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Abstract

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ON THE CHEMICAL BOND IN MOLECULES OF ACETYLACETONATES OF TRIVALENT METALS

(Presented by Academician A. N. Nesmeyanov, 4 III 1960)

In the present work an X-ray diffraction study was carried out of isomorphous crystals of the acetylacetonates of aluminum (I), chromium (II), and cobalt (III). The values of the unit-cell parameters and data on polymorphism and isomorphism in this series of compounds were reported by us earlier ($^{1-3}$). The crystals of the acetylacetonates investigated were isolated from solutions of these substances in benzene, acetone, or chloroform by slow evaporation of the solvent. Exposures were made with copper radiation. Crystals II and III, owing to insufficient perfection, gave a limited field of reflections (642 and 316, respectively). For crystals I, 1373 reflections were recorded. In cases I and II the three-dimensional set consisted of data from X-ray goniometric layer-line photographs of 0–5 layer lines along the b axis of the crystal; for III, of 0–4 layer lines. The "blind" region was filled with data from layer-line photographs along the other axes. Reduction of the structural factors to a single scale was carried out at the first stage of the work by comparing data for individual reflections common to the X-ray photographs along different axes, and subsequently by the method of comparing experimental and theoretical values of structural amplitudes for a number of intervals of $\sin\vartheta/\lambda$ (^{4}). The structures were studied by the method of difference projections and three-dimensional planar and linear sections of the electron density. The method of isomorphous replacement was used in the work.

We give the values of the mean interatomic distances and valence angles in molecules I, II, and III:

	I	II	III		I	II	III
Me–O	1.95 ± 0.02 Å	1.90 ± 0.03 Å	1.92 ± 0.03 Å	O–Me–O	89° ± 1°	93° ± 1°	90° ± 1°

	I	II	III		I	II	III
C–C	1.38 ± 0.04	1.40 ± 0.04	1.41 ± 0.04	Me–O–C	131 ± 2	131 ± 3	132 ± 3
C–O	1.28 ± 0.02	1.28 ± 0.04	1.27 ± 0.04	C–C–C	128 ± 3	127 ± 4	130 ± 4
C–CH_3	1.53 ± 0.03	1.53 ± 0.04	1.52 ± 0.04	O–C–C	122 ± 4	118 ± 4	118 ± 4

In the acetylacetonates investigated, the metal atom forms 6 equivalent covalent bonds; the double bonds C=C and C=O in the acetylacetonate ring are delocalized. On the basis of the data presented, it may be assumed that the character of the Me–O bond and the delocalization of the double bonds in the acetylacetonate ring do not depend on the state of the electrons in the *d*-orbitals of the metal atoms.

In molecules of acetylacetonates of transition metals that have unpaired pairs of electrons in the *d*-orbitals and those that do not, and in the molecule of aluminum acetylacetonate, in whose atom *d*-electrons are absent, delocalization of the double bonds is observed irrespective of the nature of the metal atom. This conclusion agrees with the data of D. N. Shigorin (^{5}), which showed an analogous character of the IR spectra of various acetylacetonates, including I, II, and III. On the basis of the values of the interatomic distances, which are close for I, II, and III, it may be assumed that the formation of multiple Me–O bonds

with the participation of unshared pairs of *d*-electrons of the metal atom and the $p\pi$-electron of the oxygen atom of the acetylacetonate ring, as assumed by a number of authors (^{6,7}), does not occur. The π-bonds Me–O, which, upon delocalization of the double bonds, supplement the system of conjugated $C = O$ and $C = C$ bonds with a third multiple bond, as a result of which a "benzenoid" structure arises in the acetylacetonate ring (^{8}), apparently have a different nature, not connected with the *d*-electrons of the metal atom. It is possible that in this general system of π-interaction in the acetylacetonate ring the *p*-orbitals of the metal atom are used (^{9}).

The supposition that the *d*-electrons of the metal atom do not participate in multiple Me–O bonds is consistent with the ideas of crystal-field theory. According to experimental data, the acetylacetonate group $C_5H_7O_2^-$ does not give a strong crystal field (^{8}) and, consequently, is not capable of causing forced pairing of *d*-electrons, of greatly changing their energy state, and of interacting with them. This is confirmed by data on magnetic moments: nickel and iron cyanides are diamagnetic or, in any case, have reduced spin, whereas nickel and iron acetylacetonates are paramagnetic, and the magnetic moment of iron acetylacetonate corresponds to five unpaired electrons.

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