1800-Cm^{-1} Region.—The most striking feature of the various chelate spectra in this region is the very low intensity of bands due to aldehydic C—H stretching. These absorptions are observable only in samples that contain an extremely high concentration of the chelate. Under these conditions overtone bands are also visible. For example, in $Fe(HMC)_3$, $Cu(HMC)_2$, and $Co(HMC)_2$ carbonyl overtones occur at 3235, 3240, and 3293 cm^{-1}, respectively, as well as at 2620, 2625, and 2580 cm^{-1}. Two aldehydic C—H stretching vibrations are observed under these conditions. The frequencies for the chelates listed above are 3110, 3100, and 3045 cm^{-1} and 2725, 2735, and 2726 cm^{-1}, respectively.

The abbreviated infrared spectra, in the region 1800–300 cm^{-1}, are presented in Table II. Only the absorptions important to the discussion have been included. The peaks omitted from Table II are observed in the spectra of camphor, HMC, and all of the chelates. These peaks are not shifted upon chelation and are independent of the metal ion. Thus, they are assumed to be methyl and camphor ring vibrations.

The 1800–1200-Cm^{-1} Region.—This region of the spectrum contains the three strongest bands for all of the chelates. These bands are assigned to chelated carbonyl and chelate ring carbon–carbon stretching frequencies. The highest frequency absorption in this region is assigned to a relatively pure, chelated $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ stretching frequency. The second strong band is assigned to the chelate ring $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretch. The lowest frequency strong band is assigned to another carbon–oxygen stretch. As expected, the positions of these three bands are all a function of the metal ion. The two carbon–oxygen absorptions may be considered an antisymmetric–symmetric pair or, more simply, perturbed C=O and C—O vibrations. The choice depends upon the importance of the tautomeric forms

Table II

Abbreviated Infrared Spectra of HMC Chelates and Some Pyridine Adducts in the 1800–300-Cm^{-1} Region (as Solids in KBr Pellets)[a,b]

Co(III)	Cr(III)	Fe(III)	Zn(II)	Mg(II)	Co(II)	Co(HMC)$_2$-(py)$_2$	Mn(II)	Ni(II)	Ni(HMC)$_2$-(py)$_2$	Cu(II)	Assignment
1615 s	1616 s	1618 s	1651 s	1663 s	1647 s	1623 s	1652 s	1644 s	1628 s	1620 s	C⋯O str
						1597 m			1600 ms		Pyridine
						1576 ms			1575 ms		Pyridine
1481 s	1493 s	1494 s	1522 s	1529 s	1526 s	1506 s	1522 s	1516 s	1508 s	1506 s	C⋯C str
						1483 m	1483 m		1482 m		Pyridine
1316 s	1318 s	1316 s 1297 s	1288 s	1298 s	1295 s	1334 s	1292 s	1301 s	1336 s	1319 s	C⋯O str
1194 m	1195 m	1190 m	1190 m	1193 m	1191 m	1191 w	1191 m	1194 m	1193 w	1194 w	C(CH$_3$)$_2$
1183 w	1184 w	1183 w	1185 w	1182 w	1184 m	1184 w	1184 w	1184 w	1183 w	1184 w	
1158 m	1157 m	1157 m	1154 m	1156 m	1154 m	1151 m	1151 m	1154 m	1152 m	1156 m	Ring or C(CH$_3$)$_2$
			1139 m	1141 m	1139 m		1138 m	1141 m			
1110 m	1108 m	1108 m	1108 m	1107 m	1107 m	1106 m	1106 m	1106 m	1108 m	1108 m	Ring def
1074 m	1074 m	1076 m	1074 m	1074 m	1073 m	1071 m, d	1071 m	1074 m	1073 m, d	1078 m	Ring def
1051 w	1049 w	1044 w	1036 m	1038 m	1035 m	1036 m, d	1031 m	1038 m	1038 m, d	1048 w	Antisym C⋯C
						1006 w			1010 w		Pyridine
						755 m			756 ms		Pyridine
748 m	747 m	744 w	745 w	742 m	746 m	741 m	742 m	744 m	743 m	745 m	Aldehyde C—H
732 m	730 m	725 w	728 w	730 m	730 m	726 m	727 m	729 m	728 m	729 m	Out-of-plane bend
						700 ms			697 ms	1010 w	Pyridine
						618 m			624 w		Pyridine
570 m	558 m	547 w	550 w	549 m	551 m	548 m	544 m	553 m	554 m	561 m	
528 w	523 m	511 w				505 w			508 w	521 w	M—O str
498 w	491 m	484 w	489 w	498 m	492 m, b	485 m	486 m, b	497 m, b	490 w	495 w	
465 m	455 ms	432 m	432 vw	448 w	437 w	425 m			430 w	444 m	
			415 vw	418 w	411 w	410 w		416 w	415 w		

[a] Peak designations: s, strong; m, medium; w, weak; b, broad; d, doublet. [b] Only peaks important to the discussion have been included.

Ib and Ic. If Ic is the predominant form in the chelates, interaction between the two carbon–oxygen groups would result in an antisymmetric–symmetric pair. If Ib is the predominant form in the chelates, the carbon to oxygen bonds are formally C=O and C—O. In this case, assignment of the two frequencies can be made on the basis of perturbed C=O and C—O vibrations. The choice ultimately depends upon the difference in the two carbon to oxygen bond lengths. The relatively large energy separation (300–370 cm^{-1}) between the two absorptions indicates that a simple antisymmetric–symmetric pair does not exist. On the other hand, the positions of the peaks do not correspond well to simple C=O and C—O vibrations. Thus, the infrared spectra indicate that the chelates most likely exist as a distorted version of form Ic. The large energy separation between the two C—O vibrations is indicative of this distortion, inasmuch as it is believed to arise from a difference in the carbon to oxygen bond lengths.

Other vibrations in this region (omitted from Table II) are associated with the camphor group and are insensitive to chelation.

The 1200 to 1000-Cm^{-1} Region.—The medium-intensity bands in this region provide an excellent "fingerprint" for this class of compound. Only the band at about 1050 cm^{-1} is sensitive to metal ion changes. It is assigned to a chelate ring C–C stretching frequency. The purity of this vibration is probably quite low. The appearance of a peak at about 1140 cm^{-1} appears to be dependent only upon molecular structure. See Figure 1. The relative intensities of the bands in this region with respect to each other vary markedly with changes in molecular configuration. This fact is illustrated in Figure 1.

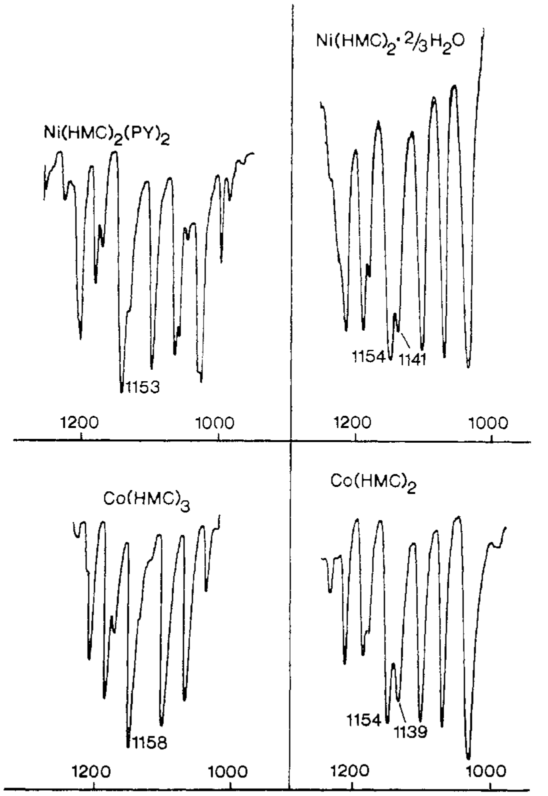

Figure 1.—Some spectra in the region 1200–1000 cm^{-1}.

The 1000–300-Cm^{-1} Region.—The doublet with peaks at about 745 and 730 cm^{-1} is extremely characteristic of these chelates. It is, however, essentially independent of metal ion changes. Neither the doublet nor other peaks in this region appears in the free ligand spectrum. For this reason, the doublet is assigned to the chelated aldehydic C–H bending frequency.

Absorptions between about 530 and 485 cm^{-1} are assigned to vibrations consisting primarily of M–O stretching. The spectral pattern depends upon molecular structure. See Figure 2. This dependence parallels the appearance of the 1140-cm^{-1} peak.

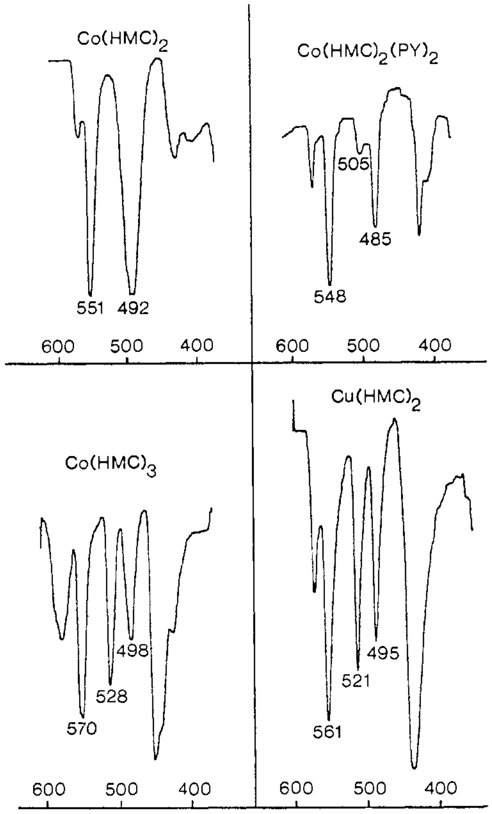

Figure 2.—Some spectra in the region 600–400 cm^{-1}.

Magnetic Studies.—The measured magnetic moments for $Co(HMC)_2$ and $Co(HMC)_2 \cdot {}^4/_3H_2O$ are 4.90 and 4.85 BM at 300°K. These values for the d^7 systems indicate at $^4T_{1g}$ ground state for the complex, arising from an octahedral ligand field. The magnetic moment of $Ni(HMC)_2 \cdot {}^2/_3H_2O$ is 3.08 BM at 300°K. This value for a d^8 system indicates an $^3A_{2g}$ ground state, also arising from an octahedral ligand field.

Analytical and Molecular Weight Results.—Cryoscopic molecular weight determinations prove that several of the $M(HMC)_2$ chelates exist as oligomers. Oligomeric structures have been indicated for the HMC^- chelates of Co(II), Ni(II), Zn(II), and Mg(II). A detailed characterization is in progress. Results from two trimers are given in Table III.

TABLE III

Analytically determined empirical formulas	Molecular formulas	Mol wt Theoret	Mol wt Found
$Co(HMC)_2$	$[Co(HMC)_2]_3$	1251	1279
			1305
$Ni(HMC)_2 \cdot {}^2/_3H_2O$	$Ni_3(HMC)_6(H_2O)_2$	1293	1452
			1266

The analytical results for these bis chelates can be explained by the existence of oligomeric structures. The unusual number of water molecules in the empirical formulas is a result of the waters occupying available coordination sites on the oligomer unit. Some basic structures for trimers in which the metal is in an octahedral field are given in Table IV. Thus, it seems likely that $Co_3(HMC)_6$ exists as a face-shared trimer. $Ni_3(HMC)_6(H_2O)_2$ is most probably an edge-shared trimer or a trimer with one shared face and one shared corner.

TABLE IV

Octahedral linkage	Trimer coordination sites: Total no. available	Used by HMC	Available for adduct	Empirical formula
Two shared faces	12	12	0	$M(HMC)_2$
Two shared edges	14	12	2	$M(HMC)_2 \cdot {}^2/_3H_2O$
Two shared corners	16	12	4	$M(HMC)_2 \cdot {}^4/_3H_2O$
One face, one edge	13	12	1	$M(HMC)_2 \cdot {}^1/_3H_2O$
One face, one corner	14	12	2	$M(HMC)_2 \cdot {}^2/_3H_2O$
One edge, one corner	15	12	3	$M(HMC)_2 \cdot H_2O$

Discussion

Garbisch[1,13] has stated that enolic HMC exists almost entirely as the hydroxymethylene tautomer (Ib). Tautomer Ia is not favored because of the strain introduced into the five-membered ring by the internal double bond. No other forms are believed to contribute to the tautomeric equilibrium. The proton magnetic resonance spectrum of HMC substantiates this conclusion. The position of the aldehydic proton resonance (6.63 ppm *vs.* TMS) is more characteristic of a vinyl proton than an aldehydic proton.[13] The enolic proton absorption peak is as narrow as the aldehydic proton absorption and occurs at a relatively high field (9.78 ppm *vs.* TMS). The absorption due to the enolic proton in HMC is quite unlike that of the enolic proton in the 1,3-diketones in which strong hydrogen bonding occurs. In the latter case, the peaks are characteristically broad and occur at low-field chemical shifts (12–18 ppm *vs.* TMS).[14] A high-field chemical shift for the enolic proton suggests a weak hydrogen bond due to a large distance between the two oxygens.[15] Intramolecular hydrogen bonding is evident, however, since the position of the absorption is not concentration dependent. These arguments support the belief that in the enol there is a strong preference for the hydroxymethylene form (Ib) and that the hydrogen bond is a good deal weaker than in 1,3-diketones. Preliminary results indicate that substitution of a phenyl group for the aldehydic proton, to produce benzoylcamphor, results in a stronger hydrogen bond. The enolic hydrogen resonance is very broad and occurs at 12.6 ppm. Presumably, this is due to a resonance interaction between the phenyl group and the enolic ring. Further work with this ligand is in progress.

If the preference for the hydroxymethylene form is carried over from the organic enol to the metal chelate, a large difference in the carbon to oxygen bond lengths would be expected. If, however, the bonding is sig-

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[13] E. W. Garbisch, *J. Am. Chem. Soc.*, **87**, 505 (1965).

[14] R. L. Lintvedt and H. F. Holtzclaw, *Inorg. Chem.*, **5**, 239 (1966).

[15] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 407 ff.

nificantly different when a metal ion replaces the enolic proton, there is the possibility of a distorted version of Ic. The latter case would more nearly approximate the bonding in 1,3-diketonate type chelates in which the two C⋯O bond distances are very similar.[16] The similarity is observed even in unsymmetrically substituted chelate rings. This phenomenon is attributed to resonance within the chelate ring. Inasmuch as 1,3-diketonate and HMC$^-$ chelates contain the same skeletal ring, it is of interest to investigate the M(HMC)$_x$ compounds in which the carbon to oxygen bond distances may be significantly different.

Meaningful information about the nonequivalence of the carbon to oxygen bond lengths may be obtained from the carbonyl stretching frequencies. Behnke and Nakamoto[17] assigned two carbon to oxygen stretching frequencies in bis(acetylacetonato)copper(II) as an antisymmetric–symmetric pair on the basis of their normal-coordinate analysis using a reasonable value for the resonance force constant. The relatively large energy separation (about 225 cm^{-1}) is attributed to slight differences in C⋯O lengths which are within the limit of error for the X-ray method. The probability of an interaction between the two C⋯O groups is consistent with the reported structural data.[16] The C⋯O stretching vibrations of the 1,3-diketonates and the hydroxymethylenecamphorates are quite similar. The differences are in the frequencies of the absorptions and the separations between the antisymmetric and symmetric vibrations. In the spectra of M(HMC)$_x$ chelates the frequencies are higher and the separations are significantly larger than in the 1,3-diketonates. The separations (in cm^{-1}) between the two C⋯O vibrations in some acetylacetonate and HMC$^-$ chelates are compared below. The values for the acetylacetonates have been determined from spectra compiled and presented by Nakamoto.[18] (See Table V.) The larger separation in the HMC$^-$ chelates is attributed to a less effective resonance interaction between the two C⋯O groups. In the hydroxymethylenecamphorates the C⋯O vibrational frequencies indicate that the carbon to oxygen bond lengths are significantly more dissimilar than in the 1,3-diketonates. The same conclusion is drawn when considering the carbon to carbon stretching frequencies in the chelate ring. These frequencies seem best explained by the existence of two different carbon to carbon bond lengths rather than conjugated C⋯C. On the basis of the separation between the carbon to oxygen vibrations it seems likely that a very distorted form of Ic, the resonance tautomer, best approximates the bonding situation in the metal chelates. Presumably, the presence of the five-membered ring fused to the chelate ring is responsible for much of the distortion.

Table V

Separation between the Two C–O Absorptions in HMC$^-$ and acac$^-$ Chelates (in cm^{-1})

	Cr(III)	Co(III)	Cu(II)	Fe(III)	Ni(II)	Co(II)	Zn(II)
HMC	298	299	301	311	343	351	364
acac	205	206	224	207	231	235	231

As mentioned above, another significant difference between the spectra of M(acac)$_x$ and M(HMC)$_x$ chelates is the position of the C—O stretching absorptions. The high-frequency C—O stretch in HMC$^-$ chelates is about 50 cm^{-1} higher than in acetylacetonates containing the same metal ion.[18] This is most likely due to a greater vibrational purity and a smaller C=O polarization in M(HMC)$_x$ chelates than in M(acac)$_x$ chelates. Arranging the metal ions in order of their decreasing ability to polarize the C=O bond in HMC$^-$ yields an Irving–Williams type of relationship. Presumably, this arrangement would also reflect a decreasing trend in thermodynamic stabilities of the HMC$^-$ chelates.

The spectra below 1200 cm^{-1} show not only changes in band positions as a function of the metal ion but also two distinctly different spectral patterns. Pattern 1 is characterized by the appearance of a band at about 1140 cm^{-1}, a chelate ring C–C vibration of medium strength (1050–1035 cm^{-1}), and one relatively strong (for this spectral region), broad band from 485 to 500 cm^{-1}. Pattern 2 is characterized by the absence of a band at 1140 cm^{-1}, a very weak chelate ring C–C vibration, and two weak absorptions in the 485–500 cm^{-1} region. These differences are apparent in Figures 1 and 2. Pattern 1 is observed for chelates of Zn(II), Mg(II), Co(II), Ni(II), and Mn(II). Chelates in which the pattern 2 spectra are observed include all of the others studied. Observation of pattern 1 or 2 does not depend simply upon the metal present or its oxidation state; *e.g.*, compare Co(HMC)$_2$ to Co(HMC)$_3$ and Co(HMC)$_2$(py)$_2$. It can, however, be rationalized as being due to different molecular configurations.

All chelates that give rise to a pattern 2 type of spectrum are monomers with idealized octahedral, distorted octahedral, or square-planar symmetries. A common feature of all of the metal ions whose HMC$^-$ chelates have a pattern 1 type of spectrum is the 2+ oxidation state. In addition, all, with the exception of Mg(II), have been reported to form six-coordinate complexes with acetylacetone.[3,5–7] This is accomplished by the formation of bridging oxygen bonds, resulting in oligomeric molecules. Preliminary molecular weight determinations of HMC$^-$ chelates indicate that those with pattern 1 type spectra also exist as oligomers. A more complete discussion of these molecules will be presented in a later paper. The HMC$^-$ chelates of Ni(II) and Co(II) are trimeric on the basis of molecular weight data. The oligomeric nature of these chelates is indicated by the magnetic data, also. Values of 3.08 and 4.9 BM at 300°K for Ni$_3$(HMC)$_6$-(H$_2$O)$_2$ and Co$_3$(HMC)$_6$ are explained by $^3A_{2g}$ and $^4T_{1g}$ ground states, respectively. These ground states

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(17) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

(18) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 217. The original assignments made by Nakamoto for the chelates have been changed in light of new calculations by Behnke and Nakamoto.[17]

arise from octahedral ligand fields in both cases. Such fields are due to the formation of bridging oxygen to metal bonds.

The analytical results for chelates that produce pattern 1 type spectra are best explained by oligomeric molecules, also. The unusual number of water molecules per metal ion is caused by the fact that the waters occupy only a few coordination sites on the oligomer. The number of water molecules is determined by the number of octahedra involved and the type of bridging, *i.e.*, face sharing, edge sharing, or corner sharing between octahedra. The rigorous conditions needed to remove the water molecules leave no doubt that they are coordinated to the metal ion. It would be extremely interesting to determine the structures of the oligomers by X-ray analysis; however, as yet no suitable single crystals have been prepared. At this point, it seems likely that $Ni(HMC)_6(H_2O)_2$ exists as three octahedral units with two shared edges and that $Co_3(HMC)_6$ exists as three octahedral units with two shared faces.

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Anhydrous and Hydrated Rare Earth Acetylacetonates and Their Infrared Spectra[1,2]

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Chemical analyses, X-ray powder diffraction patterns, and infrared spectra were used to characterize anhydrous, mono-, di-, and trihydrated rare earth acetylacetonates, and the densities of the hydrated chelates were determined. The anhydrous chelates were obtained by vacuum drying one of the hydrates. They are not appreciably volatile and slowly decompose *in vacuo* at elevated temperatures. Trihydrates precipitate from 60% aqueous ethanol, dihydrates from cold 95% ethanol, and monohydrates from hot 95% ethanol and a variety of other solvents. The infrared spectra are distinctive for each of the series of hydrates. For a given hydrate series, the spectra obtained are practically independent of the rare earth ion. The most notable exception is the 3100–3600-cm^{-1} region of the monohydrates where the high-energy O–H stretching frequency shifts to higher wave numbers and the low-energy O–H stretching frequency shifts to lower wave numbers as the ionic size of the rare earth decreases. Deuterium isotopic substitution studies on the mono- and trihydrates were used to locate the C–H and coordinated H_2O vibrations.

Rare earth acetylacetonates have been studied extensively because they are the simplest known β-diketone chelates. Because of conflicting data in the literature regarding the extent of hydration of rare earth acetylacetonates, Pope, Steinbach, and Wagner[3] carried out a study designed to resolve the problem of hydration number. Only mono- and trihydrated chelates were found, and there was no evidence that the anhydrous and dihydrated complexes existed. Pope believed that the "dihydrate" reported by several workers was actually a mixture of the mono- and trihydrates, and that the "anhydrous" chelate was a partly hydrolyzed sample of the monohydrate. There is little doubt that this has frequently been the case. However, the papers by Koehler and Bos[4] and others[5-7] contain substantial evidence that an anhydrous, unsolvated chelate has been made. The present study presents definitive evidence (chemical analyses, including Karl Fischer titrations, X-ray powder diffraction patterns, and infrared spectra) for the existence of anhydrous rare earth acetylacetonates. In addition, a dihydrated chelate has been characterized for the acetylacetonates of La, Pr, Nd, and Sm.

Many investigators have obtained infrared spectra for the rare earth acetylacetonates,[8-14] but a complete study of the effect of hydration number on the spectra has not been made. This study reports a systematic investigation of the spectra of the mono-, di-, and trihydrates, as well as of the anhydrous chelates and deuterated mono- and trihydrates.

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(2) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky, Oct 27, 1966.

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