

# Dielectric Properties of Be(II), Al(III), Cr(III), Co(III), Cu(II), Zr(IV) & Th(IV) Acetylacetonates & Their Molecular Complexes with Iodine

R. SAHAI\* & V. N. BADONI

Department of Chemistry, V.S.S.D. College, Kanpur 208002

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Dipole moments of Be(II), Al(III), Cr(III), Co(III), Cu(II), Zr(IV) and Th(IV) acetylacetonates and some of their molecular complexes with iodine have been determined in carbon tetrachloride by the refractive index method. Dielectric titration technique indicates 1:1 stoichiometry of these complexes.

**S**PECTROPHOTOMETRIC<sup>1</sup> and conductometric<sup>2</sup> studies have indicated that like aromatics, coordinatively saturated, neutral, monomeric metal acetylacetonates,  $M(acac)_n$ , form molecular complexes with iodine by donation of electron density from the chelate rings. The dielectric properties of these complexes and of individual donor component have been investigated in order to provide some information on the geometry of  $M(acac)_n-I_2$  complexes.

## Materials and Methods

The acetylacetonates of Be(II)<sup>3</sup>, Al(III)<sup>4</sup>, Cr(III)<sup>5</sup>, Co(III)<sup>6</sup>, Cu(II)<sup>7</sup>, Zr(IV)<sup>8</sup> and Th(IV)<sup>9</sup> were prepared as reported in the literature. The  $\gamma$ -substituted nitro derivatives of Be(II), Al(III), Cr(III), Co(III) and Cu(II) were prepared as reported by Singh and Sahai<sup>10</sup>. Analytical grade (BDH) acetylacetone was redistilled before use. Iodine and the solvents used were also of AR grade.

Stock solutions of metal acetylacetonates and their nitro derivatives were prepared in carbon tetrachloride. The solutions employed in the measurement of dipole moments were prepared from the freshly prepared stock solutions.

The relative densities were measured using the relative density bottle. The refractive indices were measured by the help of Abbe's refractometer at room temperature. The dielectric constants were determined by the help of a RCL bridge. The dipole moments ( $\mu$ ) were calculated using Eq. 1,

$$\mu = 0.0127 \times 10^{-18} \sqrt{(\bar{p} - \bar{p}_D)T} \quad \dots(1)$$

where  $\bar{p}$  is the total polarization and  $\bar{p}_D (= \bar{p}_E + \bar{p}_A)$  the distortion polarization.  $\bar{p}$  and  $\bar{p}_D$  were calculated using Eqs 2. and 3.

$$\bar{p} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} \quad \dots(2)$$

$$\bar{p}_D = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \quad \dots(3)$$

where  $\epsilon$  is the dielectric constant,  $M$  is the mole-

TABLE 1 — DIELECTRIC DATA OF METAL ACETYLACETONATE AND THEIR NITRO DERIVATIVES IN  $CCl_4$  AT 22°

Donor	Concentration of donor (M)	$\mu \times 10^{-18}$
H(acac)	$1.0 \times 10^{-1}$	2.63
Be(acac) <sub>2</sub>	$1.0 \times 10^{-3}$	0.88
Be(NO <sub>2</sub> -acac) <sub>2</sub>	$1.0 \times 10^{-3}$	1.58
Al(acac) <sub>3</sub>	$1.0 \times 10^{-3}$	1.30
Al(NO <sub>2</sub> -acac) <sub>3</sub>	$1.0 \times 10^{-3}$	2.01
Cr(acac) <sub>3</sub>	$1.0 \times 10^{-3}$	1.44
Cr(NO <sub>2</sub> -acac) <sub>3</sub>	$1.0 \times 10^{-3}$	1.93
Co(acac) <sub>3</sub>	$1.0 \times 10^{-3}$	1.32
Co(NO <sub>2</sub> -acac) <sub>3</sub>	$1.0 \times 10^{-3}$	1.99
Cu(acac) <sub>2</sub>	$1.0 \times 10^{-3}$	0.82
Cu(NO <sub>2</sub> -acac) <sub>2</sub>	$1.0 \times 10^{-3}$	1.22
Zr(acac) <sub>4</sub>	$1.0 \times 10^{-4}$	2.46
Th(acac) <sub>4</sub>	$1.0 \times 10^{-4}$	2.93

cular weight,  $d$  is the density and  $n$  is the refractive index of the complex. The relevant data are reported in Table 1.

## Results and Discussion

The dipole moment data (Table 1) show that acetylacetone has a greater dipole moment than those of the chelated metal acetylacetonates. The larger dipole moment of acetylacetone can be attributed to its non-planar (asymmetric) structure. The decrease in dipole moment on chelation with different metals may be due to the enhanced symmetry in the structure of the chelates. The acetylacetonates of Al(III), Cr(III) and Co(III) have the same symmetry (octahedral structure), so one may expect similar dipole moment values for these chelates. Indeed, we have observed the same order of the magnitude of dipole moments for these chelates, but the role of the metal ion can not be completely ruled out. Slight differences in dipole moments of the chelates  $M(acac)_n$  may

\*To whom all correspondence should be addressed.

TABLE 2 — DIELECTRIC DATA ON THE INTERACTION OF ACETYLACETONATES WITH IODINE\* IN  $\text{CCl}_4$ 

Donor	Concentration of donor (M)	$\Delta\epsilon$	$\mu \times 10^{-18}$
H(acac)	$0.6-5.0 \times 10^{-1}$	13.75	2.84
Be(acac) <sub>2</sub>	$0.6-5.0 \times 10^{-2}$	4.37	1.54
Al(acac) <sub>3</sub>	$0.6-5.0 \times 10^{-3}$	5.37	2.14

\*The concentration of iodine was kept constant at  $1 \times 10^{-3} M$  in each case.

be explained on the basis of difference in their respective electronegativities and the presence of  $M(d\pi)-O(p\pi)$  bonding in some of these chelates.

When hydrogen in the  $\gamma$ -position of the acetylacetonate ring is replaced by the nitro group, a shift in electron density, away from the ring takes place due to the inductive effect of the nitro group leaving a net positive charge on the ring. The nitro group acts as a  $\pi$ -acceptor. Thus, there is a slight change in the overall geometry of the chelates leading to change in the dipole moment. The larger dipole moments of the nitro derivatives of these metal acetylacetonates confirm the greater unsymmetric nature of these chelates. The extent of charge-transfer from the ring to the nitro group may provide a measure of the dipole moment as in the case of nitrobenzene<sup>11</sup>.

The dipole moments of the molecular complexes of iodine with acetylacetonate, Be(acac)<sub>2</sub> and Al(acac)<sub>3</sub> were also obtained by the same procedure as discussed above and the data are recorded in Table 2. It is evident that an increase in the dipole moment is observed on complexation with iodine which indicates that metal acetylacetonates form charge-transfer type of molecular complexes with iodine. Further, the maximum increase in dipole moment of the complex is observed in the case of Al(acac)<sub>3</sub>-I<sub>2</sub> system. This indicates stronger interaction with iodine in this particular case. The following order of the dipole moments may be inferred: Al(acac)<sub>3</sub> > Be(acac)<sub>2</sub> > H(acac). Similar order of the magnitude of dipole moments for benzene-I<sub>2</sub> system has also been observed<sup>12</sup>.

The stoichiometries of the above mentioned molecular complexes have been determined using dielectric titration technique<sup>13</sup> where change in the dielectric permittivity ( $\Delta\epsilon$ ) of a solution of one component (iodine), on addition of successive amounts of the other component (metal acetylacetonates), is measured. In the case of the addition of a dipolar donor to a non-dipolar acceptor a complex is produced which has a dipole moment value larger than that of the donor. The addition of a small amount of donor generates an equal amount of complex. The permittivity increase on successive additions of the donor and continues to increase until the equivalent quantities of the donor and acceptor are present. This situation is schematically shown by line XY of Fig. 1, which indicates the

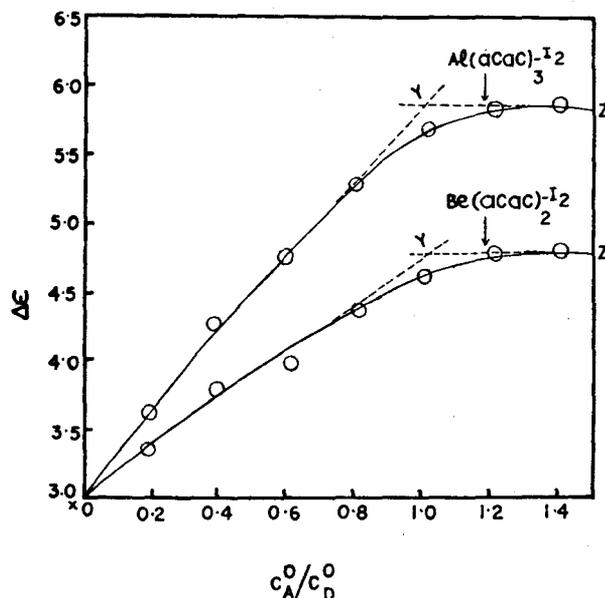
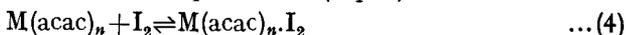


Fig. 1 — Plot of  $C_A^0/C_D^0$  versus  $\Delta\epsilon$  for the interaction of Be(acac)<sub>2</sub>-I<sub>2</sub> and Al(acac)<sub>3</sub>-I<sub>2</sub> in  $\text{CCl}_4$

1:1 stoichiometry of these complexes under the conditions of equilibrium (Eq. 4).



Further addition of the donor increases the permittivity by an amount depending on the dipole moment of the donor (line YZ in Fig. 1). A break has been observed in the graph at the donor-acceptor ratio corresponding to the ratio existing in the complex.

Thus, the above results seem to provide convincing evidence for the existence of a stable complex with sufficient polarity to orient itself in an applied electric field. Further, these observations give additional evidence for the formation of molecular complexes by metal acetylacetonate rings with iodine thereby providing support to pseudo-aromatic character of these chelate rings.

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