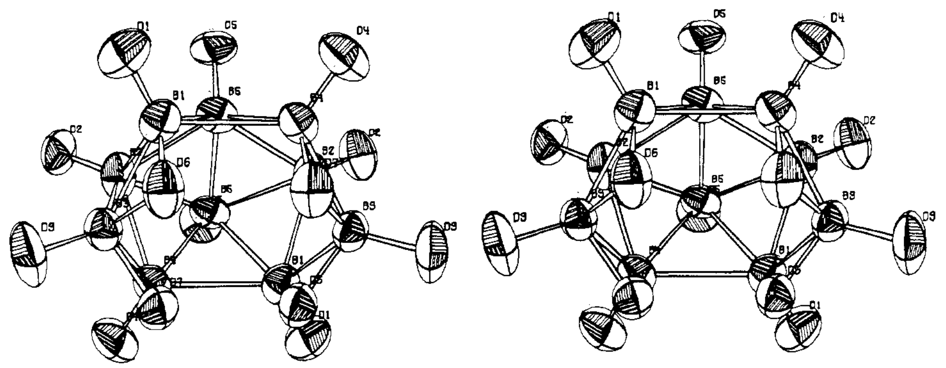

Figure 2.—Stereoview of the decaborane molecule. The ellipsoids indicate the magnitudes of thermal vibration.

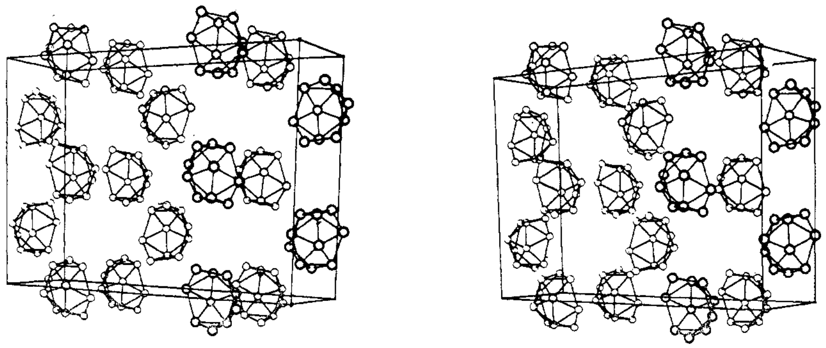

Figure 3.—Packing diagram of the decaborane unit cell (stereoview). The hydrogen atoms are not included.

Acknowledgments.—We wish to thank Professor Dr. R. Brill of Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany, for his suggestion of this problem and for his great interest and help in its solution. We are also grateful to D. R. Christman for the deuterium analyses.

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Metal Complexes of the Dibenzamido Anion

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Several new metal complexes of the dibenzamido anion, $M(C_6H_5CONCOC_6H_5)_n$, where M = Be(II), Al(III), Fe(III), Cu(II), and Hg(II), have been synthesized. The compounds were characterized by elemental analysis and from their infrared spectra. A comparison of the electronic properties of some isoelectronic and isostructural dibenzamido and dibenzoylmethano complexes is presented.

Introduction

Tris(dibenzamido)chromium(III), $Cr(dba)_3$, and tris(diacetamido)chromium(III), $Cr(daa)_3$, were reported recently as the first well-characterized complexes of diacylamide anions.[1] Further attempts to obtain other new diacetamido–metal complexes have been generally unsuccessful. However, several new complexes of the dibenzamido anion have been isolated and characterized and will be reported on at this time.[2]

Experimental Section

Reagents.—Anhydrous beryllium chloride was obtained from Alfa Inorganics, Inc. Anhydrous chromium(III) chloride[3] and iron(III) chloride[4] were prepared in the laboratory. Anhydrous aluminum chloride (Baker and Adamson) was sublimed before use. Copper(II) acetate monohydrate and mercury(II) acetate were purchased from the J. T. Baker Chemical Co. The preparation of dibenzamide has already been reported.[1] Dibenzoylmethane (Eastman Kodak Co.) was used as received.

Chloroform, *n*-hexane, and anhydrous diethyl ether were used as received from J. T. Baker Chemical Co. ("Baker

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[1] C. S. Kraihanzel and D. N. Stehly, *Inorg. Chem.*, **6**, 277 (1967).

[2] D. N. Stehly and C. S. Kraihanzel, presented in part at the 3rd Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1968.

[3] G. B. Heisig, B. Fawkes, and R. Hedin, *Inorg. Syn.*, **2**, 193 (1946).

[4] A. R. Pray, *ibid.*, **5**, 154 (1957).

Analyzed" reagent). Benzene ("Baker Analyzed" reagent) was distilled azeotropically to remove the bulk of the water impurity and then drawn through a column of activated alumina as needed. Tetrahydrofuran, THF (Matheson Coleman and Bell), was distilled from calcium hydride and redistilled from lithium aluminum hydride directly into the reaction vessels. All distillations and experimental procedures were carried out under prepurified nitrogen.

N-Deuteriodibenzamide.—Dibenzamide (0.3 g) was slurried in 6 ml of deuterium oxide (Bio Rad Laboratories, 99.7%) under a stream of nitrogen. Sodium metal was added in small pieces with shaking to form sufficient sodium deuterioxide to dissolve the dibenzamide completely. The solution was filtered under nitrogen and saturated with dry carbon dioxide to precipitate the N-deuteriodibenzamide. The solid was collected by filtration under nitrogen and washed with two 2-ml portions of fresh deuterium oxide. The above procedure was repeated twice and the resultant material was dried at 50° and 0.1 mm pressure for 8 hr.

Preparation of Complexes. Tris(dibenzamido)iron(III), Fe(dba)$_3$.—Dibenzamide (4.0 g, 18 mmol) was added to THF (100 ml) containing finely divided sodium (0.42 g, 18 mg-atoms). When the sodium metal had dissolved ($\sim$1 hr), anhydrous iron(III) chloride (0.97 g, 6.0 mmol) was added. The mixture was allowed to stir under nitrogen for 5 days. At the end of this time, the THF was removed from the mixture under vacuum. The resultant brown solid was extracted continuously with approximately 500 ml of dry benzene for a period of 24 hr. The crude product, obtained as a brown solid after concentration of the extracts, was recrystallized by first dissolving it in dry benzene at room temperature, then heating the mixture to reflux, and adding boiling *n*-hexane to the cloud point. The solution was stored overnight in the refrigerator and yielded 0.72 g (17%) of well-formed, gold crystals, mp 237–238°. *Anal.* Calcd for $C_{42}H_{30}O_6N_3Fe$: C, 69.24; H, 4.15; N, 5.77; Fe, 7.66. Found: C, 69.48; H, 4.28; N, 5.57; Fe, 7.60.

Bis(dibenzamido)copper(II), Cu(dba)$_2$.—Dibenzamide (1.12 g, 5.0 mmol) was dissolved in 80 ml of absolute ethanol. A solution of copper(II) acetate monohydrate (0.40 g, 2.0 mmol) in 60 ml of absolute ethanol was added to the dibenzamide solution in one portion at room temperature. Precipitation of blue-gray needles commenced within a few minutes and was considered complete after 2 hr. The solid was collected by filtration and then recrystallized from dry benzene to yield 0.80 g (78%) of product, mp 265–266°. Other than the recrystallization procedure, this preparation is similar to that reported by Ley and Werner[5] for a compound which thay apparently considered to be $Cu(C_{14}H_{10}O_2N)_2 \cdot 2H_2O$. *Anal.* Calcd for $C_{28}H_{20}O_4N_2Cu$: C, 65.66; H, 3.94; N, 5.47; Cu, 12.42. Found: C, 65.45; H, 3.96; N, 5.62; Cu, 12.55.

Tris(dibenzamido)aluminum(III), Al(dba)$_3$.—Dibenzamide (4.0 g, 18 mmol) was added to THF (100 ml) containing finely divided sodium (0.42 g, 18 mg-atoms). Freshly sublimed, anhydrous aluminum chloride (0.80 g, 6.0 mmol) was added to the reaction mixture after the sodium metal had been consumed. The mixture was allowed to stir under nitrogen for 24 hr. At the end of the reaction period, the THF was removed under vacuum and the resultant yellow solid was extracted with several portions of boiling benzene until no more material dissolved. Upon cooling, the yellow benzene extracts yielded white crystals. Several additional crops of the white solid were obtained by concentration of the benzene solution and addition of hot *n*-hexane. The combined crops were dissolved in a minimum amount of hot benzene following which hot *n*-hexane was added to the cloud point. The yield of white crystalline solid, mp 283–287°, was 0.54 g (13%). *Anal.* Calcd for $C_{42}H_{30}O_6N_3Al$: C, 72.10; H, 4.32; N, 6.01; Al, 3.86. Found: C, 72.27; H, 4.28; N, 5.79; Al, 3.84.

Bis(dibenzamido)beryllium(II), Be(dba)$_2$.—After 2.8 g (12 mmol) of dibenzamide dissolved in 150 ml of THF had reacted with 0.27 g (12 mg-atoms) of finely divided sodium, anhydrous beryllium(II) chloride (0.48 g, 6.0 mmol) was added and the mixture was allowed to stir under nitrogen for 24 hr. At the end of the reaction period, the THF was removed under vacuum and the resultant pale orange solid was extracted with several portions of boiling benzene to yield a yellow-gold solution. The solid obtained upon evaporation of the benzene was recrystallized from benzene–hexane mixtures. The first crops of white solid were low-melting material (120–125°) and were discarded. Further crops were obtained by concentration of the filtrates and these yielded the desired product as a white crystalline solid, mp 230–238°. Recrystallization from a benzene–hexane mixture yielded 0.93 g (34%) of product, mp 238–240°. *Anal.* Calcd for $C_{28}H_{20}O_4N_2Be$: C, 73.51; H, 4.41; N, 6.12; Be, 1.75. Found: C, 73.24; H, 4.34; N, 5.95; Be, 1.83.

Bis(dibenzamido)mercury(II), Hg(dba)$_2$.—This complex was prepared from 0.64 g (2.0 mmol) of mercury(II) acetate, and 1.13 g (5.0 mmol) of dibenzamide according to the same procedure used in the preparation of Cu(dba)$_2$. The yield of white, crystalline solid was 1.1 g (86%), mp 225–227.5°. *Anal.* Calcd for $C_{28}H_{20}O_4N_2Hg$: C, 51.81; H, 3.11; N, 4.32. Found: C, 52.03; H, 3.12; N, 4.48.

β-Diketonato Complexes.—Tris(dibenzoylmethano)iron(III), Fe(dbm)$_3$, and bis(dibenzoylmethano)beryllium(II), Be(dbm)$_2$, were prepared by known methods.[6] Bis(dibenzoylmethano)copper(II), Cu(dbm)$_2$, and tris(dibenzoylmethano)aluminum(III), Al(dbm)$_3$, were prepared by adding dropwise a solution of the metal chloride (4.0 mmol) in 10 ml of water with stirring to dibenzoylmethane (8.0 mmol) dissolved in 30 ml of 95% ethanol. The solid which precipitated immediately was collected by suction filtration and then recrystallized twice from hot benzene. The purity of each product was determined by its melting point and from a comparison of the infrared spectrum with published results.[6-8]

Physical Measurements. Spectrophotometry.—Infrared spectra were obtained in the region 4000–600 cm^{-1} with a Perkin-Elmer Model 257 spectrophotometer. Bands in the 800–400-cm^{-1} region were obtained with a Perkin-Elmer Model 337 spectrophotometer. Samples were examined as mulls in dry Nujol oil and dry hexachlorobutadiene.

Electronic spectra were obtained with a Beckman DK-2A quartz prism ratio-recording spectrometer. Chloroform and dry benzene were used as solvents.

General Measurements.—Melting points were obtained of samples sealed in tubes under nitrogen. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Results and Discussion

The new compounds Be(dba)$_2$, Al(dba)$_3$, and Fe(dba)$_3$ have been prepared, as was Cr(dba)$_3$, by the direct reaction of the pertinent anhydrous metal chloride with dibenzamidosodium in THF. Cu(dba)$_2$ and Hg(dba)$_2$ were synthesized more readily by the reaction of the metal acetate with dibenzamide in alcohol solution. The compounds have reasonably sharp melting points and are soluble in benzene, tetrahydrofuran, chloroform, and ether. Although the solid complexes appear to be hydrophobic and float unaffected on the surface of pure water, deterioration of each of the complexes does occur in wet organic solvents.

Infrared Spectra.—The conclusion that the diacetamido anion chelates Cr(III) through the two ligand oxygen atoms was reached by comparing the infrared

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(5) H. Ley and F. Werner, *Ber.*, **46**, 4040 (1913).

(6) J. MacQueen and J. W. Smith, *J. Chem. Soc.*, 1821 (1956).

(7) K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).

(8) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Phys. Chem.*, **66**, 346 (1962).

TABLE I

INFRARED ABSORBANCES OF DIBENZAMIDO COMPLEXES (CM^{-1})[a]

$Hg(dba)_2$	$Be(dba)_2$	$Cu(dba)_2$	$Al(dba)_3$	$Fe(dba)_3$	$Cr(dba)_3$	Hdba
						3229 s
						3150 w
						3118 m
3075 w	3080 w, sh	3080 w, sh	3085 w, sh	3085 w, sh	3085 w, sh	3075 w, sh
3055 w	3058 w	3062 w	3064 w	3064 w	3060 w	3045 m
3020 w	3020 w, sh	3020 w, sh	3023 w	3025 w	3030 w	3012 w
1634 s						1708 s
						1681 s
1592 s	1615 sh	1602 sh		1597 m	1596 sh	1603 m
1577 s	1592 s	1596 s	1598 s	1590 s	1587 s	1583 m
	1525 s	1545 s	1542 s	1522 s	1518 s	
						1502 m
						1480 s
1484 m	1490 m	(1465) sh	1470 s	1457 s	1455 s	
1445 s	1457 s	1456 s	1458 s	1443 s	1446 m	1445 sh
	1410 s	1406 s	1407 s	1399 s	1399 s	
1320 sh	1362 s	1346 s	1357 s	1341 s	1349 s	
1305 s	1300 m	(1303) w	1305 m	1303 m	1305 w	1303 m
1290 s						
1272 s						1231 s
1178 m	1174 w	1170 w, sh	1172 w	1170 w	1171 w	1176 m
	1160 m	1165 w	1162 w	1162 w	1160 w	1157 w
1152 m	1148 m	1148 m	1150 m	1149 m	1150 m	
						1118 m
1085 m	1098 w	(1095) w, b	1098 w	1096 w	1094 w	1104 sh
1070 m	1082 m	1076 w	1084 w	1070 m	1076 w	1072 m
	1064 w	1063 w	1066 w	1063 w	1067 w	
1025 m	1023 m	1023 m	1023 m	1029 m	1029 m	1026 m
1000 w	1000 m	(1000) w	1000 w	1000 w	1000 w	1002 m
						979 w
	959 m					
						955 m
940 m		940 w, b	944 w	937 w, b	936 w, b	940 w, b
930 m						869 w
826 m	825 s					
		(820) w. sh	829 m	824 m	822 m	
						809 m
790 m	800 m	804 m	802 w	799 m	801 m	710 s
	772 w	726 s	730 s	727 s	728 s	693 s
	728 s	704 w	712 w	712 w	709 w	609 s
	705 w	684 m	701 w	698 m	698 w	529 m
	694 w, sh	660 m	685 m	685 m	682 m	
	682 m	577 s	640 s	625 s	659 m	
	616 w		605 s	565 s	650 m	
	602 s		588 s	547 s	580 sh	
	535 m		561 s	(405) m	572 s	
	512 m		435 s		(435 w, b?)	
	(455 w, b?)					

[a] Hexachlorobutadiene mulls: 4000–1650 and 1500–1200 cm^{-1}. Nujol mulls: 2500–1490 and 1300–650 cm^{-1}. Notations: s, strong; m, medium; w, weak; sh, shoulder.

spectra of $Cr(daa)_3$ and *trans,trans*-diacetamide.[1] The particular criteria employed in this comparison were (1) the absence of ν_{NH}, (2) the shifts of ν_{CO}(sym) and ν_{CO}(asym) to lower energy, and (3) the appearance of a single sharp band, assigned to ν_{CNC}(asym) for the complexed ligand, of an energy intermediate between that of the coupled ν_{CNC}(asym) and δ_{NH}(in plane) bands of free diacetamide.

These same criteria are useful in comparing the infrared spectra (Table I) of the dba complexes of Be(II), Al(III), Cr(III), Fe(III), and Cu(II) with the spectrum of *trans,trans*-dibenzamide.[9] For example, the absence of an imide hydrogen is proved by the disappearance of the free ligand bands at 3118, 3150, and 3229 cm^{-1} as well as the coupled ν_{CNC}(asym) and δ_{NH}(in plane) bands at 1502 and 1231 cm^{-1}, respectively. For the metal complexes of the dibenzamido ion these last two bands are replaced by a single band in the region 1341–1362 cm^{-1}, which most likely is primarily ν_{CNC}(asym) in character. Other evidence in support of this last assignment is obtained from the spectrum of N-deuteriodibenzamide in which a band assigned to ν_{CNC}(asym) is observed at 1346 cm^{-1}, as coupling between ν_{CNC}(asym) and δ_{ND}(in plane) is much less than in the NH compound. The two strong carbonyl stretching bands of dibenzamide are shifted markedly from 1708 and 1681 cm^{-1} to the regions 1518–1542 and 1399–1410 cm^{-1} upon complexation. Essentially all other bands in the spectra above 650 cm^{-1} can be assigned to vibrations of the benzene rings and may be found in the spectrum of free dibenzamide. The one major exception in this last regard is the strong band at 825 cm^{-1} observed for $Be(dba)_2$. This band may be assigned to Be–O stretching and corresponds well to a band seen at 824 cm^{-1} in the spectrum of $Be(acac)_2$.[10] The conclusions based on

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(9) Although no structural proof is available, dibenzamide probably exists in the *trans,trans* form. This is suggested from Uno and Machida's observation that for acyclic imides RCONHCOR, when R is an alkyl group larger than CH_3, the *trans,trans* configuraton appears to be the exclusive form: T. Uno and K. Machida, *Bull. Chem. Soc. Japan*, **34**, 551 (1961).

(10) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

these observations are (1) that dba is attached in a similar manner to each of the metal ions listed above and (2) that the most likely mode of attachment is chelation through the ligand oxygen atoms.

The infrared spectrum of Hg(dba)$_2$ is unique among the spectra of the dibenzamido complexes. However, no unequivocal assignment for the mode of attachment of dba to Hg(II) can be made. The strong carbonyl stretching band near 1634 cm^{-1} does suggest that at least one carbonyl group per ligand is not attached tightly, if attached at all, to the mercury ion. Two strong bands at 1272 and 1290 cm^{-1} which may arise from CO and CN stretching also differentiate Hg(dba)$_2$ from the other dba complexes.

The infrared spectra of β-diketone complexes of Hg(II) also contain higher energy stretching bands than are observed for β-diketonato–metal complexes in which only simple chelation is present. For example, Hammond, Nonhebel, and Wu[11] observed a strong carbonyl band centered near 1665 cm^{-1} in the spectrum of bis(dipivaloylmethano)mercury(II).

Electronic Spectra.—The electronic spectra of the new compounds studied in this work are presented in Figures 1–3. A major conclusion of our earlier study[1] of the electronic spectra of Cr(daa)$_3$, Cr(aca)$_3$, Cr(dba)$_3$, and Cr(dbm)$_3$ was that the ligand field splitting parameter of a diamido anion was only slightly greater than that of its isoelectronic and isostructural β-diketonato analog. Furthermore, the difference between the Dq values for these two types of ligands with Cr(III) was not nearly as large as expected on the basis of strong π interaction of the metal orbitals with the π levels of the ligand. In this work, we note that toward Cu(II), dba is likewise only a slightly stronger field ligand than is dbm. The d → d transitions for Cu(dba)$_2$ are centered at 15,580 and 19,230 cm^{-1} while for Cu(dbm)$_2$ the corresponding transitions appear near 15,220 and 18,450 cm^{-1}.

Although the strong ultraviolet transitions for Fe(dbm)$_3$ and Fe(dba)$_3$ do interfere with precise positioning of the very weak spin-disallowed d → d transitions for these complexes, the center of the first band for Fe(dba)$_3$ can be placed at 13,800 cm^{-1} while for Fe(dbm)$_3$ the first band has a maximum near 12,800 cm^{-1}. Examination of the Tanabe–Sugano diagram for a d^5 ion reveals that the lowest energy transition expected for Fe(III) in a weak octahedral field, an obvious approximation for these complexes, should be the $^6A_{1g} \rightarrow {}^4T_{1g}$ transition and that the energy of this transition decreases with increasing ligand field strength. Thus, toward Fe(III) dbm is a stronger field ligand than dba. This apparent reversal of trend is not unusual for ligands with similar Dq values. For example, the data tabulated by Jørgensen[12] show that for several oxygen-donor ligands the order of Dq values

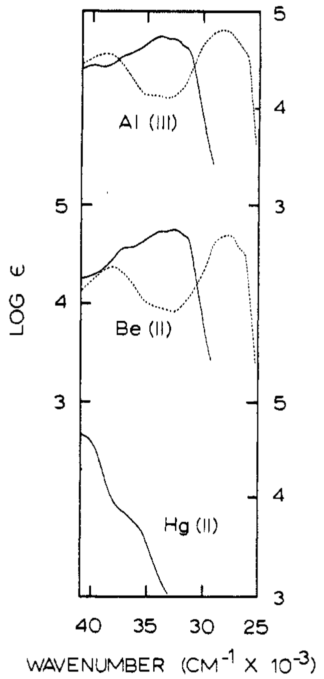

Figure 1.—Ultraviolet spectra of M(dba)$_n$ (——) and M(dbm)$_n$ (- - -) complexes in chloroform.

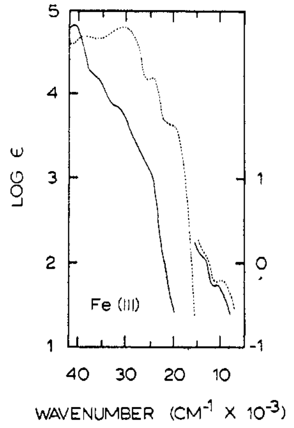

Figure 2.—Electronic spectra of Fe(dba)$_3$ (———) and Fe(dbm)$_3$ (- - -) in chloroform. Right-hand scale is for right-hand curves.

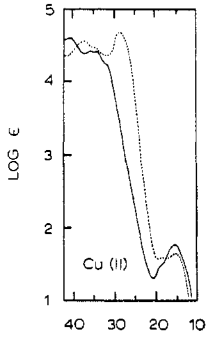

Figure 3.—Electronic spectra of Cu(dba)$_2$ (——) and Cu(dbm)$_2$ (- - -) in chloroform.

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[11] G. S. Hammond, D. C. Nonhebel, and C. S. Wu, *Inorg. Chem.*, **2**, 73 (1963).

[12] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Reading, Mass., 1962, p 110.

is $mal^{2-} = ox^{2-} > H_2O >$ urea for Cr(III) and $H_2O > mal^{2-} > ox^{2-} >$ urea for Fe(III).

Although unequivocal assignments for the ultraviolet transitions observed for the dba and dbm complexes cannot be made, there are two striking features of these spectra which may be noted. First, in each case where a comparison has been made, the lowest energy bands of high intensity for the dba complex of a particular metal are 5000–6000 cm^{-1} higher in energy than the lowest energy, high-intensity bands for the dbm complex. Second, the band profiles for the Be(II), Al(III), and Cr(III) complexes of dba, or dbm for that matter, are quite similar with less than a factor of 10 difference in the extinction of the bands. Thus, a reasonable assumption to make is that the nature of the transitions giving rise to the group of lowest energy ultraviolet bands must be the same in the complexes of these three metal ions and possibly in Cu(II) as well. Inasmuch as charge-transfer bands involving metal orbitals are not expected for the Be(II) complex, the observed spectrum should be composed only of intraligand transitions. If the similarity of the spectrum of the "tetrahedral" Be(II) complex to the spectra of the "octahedral" Al(III) and Cr(III) complexes is real and not just coincidental, then the tentative conclusion may be drawn that the ultraviolet spectra of these complexes all consist of primarily intraligand transitions.

The spectra of $Fe(dba)_3$ and $Fe(dbm)_3$ are in general similar in both profile and extinction to each other. Although each spectrum is more complicated than the spectra of the complexes of the other metals, the $Fe(dba)_3$ spectrum does follow the trend noted with the other dba complexes as the lowest energy, high-intensity bands are shifted some 6000 cm^{-1} or more to higher energy compared to the dbm complexes. Whereas the ground-state configuration of Fe(III) in these two complexes is basically $t_{2g}{}^3e_g{}^2$, $e_g \rightarrow \pi^*$ transitions are possible and may account for some of the lower energy bands not observed in the complexes of Be(II), Al(III), or Cr(III). However, a more definitive consideration of the nature of these bands is tentative at best until other complexes in the diamido class which do not contain groups, such as the benzene ring, that contribute to absorption in the ultraviolet region are available for study.

The ultraviolet spectrum of $Hg(dba)_2$ is quite different from that of any of the other dba complexes and offers support to the earlier suggestion that the ligand is not attached to Hg(II) in a normal chelated manner. In addition to the possibility of O–Hg bonds, there may be N–Hg bonds in $Hg(dba)_2$. However, no structural assignment of this compound in the solid state or in solution may be made at this time.

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Mass Spectral Studies of Metal Chelates. III.[1] Mass Spectra and Appearance Potentials of Substituted Acetylacetonates of Trivalent Chromium. Comparison with Other Trivalent Metals of the First Transition Series

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The appearance potentials of some substituted acetylacetonates of chromium are: $Cr(acac)_3$, 8.11 V; $Cr(Iacac)_3$, 8.03 V; $Cr(Bracac)_3$, 8.05 V; $Cr(Clacac))_3$, 8.21 V; $Cr(NO_2acac)_3$, 8.63 V; $Cr(tfacac)_3$, 9.09 V; $Cr(hfacac)_3$, 10.13 V; $Cr(CH_3acac)_3$, 7.81 V. The values seem to be consistent with the ionization of an electron from the π system of the chelate ring. The mass spectra of these chelates are compared with previously reported mass spectra of $Ti(acac)_3$, $V(acac)_3$, $Cr(acac)_3$, $Mn(acac)_3$, $Fe(acac)_3$, and $Co(acac)_3$, and mechanisms of decomposition are discussed.

In the previous paper[1] in this series, the mass spectra and appearance potentials of the acetylacetonates of trivalent metals of the first transition series were reported (*i.e.*, the acetylacetonates of Ti, V, Cr, Mn, Fe, and Co). The trends in the mass spectra were briefly rationalized using the established chemistry of the metals, while it was shown that the measured appearance potentials did not correlate with the simplified theoretical calculations of Barnum,[2] assuming that the electron was removed from the highest occupied molecular orbital in all cases.

MacDonald and Shannon[3] postulated valency changes in the metal to account for the observed mass spectra

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[1] Part II: *Inorg. Chem.*, **7**, 870 (1968).

[2] D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); **22**, 183 (1961).

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