complex support this formulation. The infrared spectrum exhibits bands at 2022 and 1790 cm^{-1} from the ν(CO) and ν(NO) frequencies, respectively, of the $[C_5H_5Mn(CO)(NO)L][PF_6]$ portion of VII and a band at 1742 cm^{-1} from the ν(NO) frequency of the $[C_5H_5Mn(NO)L_2][PF_6]$ portion of VII. The proton nmr spectrum of VII exhibits resonances arising from nonequivalent π-cyclopentadienyl protons; the reasons for the additional complexities in this region are not clear. Recently, Behrens and Brandl have reported a related compound $(C_5H_5)_2V_2(CO)_5$(triphos) (VIII) which they prepared from the tritertiary phosphine and $C_5H_5V(CO)_4$.[18]

The proton nmr spectra of the new compounds prepared in this work (Table III) exhibited several features of interest. The phenyl region in the nmr spectra of the monodentate monometallic derivatives of any of the ditertiary phosphines Pf—Pf, tPf=Pf, or Pf≡Pf had an extra line toward the upper portion of this region as compared with the corresponding spectra of the more symmetrical bidentate bimetallic derivative of the same ligand. This suggests a partial ability to separate coordinated and noncoordinated diphenylphosphino groups in the nmr spectra of these complexes. The chemical shifts of the π-cyclopentadienyl nmr resonances increase upon increasing substitution of carbonyl groups with the more weakly π-accepting tertiary phosphines thereby parallelling decreases in the ν(CO) and ν(NO) infrared frequencies in a manner similar to that reported for neutral cyclopentadienylmetal carbonyl derivatives of the first-row transition metals.[19] The π-cyclopentadienyl resonances of the tertiary phosphine derivatives generally exhibited the characteristic splitting ($J_{PH} \approx 2$ cps) into doublets or triplets consistent with the number of phosphorus atoms coordinated to the manganese atom.

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-1435-68. We also thank M and T Chemicals, Inc., for supplying generous research samples of triphenylarsine and triphenylstibine.

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Dipole Moments and Electric Field Effects on the Proton Chemical Shifts of Halo(acetylacetonato) Complexes of Group IV Metals[1]

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Received April 30, 1969

Dipole moments for several dihalobis(acetylacetonato) complexes of tin, titanium, zirconium, and hafnium (6.19–8.15 D) and halotris(acetylacetonato) complexes of zirconium and hafnium (4.90–6.07 D) have been measured in dilute benzene solution at 25.0°. The results strongly support a *cis*-octahedral structure for the $M(acac)_2X_2$ complexes and are consistent with a seven-coordinate structure for the $M(acac)_3X$ compounds. Low-field shifts, $\Delta\sigma$, of the $-CH=$ and $-CH_3$ proton resonances of the $M(acac)_2X_2$ complexes have been computed from the dipole moments on the basis of an electric field model. Calculated and observed values of $\Delta\sigma$ are in good agreement for the $-CH_3$ protons and for the $-CH=$ proton of the tin complexes, but when M = Ti, Zr, or Hf, only ~50–60% of the observed $\Delta\sigma$ for the $-CH=$ proton can be accounted for by electric field effects. The discrepancy in the case of the transition metal compounds may be due to metal–ligand π bonding.

Introduction

The stereochemistry of dihalobis(acetylacetonato) complexes of group IV metals, $M(acac)_2X_2$, has been the subject of a number of recent papers.[3–18] Although Kawasaki and co-workers have proposed for the dichloro-, dibromo-, and diiodotin complexes a distorted *trans* structure containing somewhat localized double bonds within the chelate rings,[3–5] nmr,[6–8] infrared,[8–10] Raman,[8] and dipole moment[11–13] results overwhelmingly support a *cis*-octahedral structure. Spectroscopic evidence also points to a *cis* structure for the analogous titanium,[9,14–16] zirconium,[17,18] and hafnium[17,18] complexes, but this has not yet been confirmed by dipole moment studies.

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[1] Presented before the Division of Inorganic Chemistry, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

[2] National Research Council of Canada predoctoral fellow, 1966–1968.

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Smith and Wilkins[7] have pointed out that the proton resonances of $Sn(acac)_2X_2$ complexes are shifted to low field relative to the resonances of symmetrical $M(acac)_n$ complexes. They have suggested that the low-field shifts are due to an intramolecular electric field which arises from the molecular dipole moment of the highly polar *cis* isomers. Even larger low-field shifts have been reported for the corresponding titanium,[16] zirconium,[17] and hafnium[17] compounds.

It seemed desirable, therefore, to measure the dipole moments of the known $M(acac)_2X_2$ complexes in order first to confirm the *cis* stereochemistry and second to test the electric field model by calculating the proton chemical shifts due to the intramolecular electric field. Also reported in this paper are dipole moments for some seven-coordinate halotris(acetylacetonato) complexes of zirconium and hafnium.[17,18]

Experimental Section

Materials.—Thiophene-free reagent grade benzene (Mallinckrodt) and Spectroquality reagent grade cyclohexane and carbon tetrachloride (Matheson Coleman and Bell) were dried by refluxing over calcium hydride for 4–5 days and distilling therefrom collecting only the middle fraction. Nitrobenzene was purified by an abbreviation[16] of the procedure of Taylor and Kraus.[19] The dried solvents were stored under dry nitrogen and were subsequently handled in a dry nitrogen-filled glove bag.

Difluorobis(2,4-pentanedionato)tin(IV) (mp 226–227°) was prepared by reaction of 2,4-pentanedione with tin(IV) fluoride in dichloromethane.[20] Dibromobis(2,4-pentanedionato)germanium(IV) (mp 224° dec; lit.[21] mp 226°) was synthesized in tetrahydrofuran by reaction of 2,4-pentanedione with germanium(IV) bromide.[20] The other complexes were prepared by published procedures.[16,17,22,23]

Measurements.—Dielectric constants, refractive indices, and specific volumes of dilute benzene solutions of the complexes were determined at 25.0 ± 0.1°. Dielectric constants were measured using a Wissenschaftlich-Technische Werkstätten dipolemeter, Type DM 01, and a modified[24] measuring cell, Type DFL 1. The measuring condenser was calibrated with air, cyclohexane, carbon tetrachloride, and benzene. Refractive indices were determined at the sodium D line with a Bausch and Lomb dipping refractometer, which was calibrated with benzene.

Solutions were prepared in 50-ml volumetric flasks in a nitrogen-filled glove bag in order to exclude moisture and minimize hydrolysis. A flask was first transferred to a constant-temperature bath, and the specific volume of the solution was measured using the procedure of Scaife and Laubengayer.[25] The flask was then returned to the glove bag, and the solution was transferred to the dipolemeter cell and refractometer cup. After the cell and cup were connected to the dipolemeter and refractometer, respectively, 1 hr was allowed for temperature equilibrium, constant temperature being maintained with a constant-temperature circulating system. Ordinarily, the total elapsed time between preparation of the solutions and the dielectric constant and refractive index measurements was ~2 hr. A duplicate set of dielectric constant measurements on $Zr(acac)_2Cl_2$, one of the compounds most susceptible to hydrolysis, taken 20 min after preparation of the solutions yielded a value of α (18.98 ± 0.86) which agreed well with that obtained by the usual, more lengthy procedure (19.44 ± 0.72).

Calculations.—Total molar polarizations of solutes, ${}_{\mathrm{T}}P_2$, were obtained from the Halverstadt–Kumler equation[26]

$$ {}_{\mathrm{T}}P_2 = \frac{3\alpha v_1 M_2}{(\epsilon_1 + 2)^2} + (v_1 + \beta)\frac{(\epsilon_1 - 1)M_2}{\epsilon_1 + 2} \qquad (1) $$

where ϵ_1 and v_1 denote the dielectric constant and specific volume of the solvent (2.2727[27] and 1.1449 cm³ g⁻¹,[28] respectively), α and β, respectively, denote the slopes of linear plots of the dielectric constant, ϵ_{12}, and specific volume, v_{12}, of the solution *vs.* weight fraction of the solute, w_2, and M_2 denotes the molecular weight of the solute. Electronic molar polarizations of solutes, ${}_{\mathrm{E}}P_2$, were calculated from the expression[29]

$$ {}_{\mathrm{E}}P_2 = \frac{6n_1\gamma v_1 M_2}{(n_1{}^2 + 2)^2} + (v_1 + \beta)\frac{(n_1{}^2 - 1)M_2}{n_1{}^2 + 2} \qquad (2) $$

where n_1 is the refractive index of the solvent (1.49794[30]) and γ is the slope of a linear plot of the refractive index of the solution, n_{12}, *vs.* weight fraction of the solute. Orientation molar polarizations, ${}_{\mathrm{O}}P_2$, were obtained using the relation ${}_{\mathrm{O}}P_2 = {}_{\mathrm{T}}P_2 - {}_{\mathrm{E}}P_2 - {}_{\mathrm{A}}P_2$, where ${}_{\mathrm{A}}P_2$ represents an assumed value for the atomic molar polarization. Dipole moments were calculated from the equation

$$ u = \frac{3}{2}\left[\frac{kT}{\pi N}{}_{\mathrm{O}}P_2\right]^{1/2} \qquad (3) $$

where the sumbols k, T, and N have their usual meaning.

The dipole moment of nitrobenzene in dilute benzene solution was determined as a check on the experimental method. Results were in good agreement with literature values: ${}_{\mathrm{T}}P_2 = 385 \pm 28$ cm³; ${}_{\mathrm{E}}P_2 = 32 \pm 3$ cm³, lit.[31] 32.59 cm³; taking[31] ${}_{\mathrm{A}}P_2 = 3.26$ cm³, ${}_{\mathrm{O}}P_2 = 350 \pm 27$ cm³ and $\mu = 4.14 \pm 0.16$ D; lit.[31] 3.85–4.11 D.

Results and Discussion

Dipole Moments.—Dielectric constant, specific volume, and refractive index data as a function of weight fraction are presented in Table I along with derived values of the respective slopes α, β, and γ. Slopes were determined by least-squares analysis, and errors are estimated at the 95% confidence level.

Molar polarizations, ${}_{\mathrm{T}}P_2$, ${}_{\mathrm{E}}P_2$, and ${}_{\mathrm{O}}P_2$, and dipole moments are presented in Table II. Two sets of orientation polarizations and dipole moments are given because values of the atomic polarization are unknown. Most workers have held that metal acetylacetonates possess remarkably large atomic polarizations, amounting to ~50% of the electronic polarizations.[22] Recently, however, Nelson and coworkers[33]

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TABLE I

DIELECTRIC CONSTANT, SPECIFIC VOLUME, AND REFRACTIVE INDEX DATA FOR HALO(ACETYLACETONATO) COMPLEXES IN BENZENE SOLUTION AT 25.0°

$w_2 \times 10^3$	ϵ_{12}	v_{12}	n_{12}
$Sn(acac)_2F_2$			
1.921	2.2928	1.1439	1.49795
3.124	2.3078	1.1433	1.49810
5.296	2.3341	1.1420	1.49803
6.799	2.3516	1.1414	1.29810
9.762	2.3859	1.1386	1.49839
	$\alpha = 11.86 \pm 0.32$	$\beta = -0.66 \pm 0.19$	$\gamma = 0.05 \pm 0.05$
$Sn(acac)_2Cl_2$			
0.865	2.2947	1.1453	1.49835
1.728	2.2990	1.1452	1.49828
2.699	2.3154	1.1449	1.49831
3.518	2.3247	1.1438	1.49849
4.786	2.3369	1.1427	1.49867
7.802	2.3743	1.1412	1.49882
10.566	2.4126	1.1401	1.49871
14.701	2.4659	1.1374	1.49914
	$\alpha = 12.52 \pm 0.55$	$\beta = -0.58 \pm 0.07$	$\gamma = 0.06 \pm 0.02$
$Sn(acac)_2Br_2$			
7.193	2.3504	1.1413	-----
8.340	2.3635	1.1406	-----
10.622	2.3873	1.1394	-----
12.380	2.4091	1.1384	-----
13.295	2.4185	1.1380	-----
3.006	----	----	1.49785
4.872	----	----	1.49806
5.289	----	----	1.49817
7.243	----	----	1.49817
10.794	----	----	1.49831
12.479	----	----	1.49835
	$\alpha = 11.18 \pm 0.57$	$\beta = -0.54 \pm 0.03$	$\gamma = 0.05 \pm 0.03$
$Sn(acac)_2I_2$			
7.770	2.3320	1.1378	1.49828
10.827	2.3553	1.1366	1.49882
12.747	2.3710	1.1364	1.49885
19.177	2.4208	1.1320	1.49943
24.361	2.4608	1.1286	1.49993
	$\alpha = 7.77 \pm 0.08$	$\beta = -0.57 \pm 0.15$	$\gamma = 0.09 \pm 0.03$
$Ti(acac)_2F_2$			
4.014	2.3396	1.1444	1.49857
5.749	2.3688	1.1439	1.49864
9.327	2.4277	1.1420	1.49885
10.580	2.4464	1.1410	1.49907
11.266	2.4636	1.1413	------
14.449	2.5089	1.1398	1.49936
	$\alpha = 16.36 \pm 0.87$	$\beta = -0.46 \pm 0.09$	$\gamma = 0.08 \pm 0.02$
$Ti(acac)_2Cl_2$			
3.560	2.3426	1.1450	1.49857
6.144	2.3891	1.1437	1.49882
6.432	2.3980	1.1437	1.49871
7.970	2.4251	1.1430	1.49896
10.006	2.4606	1.1420	1.49921
	$\alpha = 18.37 \pm 1.14$	$\beta = -0.46 \pm 0.04$	$\gamma = 0.10 \pm 0.05$
$Ti(acac)_2Br_2$			
2.755	2.3120	1.1445	-----
2.967	2.3144	1.1447	1.49864
4.468	2.3328	1.1437	1.49864
4.935	2.3420	1.1430	1.49860
6.813	2.3662	1.1417	1.49889
7.253	2.3695	1.1412	-----
7.952	2.3799	1.1415	1.49900
	$\alpha = 13.10 \pm 0.64$	$\beta = -0.69 \pm 0.15$	$\gamma = 0.08 \pm 0.07$
$Zr(acac)_2Cl_2$			
3.602	2.3401	1.1440	1.49803
7.864	2.4204	1.1419	1.49839
11.399	2.4873	1.1407	1.49882
15.284	2.5639	1.1386	1.49914
17.933	2.6196	1.1375	1.49921
	$\alpha = 19.44 \pm 0.72$	$\beta = -0.45 \pm 0.05$	$\gamma = 0.09 \pm 0.02$
$Zr(acac)_2Br_2$			
1.405	2.2941	1.1437	1.49806
1.896	2.3023	1.1434	1.49821
2.887	2.3140	----	1.49831
4.158	2.3418	1.1422	1.49857
5.878	2.3649	----	1.49835
6.403	2.3743	1.1397	1.49853
9.533	2.4262	1.1384	1.49878
	$\alpha = 16.27 \pm 0.87$	$\beta = -0.68 \pm 0.20$	$\gamma = 0.08 \pm 0.04$
$Hf(acac)_2Cl_2$			
1.582	2.3004	1.1449	1.49806
3.255	2.3203	1.1441	1.49810
5.109	2.3525	1.1421	1.49835
6.852	2.3781	1.1419	1.49842
11.913	2.4501	1.1381	1.49867
	$\alpha = 14.67 \pm 0.99$	$\beta = -0.66 \pm 0.16$	$\gamma = 0.06 \pm 0.02$
$Hf(acac)_2Br_2$			
0.653	2.2831	1.1447	1.49792
1.041	2.2904	1.1447	1.49813
1.668	2.2978	1.1434	-----
2.146	2.3104	1.1435	1.49817
3.006	2.3179	1.1428	1.49803
5.111	2.3475	1.1418	1.49821
9.228	2.3955	1.1383	1.49857
	$\alpha = 13.00 \pm 1.13$	$\beta = -0.73 \pm 0.12$	$\gamma = 0.06 \pm 0.04$
$Zr(acac)_3Cl$			
2.783	2.2927	1.1442	1.49810
4.827	2.3078	----	1.49835
5.524	2.3130	1.1426	1.49842
7.609	2.3281	1.1413	1.49853
10.233	2.3483	1.1398	1.49867
	$\alpha = 7.45 \pm 0.14$	$\beta = -0.59 \pm 0.03$	$\gamma = 0.07 \pm 0.03$
$Zr(acac)_3Br$			
1.961	2.2856	1.1443	1.49806
2.753	2.2909	1.1431	1.49817
3.243	2.2946	1.1423	1.49798
5.230	2.3114	1.1429	1.49821
5.651	----	1.1422	1.49806
6.703	2.3197	1.1416	------
8.301	2.3322	1.1403	1.49846
	$\alpha = 7.38 \pm 0.51$	$\beta = -0.49 \pm 0.27$	$\gamma = 0.06 \pm 0.06$
$Zr(acac)_3I$			
0.810	---	1.1439	---
0.930	---	1.1441	1.49846
2.054	2.2968	1.1428	----
2.574	2.2996	1.1433	1.49860
3.552	2.3082	1.1426	1.49864
4.796	2.3146	---	----
5.156	2.3171	1.1424	1.49864
7.575	2.3394	1.1405	----
9.570	2.3559	1.1392	1.49893
	$\alpha = 7.91 \pm 0.73$	$\beta = -0.52 \pm 0.11$	$\gamma = 0.05 \pm 0.02$
$Hf(acac)_3Cl$			
4.576	2.2995	1.1423	1.49803
5.761	2.3034	1.1411	1.49828
6.894	2.3105	1.1410	1.49860
9.941	2.3270	1.1396	1.49867
12.751	2.3423	1.1379	1.49882
	$\alpha = 5.35 \pm 0.48$	$\beta = -0.50 \pm 0.14$	$\gamma = 0.09 \pm 0.08$
$Hf(acac)_3Br$			
2.031	2.2860	1.1436	1.49814
2.224	2.2860	1.1436	1.49810
3.986	-----	1.1427	1.49828
5.807	2.3066	1.1417	1.49853
6.618	2.3117	1.1407	1.49846
	$\alpha = 5.67 \pm 0.63$	$\beta = -0.60 \pm 0.18$	$\gamma = 0.09 \pm 0.05$

have reported that the group dipole moments of the metal–acetylacetonate rings in certain thallium, indium, and tin acetylacetonates are less than 2 D, and they have concluded that, in view of the small values of the metal–acetylacetonate group moments, it is highly unlikely that these complexes can exhibit large values of the atomic polarization. Since the atomic polarization of metal diketonates remains a matter of some controversy, we have calculated the orientation polarizations and dipole moments on the assumption that $_AP_2 = 0.5\,_EP_2$ (columns 4 and 5 of Table II) and also on the assumption that $_AP_2 = 0$ (columns 6 and 7 of Table II). Ignoring $_AP_2$ increases the calculated dipole moments by 0.1–0.3 D; however these increases are generally less than experimental error.

The 95% confidence level estimates of error in α (Table I) are ~6%. Although per cent errors in β and γ, hence, in $_EP_2$ (Table II), are considerably larger, these errors have only a small effect on the dipole moments. In most cases the error in α accounts for more than 95% of the error in the dipole moment.

The observed moments for the dihalo complexes are large (6–8 D) and strongly support a *cis*-octahedral structure. Our results for the dihalo tin compounds are in good agreement with the results of Nelson[12] and Doron,[13] although we find a slightly larger value for the

Table II

Molar Polarizations and Dipole Moments of Halo(acetylacetonato) Complexes in Benzene Solution at 25.0°

			${}_{A}P_2 = 0.5{}_{E}P_2$		${}_{A}P_2 = 0$	
Compound	${}_{T}P_2$, cm³	${}_{E}P_2$, cm³	${}_{O}P_2$, cm³	μ, D	${}_{O}P_2$, cm³	μ, D
$Sn(acac)_2F_2$	843 ± 29[a]	60 ± 22[a]	753 ± 27[a]	6.07 ± 0.11[a]	783 ± 23[a]	6.19 ± 0.09[a]
$Sn(acac)_2Cl_2$	979[b] ± 41	77[c] ± 9	863 ± 41	6.50[d] ± 0.15	902 ± 40	6.65[e] ± 0.15
$Sn(acac)_2Br_2$	1089 ± 51	97 ± 9	943 ± 52	6.80 ± 0.19	992 ± 52	6.97[f] ± 0.18
$Sn(acac)_2I_2$	932 ± 27	127 + 26	742 ± 19	6.03 ± 0.08	805 ± 12	6.28[g] ± 0.05
$Ti(acac)_2F_2$	932 ± 47	70 ± 8	828 ± 47	6.36 ± 0.18	863 ± 47	6.50 ± 0.18
$Ti(acac)_2Cl_2$	1160 ± 68	82 ± 10	1038 ± 69	7.13 ± 0.24	1079 ± 68	7.27 ± 0.23
$Ti(acac)_2Br_2$	1055 ± 52	73 ± 24	946 ± 56	6.80 ± 0.20	982 ± 52	6.94 ± 0.18
$Zr(acac)_2Cl_2$	1392 ± 49	91 ± 7	1255 ± 49	7.84 ± 0.15	1300 ± 49	7.98 ± 0.15
$Zr(acac)_2Br_2$	1437 ± 78	81 ± 29	1317 ± 77	8.03 ± 0.23	1357 ± 74	8.15 ± 0.22
$Hf(acac)_2Cl_2$	1300 ± 86	79 ± 22	1181 ± 85	7.60 ± 0.27	1221 ± 84	7.73 ± 0.26
$Hf(acac)_2Br_2$	1378 ± 116	85 ± 23	1252 ± 116	7.83 ± 0.36	1294 ± 115	7.96 ± 0.35
$Zr(acac)_3Cl$	664 ± 12	87 ± 9	534 ± 16	5.11 ± 0.08	578 ± 13	5.32 ± 0.06
$Zr(acac)_3Br$	742 ± 59	105 ± 41	584 ± 55	5.35 ± 0.25	637 ± 48	5.58 ± 0.21
$Zr(acac)_3I$	863 ± 73	109 ± 18	699 ± 72	5.85 ± 0.30	754 ± 71	6.07 ± 0.29
$Hf(acac)_3Cl$	613 ± 51	122 ± 31	430 ± 58	4.59 ± 0.31	491 ± 51	4.90 ± 0.26
$Hf(acac)_3Br$	683 ± 72	117 ± 33	508 ± 71	4.99 ± 0.35	566 ± 68	5.27 ± 0.31

[a] Errors are estimated at the 95% confidence level. [b] Literature value[11] 1709 cm³. [c] Literature value[11] 71.2 cm³. [d] Literature value[11] 8.8 D; but see footnote 34. [e] Literature value[12] 6.77 D. [f] Literature value[12] 6.61 D. [g] Literature value[12] 6.25 D.

moment of $Sn(acac)_2Br_2$. Our moment for $Sn(acac)_2Cl_2$, 6.50 D on the assumption that ${}_{A}P_2 = 0.5{}_{E}P_2$, does not agree with the value of 8.8 D published by Cox, *et al.*[11,34]

For $Ge(acac)_2Br_2$ in benzene solution we have obtained an approximate dipole moment of 5.8 ± 0.8 D; the precision of this measurement is poor because of the low solubility of $Ge(acac)_2Br_2$ in benzene. Osipov, *et al.*,[36] have reported a value of 7.4 D for the moment of $Ge(acac)_2Cl_2$ in chloroform. Thus it appears that the dihalobis(acetylacetonato)germanium compounds also adopt a *cis* configuration in solution.[37]

Moments of the $M(acac)_2X_2$ complexes decrease as the halogen varies in the order Br $\sim$ Cl $>$ F $\sim$ I. These variations do not parallel the electronegativity of the halogens, and they are much smaller than might have been expected on the basis of electronegativity differences alone. For compounds having the same halogen, the moments generally increase as the metal varies in the order Ge $<$ Sn $<$ Ti $<$ Hf $\lesssim$ Zr.

Observed moments for the halotris(acetylacetonato) complexes are in the range expected for seven-coordinate $M(acac)_3X$ structures and result primarily from the metal–halogen bond moment. Assuming that the Zr(acac) and Hf(acac) group moments are approximately 1.7 D, the value found for the Sn(acac) group moment,[33b] with the metal at the negative end of the dipole, it is possible to estimate the Zr–X and Hf–X bond moments from the molecular moments of the dihalo complexes. The values of $\mu_{M-X} = [\mu_{M(acac)_2X_2} - \mu_{Macac}]/\sqrt{2}$ fall in the range 4.3–4.6 D. The contribution of the Macac group moments to the molecular moment of the $M(acac)_3X$ complexes is expected to be greater than zero but less than 1.7 D since there should be more effective cancellation of Macac group moments in reasonable seven-coordinate structures than in a *cis*-octahedral structure. Therefore, molecular moments for the seven-coordinate compounds should lie in the range ~5–6 D, in excellent agreement with the observed results (Table II).

Electric Field Effects on Proton Chemical Shifts.—Smith and Wilkins[7] have suggested that the low-field shifts of the proton resonances of polar metal acetylacetonates can be ascribed to the intramolecular electric field which arises from the molecular dipole moment. Since we now have in hand dipole moments for 11 *cis*-$M(acac)_2X_2$ complexes, the electric field model can be tested for a substantial number of complexes of this type.

The electric field due to the dipole moment was calculated by the procedure given in the Appendix, and the resulting chemical shift $\Delta\sigma$ was computed from the relation[39,40]

$$\Delta\sigma = -2.9 \times 10^{-12}E_{C-H} - 7.38 \times 10^{-19}E^2 \quad (4)$$

where E_{C-H} is the component of the electric field along the C–H bond, and E is the absolute magnitude of the electric field, both evaluated at the proton. The "reaction field," the additional electric field which arises from polarization of the solvent, and the associated $\Delta\sigma$ were calculated as described by Buckingham.[39,41]

The "electric field" and "reaction field" contributions to $\Delta\sigma$ in chloroform solution are presented in Table III wherein the calculated and observed values of

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(34) The moment of Cox, *et al.*, is based on an experimentally determined value for the dielectric constant of benzene of 1.8146.[35] This value is much lower than the literature value of 2.2727,[27] and because α was determined by extrapolating a plot of $(\epsilon_{12} - \epsilon_1)/w_2$ *vs.* w_2 to infinite dilution,[11] large errors in α and the dipole moment result. If α is determined from the slope of a plot of the $\Delta\epsilon$ data of Cox, *et al.*, *vs.* w_2, one obtains an α of 11.41 and a dipole moment of 6.2 D.

(35) M. Cox, private communication, Aug 1967.

(36) O. A. Osipov, V. L. Shelepina, and O. E. Shelepin, *J. Gen. Chem. USSR*, **36**, 274 (1966).

(37) The dipole moment of $Ge(acac)_2Cl_2$ was interpreted[36] in terms of a $[Ge(acac)_2Cl]^+Cl^-$ ion pair. However, this structure may be eliminated because $Ge(acac)_2Cl_2$ is a nonelectrolyte in ionizing solvents.[38] The *cis*-octahedral structure is also indicated by nmr results.[7]

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(41) In this calculation the radius of the molecule was taken as 6.1 Å, the average distance from the metal atom to the methyl protons plus the van der Waals radius of hydrogen.

TABLE III

COMPARISON OF CALCULATED AND OBSERVED CHEMICAL SHIFTS FOR $M(acac)_2X_2$ COMPLEXES IN CHLOROFORM SOLUTION[a]

	Electric field		Reaction field		Calcd $\Delta\sigma$ total		Obsd $\Delta\sigma$		
Compound	–CH=	–CH_3	–CH=	–CH_3	–CH=	–CH_3	–CH=	–CH_3	Ref
$Sn(acac)_2F_2$	−0.19	−0.08	−0.04	−0.01	−0.23	−0.09	−0.25	−0.16	20
$Sn(acac)_2Cl_2$	−0.21	−0.09	−0.04	−0.01	−0.25	−0.10	−0.24	−0.14[b]	7
$Sn(acac)_2Br_2$	−0.22	−0.10	−0.05	−0.01	−0.27	−0.11	−0.25	−0.13[b]	7
$Sn(acac)_2I_2$	−0.19	−0.09	−0.04	−0.01	−0.23	−0.10	−0.29	−0.10[b]	7
$Ti(acac)_2F_2$	−0.21	−0.10	−0.04	−0.01	−0.25	−0.11	−0.40	−0.08	16
$Ti(acac)_2Cl_2$	−0.24	−0.11	−0.05	−0.01	−0.29	−0.12	−0.53	−0.14	16
$Ti(acac)_2Br_2$	−0.23	−0.10	−0.05	−0.01	−0.28	−0.11	−0.54	−0.13	16
$Zr(acac)_2Cl_2$	−0.23	−0.10	−0.05	−0.01	−0.28	−0.11	−0.49	−0.12	17
$Zr(acac)_2Br_2$	−0.23	−0.11	−0.05	−0.01	−0.28	−0.12	−0.52	−0.13	17
$Hf(acac)_2Cl_2$	−0.22	−0.10	−0.05	−0.01	−0.27	−0.11	−0.45	−0.12	17
$Hf(acac)_2Br_2$	−0.23	−0.10	−0.05	−0.01	−0.28	−0.11	−0.47	−0.12	17

[a] Chemical shifts are in ppm. Observed $\Delta\sigma$ values for the tin and titanium complexes refer to $CDCl_3$ solutions. [b] Average $\Delta\sigma$ for the two methyl resonances. In all other cases only a single methyl resonance is observed at room temperature owing to a rapid rate process.

$\Delta\sigma$ are compared. Observed $\Delta\sigma$ values are expressed relative to the mean chemical shifts for 13 neutral, nonpolar $M(acac)_n$ complexes, *viz.*, −5.47 ± 0.08 ppm for the –CH= proton and −2.02 ± 0.09 ppm for the methyl protons.[42] It is apparent from Table III that the electric field contribution to the calculated $\Delta\sigma$ values is much more important than the reaction field contribution.

The electric-field model accounts for the sign of $\Delta\sigma$ and also for the fact that $\Delta\sigma$ is larger for the –CH= proton than for the methyl protons. Quantitatively, the agreement between the calculated and observed shifts is generally very satisfactory for the methyl protons and for the –CH= proton of the tin compounds. However, for the –CH= proton of the titanium, zirconium, and hafnium complexes, only ~50–60% of the observed low-field shift can be accounted for by electric field effects. The discrepancy may be due to acetylacetonate→metal $p\pi$–$d\pi$ bonding since only the transition elements have vacant d orbitals of principal quantum number one less than the principal quantum number of the valence shell. The possible importance of metal–ligand π bonding in titanium(IV) acetylacetonates has already been suggested[42] by the fact that the –CH= proton $\Delta\sigma$ is significantly larger for $Ti(acac)_3^+$ than for the nontransition element ions $Si(acac)_3^+$ and $Ge(acac)_3^+$.

Observed values of $\Delta\sigma$ for the $M(acac)_3X$ complexes of zirconium and hafnium are *ca.* −0.3 and −0.05 ppm for the –CH= and methyl protons, respectively.[17] These shifts are considerably smaller than those for the corresponding dihalides. Although the geometries of the seven-coordinate monohalo complexes are unknown, the smaller values of $\Delta\sigma$ appear to be consistent with their smaller dipole moments.

Finally, it should be noted that the $\Delta\sigma$ values of Table III could be interpreted *qualitatively* in terms of inductive effects. Indeed Kawasaki and coworkers[43] have suggested that the chemical shifts of organotin compounds of the type $M(acac)_2XX'$ (X, X′ = alkyl, aryl, or halogen) depend primarily on the inductive effects of the substituents X and X′. Although more data are required before the relative merits of the inductive (through bonds) and electric field (across space) models can be assessed, an obvious advantage of the electric field model is that it readily permits quantitative comparison of theory and experiment.

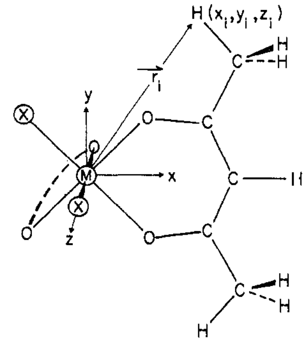
Acknowledgments.—The support of this research by National Science Foundation Grant GP-7851 is gratefully acknowledged. We also thank Professor W. H. Nelson for providing a preprint of ref 33b prior to publication.

Appendix

The electric field **E** at a point P due to a point dipole is given by[44]

$$\mathbf{E} = \nabla V = -\nabla \frac{\boldsymbol{\mu}\cdot\mathbf{r}}{r^3} \text{ (cgs units)} \qquad (5)$$

where V is the electrostatic potential at P, $\boldsymbol{\mu}$ is the dipole moment vector, and $\mathbf{r}$ is the position vector which extends from the dipole to the point P. It is convenient to locate the $M(acac)_2X_2$ complex in a right-handed coordinate system as shown below with the metal atom at the origin and one of the chelate rings in the xy plane. The dipole moment vector



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(42) R. C. Fay and N. Serpone, *J. Am. Chem. Soc.*, **90**, 5701 (1968).

(43) Y. Kawasaki, T. Tanaka, and R. Okawara, *Bull. Chem. Soc. Japan*, **40**, 1562 (1967).

(44) W. J. Duffin, "Electricity and Magnetism," McGraw-Hill Publishing Co. Ltd., London, 1965, pp 55, 87.

$$\boldsymbol{\mu} = \left(\frac{\mathbf{i}}{2} - \frac{\mathbf{j}}{2} - \frac{\mathbf{k}}{\sqrt{2}}\right)\mu \tag{6}$$

is assumed to be located at the metal atom; it bisects the X–M–X angle and points toward the positive end of the dipole. Consequently, the x, y, and z components of the electric field at the ith proton are given by

$$E_x = -\frac{\partial V}{\partial x} = \mu\left[-\frac{1}{2r_i^3} + \frac{3x_i(x_i - y_i - \sqrt{2}z_i)}{2r_i^5}\right] \tag{7}$$

$$E_y = -\frac{\partial V}{\partial y} = \mu\left[\frac{1}{2r_i^3} + \frac{3y_i(x_i - y_i - \sqrt{2}z_i)}{2r_i^5}\right] \tag{8}$$

$$E_z = -\frac{\partial V}{\partial z} = \mu\left[\frac{1}{\sqrt{2}r_i^3} + \frac{3z_i(x_i - y_i - \sqrt{2}x_i)}{2r_i^5}\right] \tag{9}$$

The component of **E** along the C–H bond, which determines the more important term in eq 4, is $E \cos \gamma$ where γ is the angle between **E** and the C–H bond direction, and E is simply $(E_x^2 + E_y^2 + E_z^2)^{1/2}$. For the ring proton these equations simplify since $x_i = r_i$ and $y_i = z_i = 0$; hence

$$E_{\mathrm{C-H}} = \frac{\mu}{r_i^3} \text{ and } E = \frac{\sqrt{7}\mu}{2r_i^3} \tag{10}$$

The coordinates used in the calculations are based on bond distances and bond angles given in a previous paper.[42] The geometry assumed for the Ti(acac)$_2$X$_2$ complexes is given in structure V of ref 42; that for the tin, zirconium, and hafnium compounds is shown in structure VI. Assumptions about the M–O bond distances and the orientation and restricted rotation of the methyl group are the same as in ref 42. The calculated $\Delta\sigma$ for the methyl protons was averaged over the six nonequivalent environments.

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Structural Analyses of Tetracobalt Dodecacarbonyl and Tetrarhodium Dodecacarbonyl. Crystallographic Treatments of a Disordered Structure and a Twinned Composite[1]

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Received March 6, 1969

A statistically disordered crystal structure and detailed molecular configuration of Co$_4$(CO)$_{12}$ have been unambiguously determined from a three-dimensional single-crystal X-ray photographic analysis. The compound crystallizes with four tetrameric molecules in an orthorhombic unit cell of symmetry Pccn and dimensions a = 8.99 (2) Å, b = 11.70 (2) Å, and c = 17.28 (4) Å. A three-dimensional X-ray photographic investigation of twinned apparent orthorhombic crystals of Rh$_4$(CO)$_{12}$ has also been completed. The successful analysis of the structure of Rh$_4$(CO)$_{12}$ was accomplished by the assumption of a simple twinning mechanism and the application of derived mathematical relations which made possible a breakdown of the observed F^2 data for the twin composite into the appropriate F coefficients for the single-crystal component. The results of the analysis conclusively showed (a) that the individual twin component contains four tetrameric molecular species in a centrosymmetric monoclinic unit cell of dimensions a = 9.24 (2) Å, b = 12.02 (2) Å, c = 17.74 (3) Å, and β = 90°, with symmetry P2$_1$/c, and (b) that the twinning mirror plane parallel to the unique b axis and perpendicular to either the a or c axis results in apparent orthorhombic D$_{2h}$-mmm Laue symmetry. Both structures solved by the heavy-atom technique (complicated in each case by the pseudomirror symmetries imposed by metal atom positions) were refined isotropically by full-matrix least squares to conventional discrepancy factors $R_1(F)$ = 0.126 for Co$_4$(CO)$_{12}$ and $R_1(F)$ = 0.096 for Rh$_4$(CO)$_{12}$, based on 529 and 962 nonzero observed photographic data, respectively. Despite the different ways in which these complexes crystallize, the molecular configurations of the two polynuclear metal carbonyls are strikingly similar and have idealized C$_{3v}$-3m symmetry. Each molecule consists of an apical M(CO)$_3$ group coordinated by the three metal–metal bonds to a basal M$_3$(CO)$_9$ fragment containing three chemically identical M(CO)$_2$ groups linked to each other by metal–metal bonds and bridging carbonyl groups. A detailed structural comparison of Co$_4$(CO)$_{12}$ and Rh$_4$(CO)$_{12}$ is given.

Introduction

During the course of stereochemical investigations of metal carbonyl complexes, the correct detailed molecular architecture of tetracobalt dodecacarbonyl has been the source of much speculation and controversy. The apparent contradictions that have arisen between theoretical considerations and experimental data for this compound are perhaps paralleled only by those surrounding triiron dodecacarbonyl.[3]

First synthesized in 1932 by thermal decomposition of Co$_2$(CO)$_8$, cobalt tricarbonyl was formulated as a tetramer by molecular weight determination in iron pentacarbonyl solution.[4] The infrared spectrum of this black compound, later investigated by Friedel,

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(1) Research jointly sponsored by the National Science Foundation (Grant GP-4919 to L. F. Dahl) at the University of Wisconsin, the National Institutes of Health, and the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) Biology Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.

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