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Abstract

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ELECTRICAL PROPERTIES OF INNER-COMPLEX COMPOUNDS

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Inner-complex compounds with a chelate bond have found not only broad application in analytical chemistry, but are also of definite interest for resolving certain questions in the theory of the chemical bond. However, the physicochemical properties, in particular the electrical properties, of inner-complex compounds have been studied quite insufficiently ($^{1-4}$).

The present work is devoted to the investigation of the electrical properties of acetylacetonates and oxine chelates of zirconium, thorium, indium, beryllium, and certain other metals. According to the stereochemistry of inner-complex compounds with a chelate bond, the acetylacetonates and oxine chelates of the above-mentioned metals should possess electrical symmetry. However, studies of the electrical properties of some acetylacetonates in nonpolar solvents have shown that the molecular polarization is considerably greater than the electronic polarization, and the difference between them for different compounds reaches 30—100 cm^3. The dipole moments calculated on the basis of these data are of the order of 1.2—2.1 debye.

The presence of such a considerable difference between the molar and electronic polarizations was attributed by a number of authors ($^{2-4}$) to an anomalously large atomic polarization, reaching 40—60% of the electronic polarization. It is of interest to determine whether these compounds really possess an unusual atomic polarization or whether their dipole moment is caused by other possible reasons: the influence of the solvent, the presence of internal hindered rotation (^{5}), or the absence of complete symmetry in the spatial structure of the complex molecule. To resolve this question, we studied the electrical properties of the above-mentioned complex compounds both in solution and in the solid phase.

The method for determining the dielectric constant, density, and refractive index was described by one of us earlier (^{6}). The dielectric constant in the solid phase was measured according to the method described in the literature (^{7}). We note only that the tablets were pressed at a pressure of 1000 kg/cm^2 and held for 1 min. The accuracy of measuring the dielectric constant in the solid phase is 1—1.5%.

The complex compounds investigated were synthesized by known methods ([8],[9]) and purified by sublimation in vacuum or by repeated recrystallization. As the solvent for determining the dipole moments of the complex compounds, we used thoroughly purified carbon tetrachloride, benzene, and dioxane.

Table 1 gives the results of determining the molar polarization extrapolated to infinite dilution P_2, the electronic polarization (refraction) P_e, and the dipole moments calculated with allowance for the atomic polarization P_a (found from our measurements in the solid phase) for the acetylacetonates of beryllium, aluminum, zirconium, and thorium in tetrachloro-

rist carbon, benzene, and dioxane, and zirconium 8-oxyquinolate in dioxane. The last column gives the ratio of the difference $P_2 - P_\mathrm{e}$ between the molar and electronic polarizations to the electronic polarization, expressed as a percentage.

Cryoscopic studies carried out by us of the molecular weights of the above-mentioned complex compounds in benzene showed that their molecules are monomeric.

Table 1

Compound	Solvent	P_2	P_e (R)	P_a	μ, in debyes	$\frac{P_2 - P_\mathrm{e}}{P_\mathrm{e}} \cdot 100$
$(C_5H_7O_2)_2Be$	CCl_4	85,22	58,85	15,40	0,71	44,8
$(C_5H_7O_2)_2Be$	C_6H_6	87,70	59,22	15,40	0,79	48,1
$(C_5H_7O_2)_2Be$	$C_4H_8O_2$	88,06	59,04	15,40	0,80	50,0
$(C_5H_7O_2)_3Al$	CCl_4	128,59	90,00	17,15	1,03	42,9
$(C_5H_7O_2)_3Al$	C_6H_6	130,52	89,24	17,15	1,08	46,2
$(C_5H_7O_2)_3Al$	$C_4H_8O_2$	130,07	88,51	17,15	1,11	46,8
$(C_5H_7O_2)_4Zr$	CCl_4	197,50	128,00	24,20	1,45	53,5
$(C_5H_7O_2)_4Zr$	C_6H_6	197,34	128,54	24,20	1,46	53,5
$(C_5H_7O_2)_4Zr$	$C_4H_8O_2$	201,03	128,43	24,20	1,52	56,6
$(C_9H_6NO)_4Zr$	$C_4H_8O_2$	279,77	189,98	9,85	1,97	47,4
$(C_5H_7O_2)_4Th$	CCl_4	202,21	127,40	23,10	1,58	58,7
$(C_5H_7O_2)_4Th$	C_6H_6	203,60	126,91	23,10	1,60	60,4
$(C_5H_7O_2)_4Th$	$C_4H_8O_2$	201,78	127,12	23,10	1,57	59,0

The data presented in Table 1 indicate that the dipole moments of the acetylacetonates studied do not depend on the nature of the solvent. Consequently, the presence of a considerable difference between the molecular and electronic polarizations cannot be explained by a solvent effect. Further, from the data given it is also clearly seen that the difference between these two types of polarization reaches 60% of the electronic polarization. If this difference is not ascribed (after subtraction of the atomic polarization found by us from the measurements in the solid phase) to an orientational origin, then it must be concluded that the complex compounds studied by us possess an anomalously high atomic polarization, i.e., a strong displacement of the atomic nuclei occurs upon application of an electric field. To clarify this question, it is necessary to investigate the electrical properties of our complexes in the solid phase. The results of such studies of the acetylacetonates and oxyquinolates of beryllium, copper, cadmium, aluminum, indium, chromium, zirconium, and thorium are presented in Table 2.

Table 2

Compound	P_d	P_e (R)	P_a	$\frac{P_d - P_e}{P_e} \cdot 100$	Compound	P_d	P_e (R)	P_a	$\frac{P_d - P_e}{P_e} \cdot 100$
$(C_5H_7O_2)_2Cu$	68,80	65,05	3,75	7,4	$(C_5H_7O_2)_4Th$	150,24	127,14	23,10	18,4
$(C_5H_7O_2)_2Be$	74,62	59,22	15,40	26,5	$(C_9H_6NO)_2Cu$	102,43	96,07	6,36	6,3
$(C_5H_7O_2)_2Cd$	67,41	55,03	12,38	22,4	$(C_9H_6NO)_2Cd$	95,50	89,65	5,85	0,54
$(C_5H_7O_2)_3Al$	106,40	89,25	17,15	19,5	$(C_9H_6NO)_3In$	152,74	145,36	7,38	4,7
$(C_5H_7O_2)_3In$	96,10	88,00	8,10	9,2	$(C_9H_6NO)_3Al$	154,60	144,00	10,60	7,7
$(C_5H_7O_2)_3Cr$	108,23	95,15	13,08	13,7	$(C_9H_6NO)_4Zr$	198,85	189,00	9,85	5,2
$(C_5H_7O_2)_4Zr$	152,70	128,50	24,20	19,3	$(C_9H_6NO)_4Th$	205,90	190,85	15,05	7,8

The data given show that the deformation polarization P_d, which for the solid state is equal to the sum of the electronic and atomic polarizations, differs little in magnitude from the electronic polarization (refraction). The value of the ratio $\frac{P_d - P_e}{P_e} \cdot 100$ in the solid phase is considerably smaller,

than the values of the ratios $\frac{P_2 - P_e}{P_e} \cdot 100$ in solution given in Table 1.

It follows from this that not all of the difference $P_2 - P_e$ is due to atomic polarization. The largest values of atomic polarization were obtained by us for zirconium acetylacetonates (^{24}, ^{20}), thorium (^{23}, ^{10}), and aluminum (^{17}, ^{15}). However, even these quantities amount to no more than 20% of the electronic polarization of the acetylacetonate of the corresponding metal. The data presented on atomic polarization are not anomalously high, since substances are not infrequently encountered in the literature whose atomic polarization reaches 20–25% of the electronic polarization (^{11}).

Thus, on the basis of the determination of the deformation polarization of the above-investigated metal acetylacetonates in the solid phase, it may be concluded that they do not possess anomalously high atomic polarization.

Our data agree well with the results of a study of the electrical properties of trivalent iron acetylacetonate in the solid phase, reported by Meridith and co-workers (^{10}). According to these authors, the part of the polarization corresponding to atomic polarization is 21, and not 57 cm^2, as had been assumed previously and on the basis of which anomalously high atomic polarization had been ascribed to iron acetylacetonate (11).

With an increase in the number of atoms and rings in the molecule, the magnitude of the atomic polarization should also increase. However, as is evident from the data in Table 2, for all oxyquinolates, in which the number of atoms is greater than in the corresponding acetylacetonates, the values of the atomic polarizations are smaller.

This also indicates that the complex compounds studied do not possess anomalously high atomic polarization. A comparison of the data in Tables 1 and 2 gives us grounds to believe that the indicated inner-complex compounds possess orientational polarization.

What has been said is confirmed by studies of the electrical properties of uranyl acetylacetonate, bis(ethylthioacetylacetonato)nickel, and other inner-complex compounds, in which the experimentally determined values of the dipole moments reach 4-6 D and more (1−4). This conclusion is contrary to the conclusion of Coop and Sutton (2), who measured the polarization of a number of acetylacetonates in the vapor phase, and to the data on the absence of a temperature dependence of the polarization of beryllium acetylacetonate (16). This latter complex is the only acetylacetonate for which a temperature study of polarization had previously been carried out. An analogous investigation, performed in a later work (10) for iron acetylacetonate, showed a change with temperature typical of orientational polarization. This casts doubt on the results obtained earlier and, on the contrary, corresponds to our point of view concerning the presence of a permanent dipole moment. The temperature dependence found by us for zirconium acetylacetonate in benzene is of a different character: the dipole moment increases with temperature.

	275	283	293	313	333
T°, K	275	283	293	313	333
μ, D	1.39	1.42	1.46	1.58	1.70

Such a change in the dipole moment indicates the possibility of the existence of internal hindered rotation of the methyl radicals in the acetylacetonate molecule. These data do not contradict the literature data concerning thorium and zirconium acetylacetonates (17).

At the same time, the presence of a dipole moment (1.97 D) in zirconium oxyquinolate compels the conclusion that internal rotation is not the only cause of the polarity of the compounds under consideration, since in the oxyquinolate molecule radicals capable of rotation are absent. It remains to assume the absence of complete symmetry in the structure of acetylacetonates and oxyquinolates.

In recent X-ray studies there are indications of a certain deformation of their structure ([14], [18], [19]).

Thus, on the basis of our experimental investigations and some literature data, it may be concluded that metal acetylacetonates and oxyquinolates do not have a completely symmetrical spatial structure, as a result of which their molecules possess a certain permanent electric moment. It should be noted that for a number of other substances to which anomalously high atomic polarization had also previously been ascribed (diphenylmercury, *p*-benzoquinone, *p*-dinitrobenzene), various causes have been found that explain the presence of orientational polarization ([16], [17], [20—22]).

Not long ago A. N. Nesmeyanov and co-workers obtained a new complex compound of zirconium, namely zirconium dinitratodiacetylacetonate [23]. In this complex compound the coordination number of zirconium is six, and the molecule may be assigned an octahedral structure. If the radicals ($C_5H_7O_2$) are represented as lying in one plane, then a trans configuration with a dipole moment equal or close to zero should be expected. If, however, the radicals lie in two mutually perpendicular planes, then the molecule of the complex will have a cis structure with a large value of the dipole moment. To clarify this question, we determined the dipole moment of zirconium dinitratodiacetylacetonate in benzene and dioxane at 25°. In benzene the moment $[(C_5H_7O_2)_2(NO_2)_2]Zr$ is 7.94, and in dioxane 7.76 D. Such a large value of the dipole moment indicates the presence of the cis form.

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Note: Figure translations are in progress. See original paper for figures.