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Distortion Effect in Ligands of Polynuclear Metal β-Diketonates

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Structures of ligands in acetylacetone (acac) chelates have been considered to be symmetric in C_{2v} [1]. Therefore, the differences between the corresponding distances for C–O and C–C(ring) in the ligands have not been noticed in the polynuclear chelates though the variation of metal–oxygen distance has been discussed [2], and their observations were ignored as experimental errors [3]. However, a recent structure study of trimeric Mn(acac)$_2$ [4] revealed that the ligands are distorted as 1.248 and 1.278 Å for C–O, 1.370 and 1.432 Å for C–C(ring) as shown in Fig. 1(b). Thus the structures reported for polynuclear β-diketonates such as Fe [5], Co [6], Ni [7], and Zn [8] acac chelates and their adducts [2, 7, 9] were examined with respect to the bond length of their ligands on the basis of the concept described below.

The assumptions are the following: (1) all of metals in a molecule have the same oxidation state, (2) the coordination bond is essentially ionic, (3) the ligands resonate independently of each other. Thus electronic charges on ligand atoms are estimated and the contribution of the resonance canonical forms for the skeleton of β-diketone will be evaluated, consequently yielding π-bond orders of the C–O and

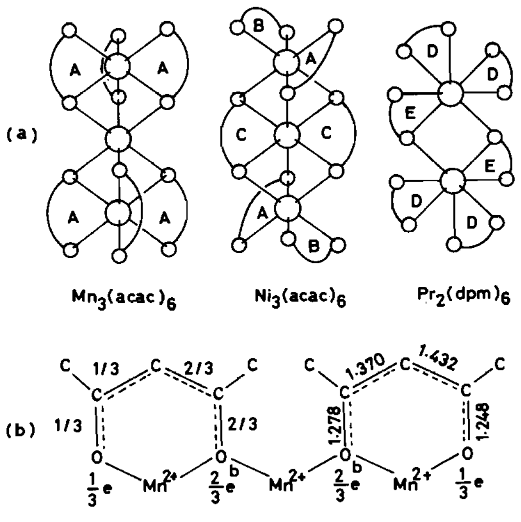
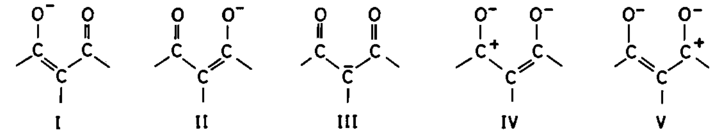


Fig. 1. (a) Polynuclear structures of Mn and Ni acetylacetonates and Pr dipivaloylmethanate with the classification of their ligands. (b) The structure of the ligands in Mn acetylacetonate with net charges on oxygen atoms, bond distances (A) (right side) and π-bond orders (left side).

C–C, as listed in Table I. Thus the ligands in divalent metal chelates can be classified into four groups, where A is asymmetric but B, C and D are symmetric. Examples are shown for Mn and Ni acac chelates in Fig. 1(a). The Cu [10] and Cr [11] acac chelates in the solid phases and all of the volatile chelates in the gas phases [12, 13] are monomeric and therefore their ligands should be symmetric, shown by D in Table I. This must have a slightly different dimension from B and C. When the experimental values of the C–O and C–C distances for the β-diketonates were related to the corresponding

TABLE I. Classification of the Ligands in β-Diketonates by Canonical Forms shown below (here O and O_b mean a non-bridged and bridged oxygen ligand atom, respectively).

Ligand type	A		B		C		D		E	
Oxygen atom	O	O_b	O	O	O_b	O_b	O	O	O	O_b
Net charge	1/3	2/3	1/3	1/3	2/3	2/3	1/2	1/2	1/2[a]	1[a]
Canonical set	$\frac{\mathrm{I}+2\mathrm{II}}{3}$		$\frac{\mathrm{I}+\mathrm{II}+\mathrm{III}}{3}$		$\frac{2(\mathrm{I}+\mathrm{II})+\mathrm{IV}+\mathrm{V}}{6}$		$\frac{\mathrm{I}+\mathrm{II}}{2}$		$\frac{2\mathrm{II}+\mathrm{IV}+\mathrm{V}}{4}$	
Related C–O bond order	2/3	1/3	2/3	2/3	1/3	1/3	1/2	1/2	1/2	0
Adjacent C–C bond order	1/3	2/3	1/3	1/3	1/2	1/2	1/2	1/2	1/4	3/4
Canonical forms										

[a] Approximate values.

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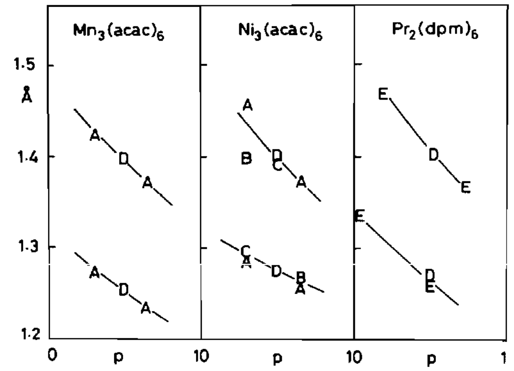

Fig. 2. Distortion effect of β-diketone ligands in Mn, Ni acac and Pr dpm chelates shown by the relation between C–O and C–C distances and their π-bond orders p. Lower curves are for C–O and upper curves are for C–C(ring). Structure data for D in Mn and Pr chelates will be published.

bond orders, it was found that there exists a good correlation between them in all the chelates described earlier. The plots for the above examples are shown in Fig. 2. This idea will be extended to chelates of trivalent metals such as Er [14] and tetravalent metals such as Zr [15]. These monomeric chelates have the symmetric ligands of D, but dimeric Pr dipivaloylmethanate(dpm) [16], shown in Fig. 1(a), involves the asymmetric ligand which is referred to as E in Table I. The distance and bond order relation for Pr(dpm)$_3$ is also shown in Fig. 2.

The conclusion is that there are essentially asymmetric ligands in polynuclear β-diketonates, *i.e., distortion effect,* which comes from the ionicity of the coordination bond in β-diketonates. This distortion is well balanced in the ligand, so the average C–O and C–C distances reported by workers are very close to their values for D with a bond order of 1/2, *i.e.,* 1.27 and 1.41 Å, respectively.

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