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Determination of molar refractions and Abraham descriptors for tris(acetylacetonato)chromium(III), tris(acetylacetonato)iron(III) and tris(acetylacetonato)cobalt(III)†

Michael H. Abraham,* [a] William E. Acree Jr.,[b] Anthony F. Fucaloro[c] and Andrew W. Zanella*[c]

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We have determined molar refractions of tris(acetylacetonato)chromium(III), tris(acetylacetonato)iron(III) and tris(acetylacetonato)cobalt(III). Although the d-electron structures of the three metal centres differ significantly, the three molar refractions are actually quite close to each other. We then used these molar refractions to determine the Abraham *E*-descriptor, we calculated the *V*-descriptor by McGowan's method, and then used literature data on solubilities and water–solvent partitions to obtain the rest of the set of descriptors for the three tris(acetylacetonato) complexes. If we take *E* as the average of those for the chromium, iron and cobalt complexes, we can use limited literature data to obtain the full set of Abraham descriptors for the tris(acetylacetonates) of vanadium(III), yttrium(III), samarium(III), lanthanum(III) and neodymium(III). For the eight complexes, the descriptors vary regularly with complex molecular weight. These show that the complexes are quite polarizable, have zero hydrogen-bond acidity and significant hydrogen bond basicity. From the sets of Abraham descriptors, a very large number of physicochemical properties can be predicted for the eight acetonylacetonates.

Introduction

Methods are now available for the calculation or prediction of numerous physico-chemical properties of organic compounds. Water–octanol partition coefficients can easily be calculated through programs such as BioLoom,[1] the EPI Suite TM,[2] ACD ChemSketch,[3] the ACD Absolv suite[4] and SPARC.[5] Some of these programs[2,5] can be used to calculate numerous other physico-chemical properties. However, extension to compounds other than organic compounds is either very limited or non-existent. We have developed a system of properties or 'descriptors' of solute molecules, known as Abraham descriptors or Absolv descriptors.[6–13] These descriptors, together with a large set of equations we have constructed enables predictions to be made of all sorts of physicochemical, environmental and biological properties. Initially the system was applied to organic compounds and to a few simple inorganic compounds, but we have since applied it to organometallic compounds such mercury compounds[14] and the tetraphenyl derivatives of silicon, germanium, tin and lead.[15] Recently we showed that the system could include derivatives of ferrocene.[16] This suggests that we might be able to include inorganic complexes into our system. If so, this would mark a very significant extension of predictive methods into the vast area of inorganic complex chemistry. We start with the tris(acetylacetonato) complexes of chromium(III), cobalt(III) and iron(III) because there was a reasonable amount of data on the solubilities of these complexes that we could use. We refer to the complexes as $Cr(acac)_3$, $Co(acac)_3$ and $Fe(acac)_3$. One of the descriptors we need can be obtained from the refractive index or molar refractivity of a compound. No such data were available for the three tris(acetylacetonato) complexes, and so we decided to determine their molar refractions experimentally.

Experimental

Compounds

The three tris(acetylacetonato) complexes, were purchased from Sigma-Aldrich. The purity of the iron compound was ≥99.9%, while that of the chromium and cobalt was 99.99%.

Solutions

For each series of measurements, the pure solvent and ten solutions of the metal compound in 200 proof ethyl alcohol, ACS/USP grade, were used. The solutions ranged from 20 mg of

[a] *Department of Chemistry, University College London, 20 Gordon St, London WC1H 0AJ, UK. E-mail: m.h.abraham@ucl.ac.uk*
[b] *Department of Chemistry, 1155 Union Circle Drive #305070, University of North Texas, Denton, TX 76203-5017, USA. E-mail: bill.acree@unt.edu*
[c] *W. M. Keck Science Department, Claremont McKenna, Pitzer, and Scripps Colleges, 925 N. Mills Ave., Claremont, CA 91711, USA. E-mail: afucaloro@kecksci.claremont.edu, azanella@kecksci.claremont.edu*
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compound in 45 mL of solvent up to 200 mg, in 20 mg increments. The iron compound, a fine powder, dissolved readily and yielded a highly colored red solution. The chromium and cobalt compounds, in crystalline form, required sonication to completely dissolve the higher concentration solutions to give violet and green solutions, respectively.

Measurements

Density and refractive index were measured at 20.00 ± 0.01 °C with an Anton Paar DMA 4500 density meter mated to an Anton Paar RXA 170 refractometer through plastic tubing. The techniques, calibration, accuracy, and precision are given elsewhere.[17] The ranges for the density and refractive index are 0.79101 to 0.79639 kg L^{-1} and 1.36135 to 1.36290, respectively. These ranges fall well within the manufacturer's recommendations for the calibration methods used here. The system was calibrated before each series of measurements with deionized water at 20 °C. For each case a value of 0.99821 g mL^{-1} were measured and agree with the accepted value for water at 20 °C of 0.998206 g mL^{-1} (one additional significant figure).

Data treatment

Table 1 reports the mole fractions, densities, and refractive index values for the ethanolic solutions of the complexes.

Table 1 x_2, ρ(g cm^{-3}), n, V^M (cm^3 mol^{-1}), and R (cm^3 mol^{-1}) for ethanolic solutions of $M(acac)_3$ [M = Cr, Fe, and Co]

x_2	ρ	n	V^M	R
M = Cr				
7.63×10^{-5}	0.79119	1.36145	58.25799	12.90393
0.000152	0.79137	1.36154	58.27361	12.91027
0.000223	0.79151	1.36163	58.29077	12.91696
0.000299	0.79167	1.36171	58.30788	12.92332
0.0003755	0.79193	1.36180	58.31811	12.92847
0.0004413	0.79205	1.36187	58.33449	12.93435
0.0005191	0.79220	1.36197	58.35320	12.94171
0.0005937	0.79239	1.36206	58.36778	12.94783
0.0006703	0.79253	1.36214	58.38679	12.95461
0.0007446	0.79271	1.36222	58.40192	12.96054
M = Fe				
7.46×10^{-5}	0.79119	1.36154	58.25771	12.90675
0.000153	0.79136	1.36163	58.27570	12.91362
0.000222	0.79153	1.36173	58.29005	12.92001
0.000294	0.79170	1.36182	58.30533	12.92628
0.000370	0.79187	1.36192	58.32239	12.93327
0.0004486	0.79202	1.36202	58.34165	12.94075
0.0005131	0.79220	1.36211	58.35342	12.94625
0.0005826	0.79236	1.36219	58.36858	12.95218
0.0006546	0.79254	1.36229	58.38320	12.95863
0.0007446	0.79272	1.36238	58.40482	12.96632
M = Co				
7.386×10^{-5}	0.79116	1.36144	58.25991	12.90403
0.000142	0.79142	1.36154	58.26738	12.90889
0.000219	0.79168	1.36165	58.27835	12.91485
0.000296	0.79188	1.36175	58.29407	12.92154
0.000364	0.79201	1.36184	58.31115	12.92821
0.0004389	0.79213	1.36194	58.33153	12.93594
0.0005135	0.79231	1.36203	58.34747	12.94236
0.0005862	0.79252	1.36213	58.36045	12.94845
0.0006493	0.79265	1.36221	58.37558	12.95437
0.0007486	0.79290	1.36233	58.39603	12.96276

The molar volumes, V^M, for each solution were calculated from

$$V^M = \frac{x_1 M_1 + x_2 M_2}{\rho}, \quad (1)$$

where x_i and M_i are the mole fractions and molar masses of the solutions' components, respectively, and where i = 1, 2 refer to the solvent and solute, respectively. The molar refractions of the solutions, R, were calculated from the molar volumes and refractive indexes (n) according to

$$R = \left(\frac{n^2 - 1}{n^2 + 2}\right) V^M \quad (2)$$

The V^M and R-values for each solution are also given in Table 1. Since V^M is a homogeneous function of n_1 and n_2, following Euler, one gets

$$V^M = x_1 V_1^M + x_2 V_2^M = V_1^M + x_2 (V_2^M - V_1^M), \quad (3)$$

where V_1^M and V_2^M are the partial molar volumes for the solvent and solute, respectively. An analogous equation obtains for molar refraction (R).[18] All V^M and R-values exhibit nearly linear dependence on the mole fraction of solute. Consequently, intercepts and slopes were calculated employing Excel's linear regression routine, and standard deviations were determined from Excel's ANOVA routine. The refractive index (n_2) for each complex was calculated according to

$$R_2 = \left(\frac{n_2^2 - 1}{n_2^2 + 2}\right) V_2^M. \quad (4)$$

Descriptor methodology

Our method for the determination of descriptors for neutral solutes uses two linear free energy relationships, eqn (5) and (6).

$$\log SP = c + eE + sS + aA + bB + vV \quad (5)$$

$$\log SP = c + eE + sS + aA + bB + lL \quad (6)$$

Eqn (5) is used when the dependent variable, log SP, refers to condensed phase processes, such as the water–solvent partition coefficient for a series of solutes in a given system; then SP itself is the water–solvent partition coefficient. Eqn (6) is used when log SP refers to a gas to system partition, where SP is the gas to system partition coefficient.

The independent variables in eqn (5) and (6) are solute descriptors as follows:[6–13] E is the solute excess molar refractivity in units of (cm^3 mol^{-1})/10, S is the solute dipolarity/polarizability, A and B are the overall or summation hydrogen bond acidity and basicity, V is the McGowan characteristic volume in units of (cm^3 mol^{-1})/100 and L is the logarithm of the gas-hexadecane partition coefficient, at 298 K. The coefficients in eqn (5) and (6) are obtained by multiple linear regression analysis, and serve to characterize the system under consideration.

In order to apply eqn (5) or (6), values of the dependent variable are needed. The most direct source is a directly determined water–solvent partition coefficient, P, as log P. However, most of the relevant data consists of solubilities in (dry) solvents and in water. Then partition coefficients can be

obtained indirectly through eqn (7), where C_w and C_s are solubilities in mol dm^{-3}, in water and a given solvent. If a value of C_w is not known, or is perhaps doubtful, then $\log C_w$ can be allowed to float, and becomes another unknown parameter to deduce.

$$\log P = \log C_s - \log C_w \quad (7)$$

We can greatly increase the number of simultaneous equations, by converting every $\log P$ value from eqn (7) into a corresponding $\log K_s$ value through eqn (8), where K_s is the gas to solvent partition coefficient and K_w is the gas to water partition coefficient. Now $\log K_w$ itself is another variable to be determined.

$$\log P = \log K_s - \log K_w \quad (8)$$

This leaves E, S, A, B, V, L, and possibly $\log C_w$ and $\log K_w$ to be determined through a set of simultaneous equations with $\log P$ and $\log K_s$ as the dependent variables in eqn (5) and (6). The Microsoft 'Solver' add-on is particularly useful, and any number of simultaneous equations can be solved to give a 'best-fit' solution.

Since we have as many as eight variables to obtain, it is useful to be able to deduce one or more variables independently, and so reduce the number that have to be obtained through the set of simultaneous equations. For organic compounds, E can be calculated through two programs[4,19] and can also be obtained from a calculated liquid refractive index at 293 K.[3] Now that we have experimental molar refractions there is no problem in obtaining values of E.

The volume descriptor, V, can very easily be calculated for organic compounds through McGowan's method,[20] but as we showed in the case of ferrocene, it is not straightforward to use McGowan's method for inorganic complexes.

The McGowan volume, $V_x = 100 \times V$, is calculated from atomic increments, as shown in Table 2,[16,20,21] with 6.56 subtracted for each bond (single, double and triple bonds all counting as one bond). If the structure of an acac derivative of cobalt(III) is as shown in Fig. 1, then for tris(acetylacetonato)Co(III) there are $15 \times 3 = 45$ bonds. Then with V_x for Co(3+) = 0.78 mL mol^{-1}, for the complex we have $V_x = 21 \times 8.71 + 15 \times 16.35 + 6 \times 12.43 + 0.78 - 6.56 \times 45 = 208.3$ cm^3 mol^{-1}. However, the C=O → Co coordinate bond is not a 'McGowan' bond, and the oxygen atom in =O → has three bonds instead of two. So there is a difficulty in calculating the McGowan volume for the cyclic structure.

Suppose we use the non-cyclic structure, Fig. 2. Now the number of bonds is $14 \times 3 = 42$, and $V_x = 21 \times 8.71 + 15 \times 16.35 + 6 \times 12.43 + 0.78 - 6.56 \times 42 = 228.0$ cm^3 mol^{-1}, substantially larger than that calculated for the cyclic structure.

We can resolve this by using the equations we have constructed[16] for the correlation of V_x against the partial molal volumes, V_2^M (MeCN), of a series of organic and inorganic compounds in acetonitrile solvent,[22] eqn (5) and (6). For Co(acac)$_3$ we have that V_2^M (MeCN) = 256.6 cm^3 mol^{-1} in acetonitrile,[22] and so calculated values of V_x are 233.1 ± 6.2 on eqn (9) and 228.2 ± 7.9 on eqn (10), very close to the McGowan volume of 228.0 cm^3 mol^{-1} as calculated for the non-cyclic structure in Fig. 2. Similar calculations for Cr(acac)$_3$ and Fe(acac)$_3$ confirm the use of the non-cyclic structure in the calculation of V_x. We make it clear that the structure in Fig. 2 is only for the purpose of calculating V_x and is not intended as the representation of the actual structure of Co(acac)$_3$. However, now that we have shown that the structure in Fig. 2 can be used to calculate V for M(acac)$_3$ complexes, we can use the same method to calculate V for complexes of various substituted acetylacetones.

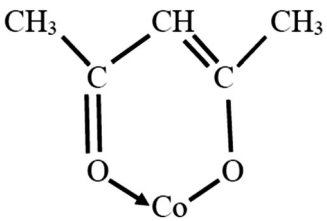

Fig. 1 A possible configuration of Co(acac)$_3$ for the calculation of McGowan's volume, illustrated for just one of the acac molecules.

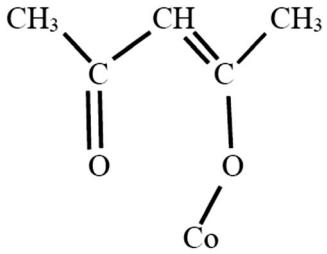

Fig. 2 A possible 'open chain' configuration of Co(acac)$_3$ for the calculation of McGowan's volume.

$$V_x = -10.237 + 0.9482V_2^M\,(\text{MeCN}) \quad N = 58,\ \text{SD} = 6.05,\ R^2 = 0.993,\ F = 7531.6,\ \text{PRESS} = 2181.40,\ Q^2 = 0.992,\ \text{PSD} = 6.24 \quad (9)$$

$$V_x = 0.8895V_2^M\,(\text{MeCN}) \quad N = 58,\ \text{SD} = 7.74,\ \text{PRESS} = 3534.0,\ \text{PSD} = 7.87 \quad (10)$$

Table 2 Atomic volumes, V_x, in cm^3 mol^{-1}[16,20,21]

H 8.71					
C 16.35	N 14.39	O 12.43	F 10.48	Fe^{3+} 0.78	Y^{3+} 3.58
Si 26.83	P 24.87	S 22.91	Cl 20.95	Co^{3+} 0.78	Sm^{3+} 3.66
Ge 31.02	As 29.42	Se 27.81	Br 26.21	Cr^{3+} 1.08	Nd^{3+} 3.89
Sn 39.35	Sb 37.74	Te 36.14	I 34.53	V^{3+} 1.18	La^{3+} 5.11
Pb 43.44					

Results and discussion

Molar refractions

The molar volumes, molar refractions, and refractive indices are listed in Table 3. The molar volumes of the three tris-acac metal compounds follow the trend of Co < Fe ≈ Cr, which inversely follows the molecular masses of the three compounds. This observation is in accord with the results of crystal structures[23–25] of the compounds in which the metal oxygen bond distances increase in roughly the same direction: Co 1.888 (4) Å, Cr 1.951 (7) Å, Fe 1.95 (1) Å. Assuming that the other bond (C–H, C–C, and C–O) distances within the acac

Table 3 V_2^M, R_2, and n_2 for M(acac)$_3$ complexes[a]

M	V_2^M, cm^3 mol^{-1}	R_2, cm^3 mol^{-1}	n_2
Cr	272.9(2.9)	97.6(0.7)	1.6338
Fe	276.3(1.4)	102.3(0.4)	1.6638
Co	269.3(5.9)	101.9(1.1)	1.6809

[a] Standard deviations in parentheses.

ligand itself do not vary appreciably, then the cobalt compound would be expected to have the smallest volume.

The d-electron structures of the three metal centers also differ significantly with the chromium(III) and iron(III) centers being paramagnetic high-spin d^3 and d^5, respectively, while the cobalt(III) center is diamagnetic low-spin d^6.

Descriptors

Water–solvent partition coefficients into water–methanol mixtures, dimethylsulfoxide (DMSO) and dioxane for Cr(acac)$_3$ have been listed by Alousy and Burgess.[26] Watarai *et al.*,[27] have determined partitions into dodecane, tetrachloromethane and benzene. Solubilities of Cr(acac)$_3$ are known in water–ethanol mixtures[28] but only in those of low ethanol content, and we did not use any of these values. Solubilities are also known in the solvents dimethylformamide[29,30] dichloromethane, 1,1,1-trichloroethane and tetrahydrofuran.[30] The solubility of Cr(acac)$_3$ in water at 298 K is given as $\log C_w = -2.55$,[29] with C_w in mol dm^{-3}, and so the various solubilities can be converted into values of $\log P$ through eqn (7). Then if we take $\log K_w$ as unknown to be determined, we can convert all the $\log P$ values into $\log K_s$ values through eqn (8). We can calculate $V_x = 2.2830$ by McGowan's method, and from the refractive index in Table 3 calculate that $E = 2.222$. This leaves the descriptors S, A, B, L and $\log K_w$ to be obtained from a set of simultaneous equations in $\log P$. In Table 4 are the values of $\log P$ that we used. A preliminary analysis showed that three values were out of line, leaving 14 values of $\log P$ and 14 values of the corresponding $\log K_s$. We also had two equations in $\log K_w$ giving a total of 30 simultaneous equations. The equation coefficients[16,31–33] for eqn (5) and (6) are collected in Tables 5 and 6. The best fit solution of the 30 simultaneous equations yielded the descriptors shown in Table 7, and the calculated values of $\log P$ from these descriptors are in Table 4.

Table 4 Calculated and observed values of water–solvent partition coefficients, as $\log P$, for Cr(acac)$_3$

Solvent	$\log P$ (calc)	$\log P$ (obs)	Ref.	
Dichloromethane	2.988	2.500	30	Not used
Tetrachloromethane	1.975	2.041	27	
Dodecane	0.322	−0.733	27	Not used
Benzene	2.397	2.534	27	
Tetrahydrofuran	1.946	1.740	30	Not used
Dioxane	1.865	1.870	26	
Dimethylfomamide	1.915	1.934	30	
Dimethylsulfoxide	1.627	1.610	26	
90% methanol–water	1.729	1.600	26	
80% methanol–water	1.498	1.510	26	
70% methanol–water	1.288	1.350	26	
60% methanol–water	1.095	1.160	26	
50% methanol–water	0.902	0.860	26	
40% methanol–water	0.733	0.560	26	
30% methanol–water	0.536	0.330	26	
20% methanol–water	0.385	0.140	26	
10% methanol–water	0.211	0.070	26	

The 14 calculated and observed values of $\log P$ for Cr(acac)$_3$ in Table 4 yield an average error AE of 0.042, an average absolute error AAE of 0.094 and a standard deviation of 0.125 log units. For the total of 30 simultaneous equations the SD is 0.123 log units. This is shown in Table 7, where N is the total number of equations used. We left out data in three solvents in Table 4, where the difference between $\log P$(calc) and $\log P$(obs) was very large.

For Fe(acac)$_3$, water–solvent partition coefficients are known into propan-2-ol, DMSO, and various water–methanol mixtures.[26] Solubilities have been determined in several solvents[30,34] but apparently not in water itself. However, we can take $\log C_w$ as another descriptor to be determined through our analysis. We find that with $\log C_w = -2.38$, the observed values of $\log P$ and those

Table 5 Coefficients in eqn (5) for water–solvent partitions as $\log P$

	Coefficients					
Solvent	c	e	s	a	b	v
Hexane	0.333	0.560	−1.710	−3.578	−4.939	4.463
Heptane	0.297	0.634	−1.755	−3.571	−4.946	4.488
Cyclohexane	0.159	0.784	−1.678	−3.740	−4.929	4.577
Formamide	−0.171	0.070	0.308	0.589	−3.152	2.432
Dimethylformamide	−0.305	−0.058	0.343	0.358	−4.865	4.486
Dimethylacetamide	−0.271	0.084	0.209	0.915	−5.003	4.557
Acetonitrile	0.413	0.077	0.326	−1.566	−4.391	3.364
Nitromethane	0.023	−0.091	0.793	−1.463	−4.364	3.460
Dimethylsulfoxide	−0.194	0.327	0.791	1.260	−4.540	3.361
Propylene carbonate	−0.149	0.754	−0.966	0.684	−3.134	3.247
Propanone	0.313	0.312	−0.121	−0.608	−4.753	3.942
Tetrahydrofuran	0.223	0.363	−0.384	−0.238	−4.932	4.450
1,2-Dichloroethane	0.183	0.294	−0.134	−2.801	−4.291	4.180
Benzene	0.142	0.464	−0.588	−3.099	−4.625	4.491
Toluene	0.125	0.431	−0.644	−3.002	−4.748	4.524
Chlorobenzene	0.065	0.381	−0.521	−3.183	−4.700	4.614
Nitrobenzene	−0.152	0.525	0.081	−2.332	−4.494	4.187
Ethylene glycol	−0.270	0.578	−0.511	0.715	−2.619	2.729
2-Ethoxyethanol	0.133	0.392	−0.419	0.125	−4.200	3.888
2-Butoxyethanol	−0.055	0.377	−0.607	−0.080	−4.371	4.234
Octan-1-ol, wet	0.088	0.562	−1.054	0.034	−3.460	3.814
Ethanol	0.222	0.471	−1.035	0.326	−3.596	3.857
96% ethanol	0.238	0.353	−0.833	0.297	−3.533	3.724
95% ethanol	0.239	0.328	−0.795	0.294	−3.514	3.697
90% ethanol	0.243	0.213	−0.575	0.262	−3.450	3.545
80% ethanol	0.172	0.175	−0.465	0.260	−3.212	3.323
70% ethanol	0.063	0.085	−0.368	0.311	−2.936	3.102
60% ethanol	−0.040	0.138	−0.335	0.293	−2.675	2.812
50% ethanol	−0.142	0.124	−0.252	0.251	−2.275	2.415
40% ethanol	−0.221	0.131	−0.159	0.171	−1.809	1.918
30% ethanol	−0.269	0.107	−0.098	0.133	−1.316	1.414
20% ethanol	−0.252	0.042	−0.040	0.096	−0.823	0.916
10% ethanol	−0.173	−0.023	−0.001	0.065	−0.372	0.454
Methanol	0.276	0.334	−0.714	0.243	−3.320	3.549
95% methanol	0.270	0.278	−0.520	0.230	−3.368	3.365
90% methanol	0.258	0.250	−0.452	0.229	−3.206	3.175
80% methanol	0.172	0.197	−0.319	0.241	−2.912	2.842
70% methanol	0.098	0.192	−0.260	0.266	−2.558	2.474
60% methanol	0.053	0.207	−0.238	0.272	−2.157	2.073
50% methanol	0.023	0.223	−0.222	0.264	−1.747	1.662
40% methanol	0.020	0.222	−0.205	0.218	−1.329	1.259
30% methanol	0.016	0.187	−0.172	0.165	−0.953	0.898
20% methanol	0.022	0.142	−0.138	0.088	−0.574	0.559
10% methanol	0.012	0.072	−0.081	0.026	−0.249	0.266

Table 6 Coefficients in eqn (6) for gas–solvent partitions as log *K*

Solvent	Coefficients					
	c	*e*	*s*	*a*	*b*	*l*
Hexane	0.320	0.000	0.000	0.000	0.000	0.945
Heptane	0.284	0.000	0.000	0.000	0.000	0.950
Cyclohexane	0.163	−0.110	0.000	0.000	0.000	1.013
Formamide	−0.800	0.310	2.292	4.130	1.933	0.442
Dimethylformamide	−0.391	−0.869	2.107	3.774	0.000	1.011
Dimethylacetamide	−0.308	−0.736	1.802	4.361	0.000	1.028
Acetonitrile	−0.007	−0.595	2.461	2.085	0.418	0.738
Nitromethane	−0.340	−0.297	2.689	2.193	0.514	0.728
Dimethylsulfoxide	−0.556	−0.223	2.903	5.037	0.000	0.719
Propylene carbonate	−0.356	−0.413	2.587	2.207	0.455	0.719
Propanone	0.127	−0.387	1.733	3.060	0.000	0.866
Tetrahydrofuran	0.189	−0.347	1.238	3.289	0.000	0.982
1,2-Dichloroethane	0.017	−0.337	1.600	0.774	0.637	0.921
Benzene	0.107	−0.313	1.053	0.457	0.169	1.020
Toluene	0.085	−0.400	1.063	0.501	0.154	1.011
Chlorobenzene	0.064	−0.399	1.151	0.313	0.171	1.032
Nitrobenzene	−0.296	0.092	1.707	1.147	0.443	0.912
2-Ethoxyethanol	−0.064	−0.257	1.452	3.672	0.662	0.843
2-Butoxyethanol	−0.109	−0.304	1.126	3.407	0.660	0.914
Octan-1-ol, wet	−0.222	0.088	0.701	3.473	1.477	0.851
Ethanol	0.222	0.471	−1.035	0.326	−3.596	3.857
96% ethanol	0.238	0.353	−0.833	0.297	−3.533	3.724
95% ethanol	0.239	0.328	−0.795	0.294	−3.514	3.697
90% ethanol	0.243	0.213	−0.575	0.262	−3.450	3.545
80% ethanol	0.172	0.175	−0.465	0.260	−3.212	3.323
70% ethanol	0.063	0.085	−0.368	0.311	−2.936	3.102
60% ethanol	−0.040	0.138	−0.335	0.293	−2.675	2.812
50% ethanol	−0.142	0.124	−0.252	0.251	−2.275	2.415
40% ethanol	−0.221	0.131	−0.159	0.171	−1.809	1.918
30% ethanol	−0.269	0.107	−0.098	0.133	−1.316	1.414
20% ethanol	−0.252	0.042	−0.040	0.096	−0.823	0.916
10% ethanol	−0.173	−0.023	−0.001	0.065	−0.372	0.454
Methanol	0.276	0.334	−0.714	0.243	−3.320	3.549
95% methanol	0.270	0.278	−0.520	0.230	−3.368	3.365
90% methanol	0.258	0.250	−0.452	0.229	−3.206	3.175
80% methanol	0.172	0.197	−0.319	0.241	−2.912	2.842
70% methanol	0.098	0.192	−0.260	0.266	−2.558	2.474
60% methanol	0.053	0.207	−0.238	0.272	−2.157	2.073
50% methanol	0.023	0.223	−0.222	0.264	−1.747	1.662
40% methanol	0.020	0.222	−0.205	0.218	−1.329	1.259
30% methanol	0.016	0.187	−0.172	0.165	−0.953	0.898
20% methanol	0.022	0.142	−0.138	0.088	−0.574	0.559
10% methanol	0.012	0.072	−0.081	0.026	−0.249	0.266

Table 7 Determined descriptors for the tris(acetylacetonates)

Complex	*E*	*S*	*A*	*B*	*V*	*L*	log K_w	*N*	SD
$Cr(acac)_3$	2.222	1.67	0.00	1.74	2.2830	11.77	10.89	30	0.123
$Fe(acac)_3$	2.524	2.25	0.00	1.74	2.2800	12.34	12.38	46	0.136
$Co(acac)_3$	2.694	2.21	0.00	1.91	2.2800	12.69	13.36	68	0.205
$V(acac)_3$	2.480	2.55	0.00	1.57	2.2840	12.82	12.57	6	0.013
$Y(acac)_3$	2.480	2.85	0.00	1.94	2.2834	13.26	15.13	10	0.182
$Sm(acac)_3$	2.480	2.83	0.00	2.36	2.2835	13.27	17.07	12	0.196
$La(acac)_3$	2.480	3.01	0.00	2.38	2.3233	13.53	17.61	10	0.190
$Nd(acac)_3$	2.480	2.98	0.00	2.37	2.3088	13.49	17.49	12	0.158

calculated from log C_s through eqn (7) are very consistent. We calculate V = 2.2800 and from the refractive index that we have determined, Table 2, we calculate E = 2.524; then the unknowns to be found by solution of the set of simultaneous equations in log P are S, A, B, L, log K_w and log C_w. We used a total of 22 values of log P, 22 values of the corresponding log K_s through eqn (8) and two equations in log K_w leading to a set of 46 simultaneous equations.

Table 8 Calculated and observed values of water–solvent partition coefficients, as log P, for $Fe(acac)_3$

Solvent	log P(calc)	log P(obs)	Ref.	
Hexane	−0.519	−0.367	34	
Heptane	−0.425	−0.430	34	
Cyclohexane	0.221	−0.005	34	
Dichloromethane	2.898	2.313	30	Not used
Tetrachloromethane	1.447	1.900	34	Not used
Benzene	2.182	2.263	34	
Toluene	1.817	1.923	34	
Chlorobenzene	2.196	2.309	34	
Tetrahydrofuran	1.818	1.858	30	
Dimethylformamide	2.083	2.060	30	
Dimethylsulfoxide	2.175	1.890	26	
Propan-1-ol	1.379	0.930	26	Not used
Propan-2-ol	1.143	0.928	26	
tert-Butanol	0.772	0.648	26	
Methanol	1.827	1.840	26	
95% methanol	1.614	1.761	26	
90% methanol	1.633	1.689	26	
80% methanol	1.364	1.489	26	
70% methanol	1.187	1.350	26	
60% methanol	1.013	1.104	26	
50% methanol	0.836	0.791	26	
40% methanol	0.677	0.508	26	
30% methanol	0.490	0.333	26	
20% methanol	0.346	0.193	26	
10% methanol	0.185	0.096	26	

These 46 equations yielded the descriptors shown in Table 7 and log C_w = −2.37, with a standard deviation between calculated and observed dependent variables of 0.136 log units. The calculated and observed values of log P are in Table 8. For the 22 used values, AE = 0.018, AAE = 0.117 and SD = 0.140 log units.

In the case of $Co(acac)_3$, solubilities are known in water (log C_w = −2.41),[29] dimethylformamide,[29] dodecane,[27] various ethanol–water mixtures[28] and alkoxyethanols.[35] Alousy and Burgess.[26] have listed partition coefficients into methanol–water mixtures and into a large number of pure solvents. The solubilities were converted into log P values, and we were able to use 33 such values. We also had 33 of the corresponding log K_s values, and two equations in log K_w giving a total of 68 simultaneous equations. These were solved to yield the descriptors in Table 7 with an SD between the 68 calculated and observed values of 0.205 log units. The observed and calculated values of log P are in Table 9. For the 33 calculated and observed values that we used, AE = 0.006, AAE = 0.136 and SD = 0.158 log units.

The determined descriptors for the complexes of Cr, Fe and Co, Table 7, do not very greatly between the three. All the complexes are quite polarizable, with S ranging from 1.67 to 2.25, as evidenced also by their dipole moments that vary from 0.95 to 1.10.[36] There is little variation in hydrogen bond basicity, and all the complexes have A as zero. It might have been expected that a concentrated positive charge in the middle of the molecule would induce some hydrogen bond acidity for the –CH═ hydrogen atom, but there is no doubt that A = 0.

There are limited data for other $M(acac)_3$ complexes, but only in a few cases are there enough to attempt to deduce descriptors. Even then, without a knowledge of E and V, little can be done. Values of V can be calculated exactly as for

Table 9 Calculated and observed values of water–solvent partition coefficients, as log *P*, for $Co(acac)_3$

Solvent	log *P*(calc)	log *P*(obs)	Ref.	
Decane	−1.004	−0.84	26	
Dodecane	−1.115	−1.090	27	
Tetrachloromethane	0.801	1.556	26	Not used
Dimethylformamide	1.233	1.282	29	
Dimethylsulfoxide	1.427	1.156	26	
Propan-1-ol	0.849	0.280	26	Not used
Propan-2-ol	0.593	0.280	26	Not used
Butan-1-ol	0.672	0.928	26	
Hexan-1-ol	0.689	0.948	26	
Octan-1-ol	0.504	0.543	26	
Decan-1-ol	0.510	0.367	26	
2-Ethoxyethanol	1.106	0.910	35	
2-Butoxyethanol	0.924	0.690	35	
Methanol	1.348	1.346	26	
95% methanol	1.109	1.240	26	
90% methanol	1.048	1.210	26	
80% methanol	0.916	1.190	26	
70% methanol	0.796	1.000	26	
60% methanol	0.691	0.808	26	
50% methanol	0.586	0.664	26	
40% methanol	0.497	0.420	26	
30% methanol	0.367	0.221	26	
20% methanol	0.278	0.140	26	
10% methanol	0.158	0.065	26	
Ethanol	1.129	1.051	28	
96% ethanol	1.091	0.932	28	
95% ethanol	1.084	0.999	28	
90% ethanol	1.039	1.195	28	
80% ethanol	1.057	1.201	28	
70% ethanol	0.944	1.027	28	
60% ethanol	0.894	0.832	28	
50% ethanol	0.796	0.642	28	
40% ethanol	0.698	0.472	28	
30% ethanol	0.513	0.325	28	
20% ethanol	0.289	0.201	28	
10% ethanol	0.087	0.093	28	

$Fe(acac)_3$ with the atomic increments for M^{3+} atoms as shown in Table 2,[21] but without any experimental values of molar refraction, *E* cannot be determined. However, *E* does not seem to alter very much with the nature of the M^{3+} atom, and in the case of the Cr, Fe and Co complexes, values of the obtained descriptors vary only slightly with change in the taken value of *E*. We therefore took *E* as 2.48, the average of the Cr, Fe and Co complexes,

Imura and N. Suzuki[37] have determined log *P* values for $V(acac)_3$, and there is just enough information to obtain the descriptors given in Table 7. There is a little more data for the $M(acac)_3$ complexes of yttrium, samarium, lanthanum and neodymium[38] and these yield the descriptors in Table 7. The descriptors *S*, *B*, *L* and $\log K_w$ for these extra five complexes fall into the same pattern as shown by the Cr, Fe and Co complexes. All four descriptors alter regularly with increase in the complex molecular weight, MW, over the eight complexes. The *B*-descriptor varies the most regularly, see eqn (11). This equation might be useful in the assignment of descriptors to other $M(acac)_3$ complexes.

$$B = -0.904 + 0.00750\text{MW} \quad N = 8,\ \text{SD} = 0.087,\quad R^2 = 0.937,\ F = 89.72 \qquad (11)$$

Table 10 Values of $\log P_{oct}$ for acetylacetonate complexes and some organic compounds

Compound	$\log P_{oct}$
$Cr(acac)_3$	2.26
$Fe(acac)_3$	1.81
$Co(acac)_3$	1.36
$V(acac)_3$	2.07
$Y(acac)_3$	0.47
$Sm(acac)_3$	−0.96
$La(acac)_3$	−1.06
$Nd(acac)_3$	−1.05
Glycerol tributanoate	3.60
Dibutyl adipate	3.88
Diheptyl ether	6.42
Pentadecane	8.56

By comparison to organic compounds, there have been comparatively few studies on physicochemical properties of inorganic complexes. Analysis of solubilities has provided estimates of the solubility parameter of complexes,[27,34,39] but the various predictive methods that have been so useful for organic compounds[1–5] have not been applied to inorganic complexes. Now that we have descriptors for the three complexes, Table 7, these can be used to predict log *P* values from the gas phase and from water to a very large number of both dry and wet solvents, as well as to several ionic liquids. We can illustrate this by the calculation of the water to wet octanol partition coefficient, as $\log P_{oct}$, commonly used as a measure of hydrophobicity. It is a simple matter to combine the descriptors in Table 7 with the equation coefficients given in Table 5 to yield the values given in Table 10. Our calculated $\log P_{oct}$ values vary regularly with complex molecular weight, from the somewhat hydrophobic $Cr(acac)_3$ to the decidedly hydrophilic Sm, La and Nd complexes, as shown in eqn (12) and by Fig. 3.

$$\text{Log}\,P_{oct} = 13.989 - 0.0345\text{MW} \quad N = 8,\ \text{SD} = 0.230,\quad R^2 = 0.979,\ F = 247.2 \qquad (12)$$

The quite good statistics of eqn (12) suggest that our assignment of *E* = 2.48 for five of the complexes is at least reasonable.

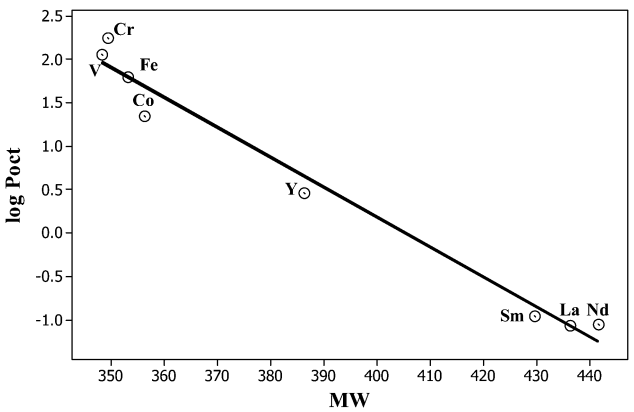

Fig. 3 A plot of calculated values of the water–octanol partition coefficient, as $\log P_{oct}$, for the eight $M(acac)_3$ complexes against the complex molecular weight.

We can compare the values of $\log P_{oct}$ for the complexes with those for organic compounds with around 15 carbon atoms. This indicates that all the $M(acac)_3$ complexes are much less hydrophobic than even glycerol tributanoate, which also has six oxygen atoms. Indeed, several of the complexes are hydrophilic.

Conclusions

We have shown that it is possible to employ the same methodology used to obtain Abraham descriptors for organic compounds to obtain Abraham descriptors for inorganic complexes. Then the various equations we have constructed for organic compounds can be used to predict a very large range of physicochemical properties for inorganic complexes. We have already shown[40] that the methods used here can be extended to obtain descriptors for electrolytes and there is no fundamental reason why our extended method cannot be used to obtain descriptors for charged inorganic complexes (electrolytes) as well as for inorganic complexes that are nonelectrolytes, The main difficulty in obtaining descriptors for the inorganic complexes is in the estimation of the *E*-descriptor. In the present work we have determined the *E*-descriptor from our experimentally determined molar refractions for the tris(acetylacetonato)chromium(III), tris-(acetylacetonato)iron(III) and tris(acetylacetonato)cobalt(III) complexes. This is a time-consuming procedure and at the moment is a limiting factor on the determination of the Abraham descriptors.

Conflicts of interest

There are no conflicts to declare.

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