interaction suggested by the susceptibility measurements. The failure to observe a higher conductivity may be due to surface contamination of the particles in the compacted powder. The contamination may arise from the inability to attain an absolutely inert atmosphere in the plastic glove bag which was used for handling the product.

An attempt was made to determine the infrared spectrum of the compound in a KBr pellet. No bands were observed in the 2000–2200-cm^{-1} range where the Ir–H stretch is reported to occur for the hydrido complexes of iridium,[7] but this may have been a limitation of the technique used.

The stoichiometery of the compound was initially indicated by the powder pattern data. When molar ratios of strontium hydride to iridium ranging from 2:1 to 5:3 are used, the resulting product gives rise to a characteristic X-ray powder pattern, and neither strontium hydride nor iridium can be detected in this powder pattern. Iridium was shown to be easily detected by X-ray analysis; free strontium hydride was not so easily observed. Experiments were carried out over a range of strontium hydride to iridium ratios of 10:1 to 1:2. These results indicate that the stoichiometry lies somewhere between an Sr:Ir mole ratio of 3:1 to 5:3. When either strontium hydride or iridium is used in amounts greater than indicated by the above ratio range, the characteristic lines for these constituents are seen in the X-ray powder pattern. Chemical analysis indicated material balance. There was no increase in the hydridic hydrogen. The analytical determinations showed that within experimental error the final product contained the same amount of hydridic hydrogen as the starting material. Uptake of hydrogen was also monitored. The early experiments showed a small decrease in hydrogen pressure, but this was also shown to occur in the system without reactants. Later experiments were carried out by not only regreasing the joint closest to the furnace before each run but also air cooling it during the run. This eliminated the loss of hydrogen and showed unequivocally that there was no hydrogen uptake during a reaction. The experimentally determined density and the size of the unit cell indicated that stoichiometry was two strontium hydrides to one iridium. These results are consistent with the stoichiometry of Li_4RhH_4 reported by Farr and Magee. However, unlike Magee, we have not been able to show the analog of the second hydride phase which he formulates as Li_4RhH_5.

A variety of conditions were tried for the synthetic procedure. The most favorable conditions seem to be a 24-hr heating period at 820°. At temperatures of 1000° the ternary phase undergoes decomposition. This was discovered when an attempt was made to prepare a pure compound by using an excess of strontium hydride, heating to destroy the strontium hydride preferentially, and distilling to remove the strontium. This procedure did not work since the ternary hydride was more easily decomposed than strontium hydride.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[7] A. P. Ginsberg, *Transition Metal Chem.*, **1**, 124 (1965).

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Mass Spectral Studies of Metal Chelates. IV. Mass Spectra, Appearance Potentials, and Coordinate Bond Energies of Bis(acetylacetonate)metal(II) Complexes of the First Transition Series

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A number of papers dealing with the mass spectrometric investigation of metal β-diketonates have recently been published.[1–8] Here we report further results on the mass spectra of the bis acetylacetonates of Mn, Fe, Co, Ni, Cu, and Zn and the appearance potentials of selected ions derived therefrom.

Experimental Section

The acetylacetonates of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) were prepared by the aqueous solution synthesis of Fernelius and Bryant.[9]

The same procedure was used for Fe(acac)$_2$ except that zinc amalgam was also present to prevent oxidation of Fe(II) to Fe(III). Reagent grade acetylacetone was distilled before use. All samples, except Fe(acac)$_2$, were sublimed at least once before use. The mass spectral studies were performed on a Hitachi Perkin-Elmer RMU-6D single-focusing mass spectrometer using the techniques described previously.[6] For all of these samples the direct-insertion method was used, the sample being heated to 30–150° depending upon its volatility. The ionization chamber temperature was 150° for all reported experimental results, which, however, were insensitive to variations in chamber temperature.

Results

The mass spectra obtained for the chelates for 50-V electrons and an ionizing chamber temperature of 150°

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(1) C. G. MacDonald and J. S. Shannon, *Australian J. Chem.*, **19**, 1545 (1966).

(2) J. Macklin and G. Dudek, *Inorg. Nucl. Chem. Letters*, **2**, 403 (1966).

(3) S. Sasaki, Y. Itagaki, T. Kwokawa, K. Nakanishi, and A. Kasahara, *Bull. Chem. Soc. Japan*, **40**, 76 (1967).

(4) C. Reichert, J. B. Westmore, and H. D. Gesser, *Chem. Commun.*, 782 (1967).

(5) M. J. Lacey, C. G. MacDonald, and J. S. Shannon, *Org. Mass Spectrometry*, **1**, 115 (1968).

(6) G. M. Bancroft, C. Reichert, and J. B. Westmore, *Inorg. Chem.*, **7**, 870 (1968).

(7) S. M. Schildcrout, R. G. Pearson, and F. E. Stafford, *J. Am. Chem. Soc.*, **90**, 4006 (1968).

(8) B. F. G. Johnson, J. Lewis, and M. S. Subramanian, *J. Chem. Soc., A*, 1933 (1968).

(9) W. C. Fernelius and B. E. Bryant, *Inorg. Syn.*, **5**, 105 (1957).

TABLE I

RELATIVE INTENSITIES OF METAL CONTAINING IONS IN THE MASS SPECTRA, AT AN ELECTRON ENERGY OF 50 V AND IONIZATION CHAMBER TEMPERATURE OF $\sim$150°[a]

	Ion	Mn	Fe	Co	Ni	Cu	Zn	Assignment
a	P	84 (0.6)	60	96	98	48	52	ML_2^+
b	P − 15	58 (1.6)	42^{a} $(0.8)^{2+}$	91^{a}	90	35	69	$(ML_2 - CH_3)^+$
	P − 18	1	. . .	. . .	. . .	$\ngtr 1$	. . .	$(ML_2 - H_2O)^+$
c	P − 30	. . . (3.3)	. . .	2	. . .	35	. . .	$(ML_2 - 2CH_3)^+$
	P − 42	9	1	2	. . .	10^{a}	9^{a}	$(L_2M - CH_2CO)^+$
d	P − 57	. . .	. . .	2^{b}	3	. . .	33	$(LMCOCH_2)^+$
	P − 82	. . .	9	. . .	. . .	. . .	. . .	$LMOH^+$
	P − 98	. . .	. . .	. . .	41	6	. . .	LMH^+
e	P − 99	100^{b}	100	100^{b}	100^{b}	50^{bc}	100^{d}	LM^+
	P − 100	. . .	. . .	3	. . .	5	. . .	$(LM - H)^+$
	P − 101	. . .	. . .	2	. . .	. . .	. . .	$(LM - 2H)^+$
f	P − 114	5	. . .	12	33	100^{ce}	. . .	$(LM - CH_3)^+$
	P − 115	. . .	. . .	3	24	. . .	. . .	$(L_2M - CH_3 - HL)^+$
	P − 117	4	. . .	2	. . .	. . .	9	$(LM - H_2O)^+$
	P − 128	. . .	. . .	. . .	. . .	12	. . .	$(L_2M - 2CH_3 - (L - H))^+$
	P − 141	. . .	. . .	. . .	. . .	. . .	4	$(LM - CH_2CO)^+$
	P − 156	. . .	. . .	. . .	30	50^{f}	. . .	$(MCOCH_2)^+$
	P − 157	. . .	. . .	. . .	. . .	8	. . .	$(MCOCH)^+$
	P − 181	$\ngtr 3$	. . .	. . .	. . .	. . .	. . .	MOH^+
	P − 182	. . .	10	. . .	. . .	. . .	. . .	MO^+
	P − 183	14	. . .	. . .	. . .	. . .	. . .	MCH_3^+
	P − 198	8	15	6	17	10	$\ngtr 5$	M^+

[a] Identified metastable transitions are indicated by superscripts which relate the daughter ion to the parent ion as labeled in column 1. The intensities of doubly charged ions are shown in parentheses (L = · acac).

are given in Table I. The mass spectrum of $Fe(acac)_2$ has not been reported previously but the other spectra can be compared with those given by MacDonald and Shannon.[1] The spectra are quite similar and the variations which do occur can probably be attributed in most cases to differences in experimental conditions. There are, however, a few cases where these latter authors found a peak and we did not, and *vice versa.* MacDonald and Shannon discussed fragmentation mechanisms in some detail and so a full discussion will not be given here. We would, however, draw attention to the $(P - 98)^+$, $(P - 100)^+$, and $(P - 116)^+$ ions in some of the spectra. These ions are believed to arise from hydrogen migration reactions and were not tabulated by MacDonald and Shannon although close examination of their diagrams show that they were sometimes present. In a later paper on metal complexes of dibenzoylmethane[5] they did discuss mechanisms for the formation of ions analogous to the $(P - 98)^+$ and $(P - 100)^+$ ions, though for the $(P - 98)^+$ ion in the acetylacetonates an analogous mechanism is not available.

Appearance Potentials.—We have previously reported the appearance potentials of a number of tris acetylacetonates[6] and substituted acetylacetonates.[10] These results suggested that on ionization the electron was removed from a π orbital localized mainly on the ligand since the nature of the ligand had a far greater effect than the metal on the appearance potentials of the metal chelates. A similar conclusion was reached by Schildcrout, *et al.*[7] However, there was a remarkable parallel between the appearance potential of $M(acac)_2^+$ from $M(acac)_3$ and the energy of the highest occupied molecular orbital of $M(acac)_3$.[6] The ion $M(acac)_2^+$ is formed by dissociation of a ligand radical from the parent molecular ion. It is possible that a similar parallelism may exist between the energy of the highest occupied molecular orbital of $M(acac)_2$ and the appearance potentials of ions formed by dissociation of neutral radicals from the parent molecular ion ML_2^+. For purposes of comparison the intensities of ions of this type should be high enough in all of the spectra that appearance potential measurements of sufficient accuracy can be made. Thus, in Table II we report the appearance potentials of the molecular ion and those ions formed by loss of CH_3 or a ligand radical.

TABLE II

APPEARANCE POTENTIALS OF IONS FROM $M(acac)_2$ AT AN IONIZATION CHAMBER TEMPERATURE OF APPROXIMATELY 150°

Metal	Sample temp, °C (approx)	AP, eV		
		P^+	$(P-CH_3)^+$	$(P-L)^+$
Mn	120	8.34 ± 0.05	11.7 ± 0.1	13.7 ± 0.1
Fe	100	8.10 ± 0.05	11.7 ± 0.1	13.9 ± 0.1
Co	25	8.54 ± 0.05	11.5 ± 0.1	13.9 ± 0.2
Ni	100	8.23 ± 0.05	11.6 ± 0.1	13.5 ± 0.2
Cu	30	8.31 ± 0.05	10.9 ± 0.1	13.1 ± 0.2
Zn	100	8.62 ± 0.05	10.9 ± 0.1	14.1 ± 0.2
H	. . .	9.2 ± 0.1	10.7 ± 0.1	. . .

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(10) G. M. Bancroft, C. Reichert, J. B. Westmore, and H. D. Gesser, *Inorg. Chem.*, **8**, 474 (1969).

Table III

Coordinate Bond Energies

Metal	AP[M(acac)$_2^+$],[a] eV	ΔH_{diss}, kcal/mol	$E_{\text{M-O}}^{\text{tris}}$,[b] kcal/mol	$E_{\text{M-O}}^{\text{bis}}$, kcal/mol
Mn	$\geqslant 8.7 \pm 0.1$	$\geqslant 9 \pm 4$	44.8 ± 0.5	$\leqslant 65 \pm 2$
Fe	$\geqslant 9.4 \pm 0.1$	$\geqslant 30 \pm 4$	55.9 ± 0.6	$\leqslant 76 \pm 2$
Co	10.7 ± 0.1	$\geqslant 51 \pm 4$	50.9 ± 0.7	$\leqslant 63 \pm 2$

[a] See reference 6. [b] J. L. Wood and M. M. Jones, *Inorg. Chem.*, **3**, 1553 (1964).

Most of these complexes have different structures in the gaseous and condensed phases. The available evidence[11] suggests that in the gaseous state the acetylacetonates of Mn(II), Fe(II), Co(II), and Zn(II) are tetrahedral (high spin) while those of Ni(II) and Cu(II) are square planar, and in the solid state they are all polymeric with the exception of Cu(acac)$_2$. Thus, the usual experimental data are not available with which to compare the measured appearance potentials. For example, electronic absorption spectra can, in principle, be used to evaluate ligand field effects, but solution spectra are not likely to be helpful here. Moreover, we are not aware of any theoretical treatment of the gaseous chelate molecules.

In the ionization process two possibilities may be considered, namely, (a) the electron is removed from a molecular orbital localized mainly on the metal and (b) the electron is removed from a molecular orbital localized mainly on the π system of the ligand. It seems that these results do not allow us to distinguish between these possibilities although previous experimental results[6,7,10] on other β-diketonates have suggested the second possibility, and the present results do not seem to be in conflict with this suggestion.

The appearance potentials of the $(\text{P} - \text{CH}_3)^+$ ions fall into two groups. For Mn$^{\text{II}}$, Fe$^{\text{II}}$, Co$^{\text{II}}$, and Ni$^{\text{II}}$ the values are 11.6 ± 0.1 V and for Cu(II) and Zn(II) the values are both significantly lower at 10.9 ± 0.1 V. For the ML$^+$ ions the values for Mn$^{\text{II}}$, Fe$^{\text{II}}$, Co$^{\text{II}}$, and Ni$^{\text{II}}$ can again be grouped together at 13.7 ± 0.2 V. These observations may be fortuitous, however.

In an earlier paper[6] we have quoted values of the appearance potentials of the M(acac)$_2^+$ ions from the tris chelates of Mn(III), Fe(III), and Co(III). For these chelates we can thus calculate the energy of the dissociation: $\text{M(acac)}_3 \rightarrow \text{M(acac)}_2 + \text{acac}$. Making the usual assumptions that the products of the ionization reactions are formed in their ground states and that their total kinetic energy is small, a lower limit for the energy of the homolytic dissociation is given by

$$\Delta H_{\text{diss}} = \text{AP}[\text{M(acac)}_2^+ \text{ from M(acac)}_3] - \text{IP}[\text{M(acac)}_2]$$

The metal–oxygen coordinate bond energies in the M(acac)$_2$ complexes are given by

$$E_{\text{M-O}}^{\text{bis}} = {}^1/_4(6E_{\text{M-O}}^{\text{tris}} - \Delta H_{\text{diss}})$$

These values and the data necessary to calculate them are given in Table III.

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[11] J. P. Fackler, *Progr. Inorg. Chem.*, **7**, 361 (1966), and references therein.

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On the Spontaneous Reduction of Hexachloroiridate(IV) in Aqueous Solution

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Previous work on the aqueous solution chemistry of iridium(IV) has indicated that hexachloroiridate(IV), IrCl$_6^{2-}$, undergoes spontaneous reduction to the +3 state in neutral and weakly acidic solution.[1–4] The rate and extent of the reduction appear to be dependent on acidity.[4] Suggested explanations for the reaction include oxidation of ligand chloride[3] and oxidation of water.[4] Recent irradiation experiments have shown that the redox process is not photochemical in nature.[5] In the course of some investigations of the chemistry of iridium(IV) in basic solution, we have observed that hexachloroiridate(IV) is rapidly and quantitatively reduced in solutions of pH >11. Through mass spectrometry, vapor-phase chromatography, and spectrophotometry we have obtained evidence as to the process of reduction in aqueous solution.

Mass spectrometry was employed to obtain qualitative identification of gaseous reaction products in basic solution. Hexachloroiridate(IV) salts were dissolved in degassed sodium hydroxide solution, and the gaseous contents of the reaction vessel were analyzed (see Experimental Section for details). When hexachloroiridate(IV) salts are dissolved in alkali hydroxide more concentrated than 10^{-2} *M*, an evolution of gas bubbles takes place and the color of the solution quickly goes from the dark reddish brown characteristic of hexachloroiridate(IV) to the pale yellow-green characteristic of the +3 state. The only gaseous products detected by the mass spectrometer were oxygen and water vapor. In more dilute alkaline solutions, evolution of gas bubbles is not visible, and the color fades more slowly; again, only oxygen and water vapor were detected by the mass spectrometer.

Vapor-phase chromatography was employed to obtain

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(1) E. A. Belousov and A. A. Grinberg, *Tr. Leningr. Tekhnol. Inst. im. Lensoveta*, **40**, 32 (1957).

(2) M. R. Martinez, Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1958.

(3) I. A. Poulsen and C. S. Garner, *J. Am. Chem. Soc.*, **84**, 2032 (1962).

(4) J. M. Peixoto Cabral, *J. Inorg. Nucl. Chem.*, **26**, 1657 (1964).

(5) T. P. Sleight and C. R. Hare, *Inorg. Nucl. Chem. Letters*, **4**, 165 (1968).