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Article

Monomeric Square-Planar Cobalt(II) Acetylacetonate: Mystery or Mistake?

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No evidence was found for the existence of a previously reported mononuclear square-planar form of unsolvated cobalt(II) acetylacetonate, $Co(acac)_2$, in all samples that have been obtained by using a variety of preparative techniques and crystallization conditions. It was confirmed that the structure of tetramer $Co_4(acac)_8$, reported back in 1964 by Cotton and Elder, is correct, the synthesis is reproducible, and the bulk material corresponds to single-crystal data. Additionally, the title compound can be isolated in tetranuclear form by reducing cobalt(III) acetylacetonate with cobalt metal in solvent-free conditions or by crystallization from a hexanes solution. At the same time, from noncoordinating halogenated solvents, $Co(acac)_2$ crystallizes as a trinuclear core molecule, in which all Co atoms also exhibit octahedral coordination. From coordinating solvents such as ethanol, cobalt(II) acetylacetonate was found to appear in the form of its bis-adduct $Co(acac)_2(EtOH)_2$. On the basis of observations made in this work and the details presented in the original paper, we suggest that the reported mononuclear structure of square-planar acetylacetonate should likely contain copper instead of cobalt.

Introduction

Cobalt(II) acetylacetonate, $Co(acac)_2$ (**1**), attracts considerable interest because of its multiple applications as a mediator in controlled radical polymerization,[1] a catalyst for cross-coupling of arylcopper reagents with aryl halides[2] and aryl sulfonate/copper exchange[3] reactions, a metal−organic precursor for Co_3O_4 deposition by the chemical vapor deposition technique,[4] and a starting material in the preparation of single-source precursors[5] for the synthesis of spinels. **1** enjoys a modest role in the history of modern coordination chemistry and a prominent position in the development of the chemistry of β-diketonate complexes. The molecular structure of unsolvated **1** was reported by Cotton and Elder back in 1964 as a tetramer,[6] in which all Co atoms maintain an octahedral coordination because of additional interactions with diketonate O atoms from neighboring units. Surprisingly, another modification of unsolvated **1** was reported in 2000[7] and consisted of mononuclear square-planar $Co(acac)_2$ units. This structure received multiple citations[1a,8] and even became a subject of density functional theory calculations[8b,f] at different levels of theory undertaken to rationalize its spin states and intermolecular interactions that cause a stacking arrangement of the planar units. All of this attention casts some doubt over the tetrameric structure published by Cotton and Elder, which, at times, is referred to as the “old data”.

Our interest in this mononuclear structure was initiated by one of the reviewers of our paper[9] on crystal structures of

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unsolvated divalent first-row transition-metal hexafluoroacetylacetonates, M(hfac)$_2$ (M = Mn, Fe, Co, Ni). In the latter, we noted that M(hfac)$_2$ solid-state structures are similar to the corresponding M(acac)$_2$, except for Co(hfac)$_2$, which is trinuclear. A detailed analysis of the paper[7] reporting a square-planar arrangement of **1** revealed a number of suspicious features:

1. Square-planar rather than tetrahedral coordination of Co atoms was present. Out of thousands of cobalt(II) compounds with O-donor ligands, there are just a few examples[10] of the square-planar arrangement when such a geometry was imposed by the ligand or dictated by steric factors. Interestingly, one of those examples[10c] was recently retracted.[11]
2. Intermolecular interactions are characteristic of homo- and heterometallic cobalt(II) β-diketonates with sterically uncongested ligands. These additional intermolecular interactions are absent in reported mononuclear Co(acac)$_2$.
3. The color of the crystal was reported as green, uncharacteristic of cobalt(II) compounds with O-donor ligands, which are either purple or blue.
4. **1** was isolated in its unsolvated form from the solution that contained molecules such as ethanol, aniline, and likely water [from cobalt(II) acetate]. In the presence of such basic donors, cobalt acetylacetonate usually converts to its mono- or bisadducts featuring octahedrally coordinated metal centers.[8d,12]
5. Just a "small number" of crystals were isolated from the reaction with a 1 g total load of cobalt(II) acetate. No additional characterization to supplement single-crystal analysis was provided.

All of these indiscretions prompted us to examine the structure of **1** obtained at different conditions: solid-state and solution syntheses and crystal growth by high-temperature gas-phase deposition or by low-temperature crystallization from both coordinating and noncoordinating solvents. To check the bulk products, we performed phase analysis by powder X-ray diffraction (XRD) using single-crystal data as the reference.

Results and Discussion

Synthesis and Crystal Growth of 1 by High-Temperature Solid-State Methods. First, we analyzed **1** obtained according to the procedure described by Cotton and Elder.[6] An anhydrous form of **1** was isolated upon heating of its dihydrate at 70 °C under vacuum followed by sublimation at 110 °C.

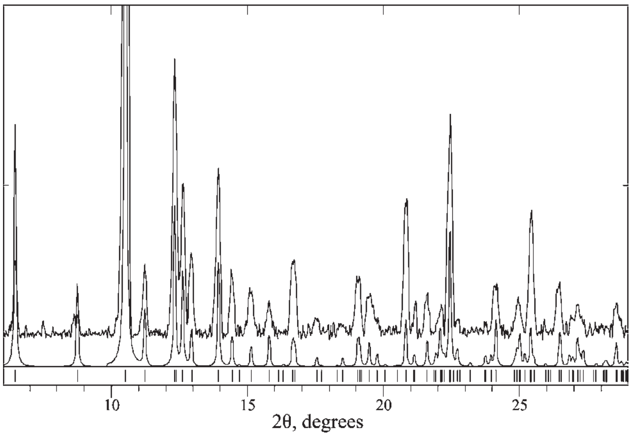

Figure 1. Comparison of the powder XRD pattern of **1** with the one calculated (gray) from single-crystal data.

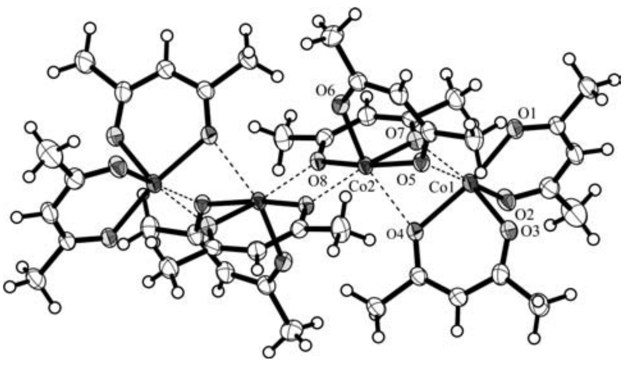

Figure 2. Molecular structure of terameric **1**. Atoms are represented by thermal ellipsoids at the 40% probability level. H atoms are shown as spheres of arbitrary radius. Only crystallographically independent Co and O atoms are labeled for clarity. Additional Co−O interactions are drawn by dashed lines.

In addition, the title compound was synthesized by the solid-state technique that we recently suggested[9] for the preparation of divalent transition-metal β-diketonates. A redox reaction between cobalt(III) acetylacetonate and a metal powder at 120 °C afforded unsolvated **1** in essentially quantitative yield according to eq 1:

$$2\text{Co(acac)}_3 + \text{Co} \rightarrow 3\text{Co(acac)}_2 \qquad (1)$$

In both cases, the identity of the purple bulk product was checked by powder XRD. It was unambiguously confirmed that the highly crystalline material represents a single phase (Figure 1) that corresponds to the tetrameric crystal structure (**1**) reported by Cotton and Elder.[6]

Because the crystal structure of the tetramer in Cotton and Elder's investigation[6] was obtained using a twinned crystal, we decided to re-collect the data set. Analysis of our experiment fully confirmed the crystal structure of **1** (Figure 2), as it was reported in ref 6.

The solid-state structure of **1** consists of tetrameric molecules that are formed by the association of four Co(acac)$_2$ units. Besides two chelating diketonate ligands, each Co atom has two additional Co−O interactions with neighboring unit(s). Thus, all metal atoms maintain a distorted octahedral coordination. In the polyhedral view, the structure can be represented by two pairs of

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Table 1. Selected Bond Distances (Å) for Cobalt Compounds with acac Ligands[a]

	Co−O$_c$	Co−O$_{c-b}$	Co−O$_b$	Co···Co
$Co_4(acac)_8$ (**1**)	2.00−2.03	2.02−2.11	2.09−2.20	2.988, 3.318
$Co_4(acac)_8$ (**1**) from ref 6b	1.95−2.07	1.99−2.12	2.11−2.28	3.20, 3.50
$Co_3(acac)_6 \cdot 2CHCl_3$ (**2**·$2CHCl_3$)	2.04−2.05	2.09	2.08−2.12	2.876
$Co_3(acac)_6 \cdot 2ClH_2CCH_2Cl$ (**2**·$2ClH_2CCH_2Cl$)	2.04−2.05	2.10	2.09−2.11	2.894
$Na^+[Co^{II}(acac)_3]^-$ from ref 15	2.06			
$Co(acac)_2(EtOH)_2$ (**3**)	2.01, 2.04			
$Co^{III}(acac)_3$ from ref 17	1.88			

[a] c = chelating; c−b = chelating−bridging; b = bridging.

face-sharing octahedra that share the common edge. For all Co atoms, the additional interactions are in the cis-oriented positions of the octahedra and are about 0.1−0.2 Å longer than the chelating bonds (Table 1). Interestingly, such a tetrameric type of association is unique among all other transition-metal (and heterometallic) β-diketonates. In particular, two other known examples of unsolvated cobalt(II) diketonates are trinuclear $Co_3(hfac)_6$ (hfac = hexafluoroacetylacetonate)[9] and mononuclear $Co(thd)_2$, in which the Co atom exhibits tetrahedral coordination by two bulky 2,2,6,6-tetramethylheptane-3,5-dionate ligands.[13]

Crystal Growth of 1 from Solutions. In the procedures described above, single crystals of the tetrameric form of **1** were obtained from the vapor phase at high temperature. It is known that crystallization of metal β-diketonates at different conditions can lead to the formation of other polymorph modifications.[8e,9,14] In order to check the existence of other forms, we studied the crystal growth of **1** from solutions of coordinating and noncoordinating solvents at room or lower temperatures.

Finely grounded **1** was found to be soluble in donor solvents, like alcohols. It is also quite soluble in noncoordinating solvents, such as toluene, dichloromethane, 1,2-dichloroethane, chloroform, and carbon tetrachloride, while dissolution in hexanes requires boiling temperatures. All solutions exhibit a typical purple color, indicating the retention of octahedral coordination for Co atoms. The saturated solution of **1** in hexanes upon cooling results in the formation of a highly crystalline product, which was confirmed by powder XRD to contain only the tetrameric form of diketonate (**1**), identical with that found upon high-temperature sublimation. On the other hand, attempts to grow **1** from chloroform led to the formation of trimer (**2**) solvated with $CHCl_3$ molecules (Figure 3). Powder XRD analysis confirmed the absence of other products in the bulk crystalline material (Figure 4).

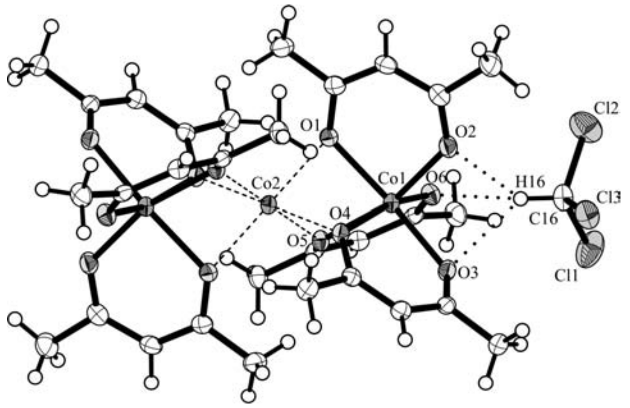

Figure 3. Molecular structure of **2**·$2CHCl_3$. The C−H···O interactions are shown by dotted lines.

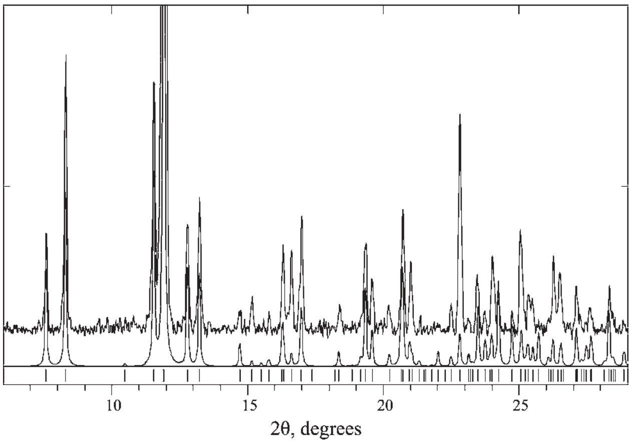

Figure 4. Comparison of powder XRD pattern of **2**·$2CHCl_3$ with the one calculated (gray) from single-crystal data.

The structure of trinuclear molecule **2** consists of a central Co atom sandwiched between two tris-chelated $[Co(acac)_3]$ units. As in the tetrameric form (**1**), all Co atoms in **2** exhibit an octahedral coordination environment. In the polyhedral representation, the structure of **2** can be viewed as a chain of three octahedra, in which the central one is sharing opposite faces with two others. The central Co atom is coordinated by six O atoms of the diketonate ligands that are all acting in a chelating−bridging manner. The bridging Co−O distances are just slightly longer than the chelating ones (Table 1). The Co−O distances in **2** are close to those reported for the $[Co^{II}(acac)_3]^-$ anion[15] and the $Co^{II}(acac)_2L_2$ (L = MeOH, EtOH, H_2O, py, Im) adducts[12g,16] but are significantly longer than the corresponding distances in $Co^{III}(acac)_3$[17] (Table 1), which indicates that the oxidation state of cobalt is 2+ in complex **2**. Such a type of aggregation

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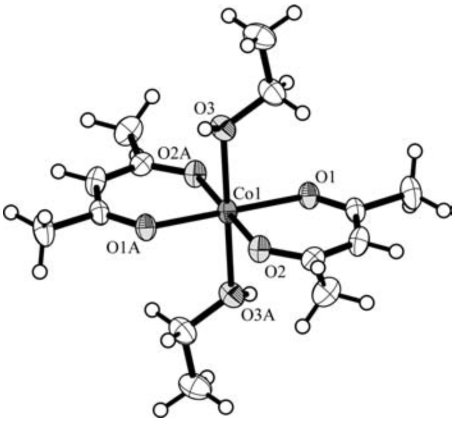

Figure 5. Molecular structure of **3**.

can be formulated as $\{Co^{2+}[Co(acac)_3^-]_2\}$ and was also found for $Mn_3(\beta\text{-dik})_6$ (β-dik = acac, hfac),[18,9] while in trinuclear nickel and cobalt hexafluoroacetylacetonates, each metal center is chelated by two ligands.[9,14a,19]

An interesting feature of this structure is that chloroform molecules form weak hydrogen C−H···O bonds with the diketonate core (Figure 3). Three oxygen centers from the outer part of the trinuclear molecule are involved in the formation of a trifurcated hydrogen bond (O···C 3.14−3.40 Å). This type of interaction was reported before[20] and represents a suitable structural model for the solvation of metal β-diketonates in a solution of weak H donors.

From other halogenated solvents such as CH_2Cl_2 and ClH_2CCH_2Cl, **1** was also crystallized as a trimer. The geometry of the trinuclear core (Table 1) is very similar to the one described for **2**·$2CHCl_3$. However, no additional interactions between the diketonates and solvent molecules were found. This observation indicates that the formation of trimer and diketonate ligand rearrangement is not caused by involvement of the core in weak hydrogen bonding. Nevertheless, we should note that all trinuclear forms contain solvent molecules in their crystal structures, while the one with tetranuclear units is solvent-free. Interestingly, the trinuclear structure can be converted back to tetramer **1** upon heating of the solvates of **2** at 70 °C under vacuum for 24 h.

We also tested the crystallization of **1** from solutions of coordinating solvents, such as ethanol, from which the mononuclear square-planar modification has been isolated.[7] The ethanol solution of **1** is air-sensitive and gradually turns green, indicating the formation of cobalt(III) complexes.[8e] In strictly air-free conditions, **1** was found to crystallize from ethanol in the form of its bis-adduct, *trans*-$Co(acac)_2(EtOH)_2$ (**3**). In the crystal structure of **3** (Figure 5), the octahedrally coordinated cobalt(II) center is surrounded by two chelating β-diketonate rings in an equatorial plane and two ethanol molecules in apical positions.

Table 2. Comparison of **1**[7] with Known Monomeric Square-Planar Metal(II) Acetylacetonates

	$Co(acac)_2$ (**1**)[7]	$Cu(acac)_2$ (**4**)[a]	$Cr(acac)_2$[22]	$Pd(acac)_2$[23]
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	10.276(2)	10.314(3)	10.325(3)	10.125(2)
b (Å)	4.677(1)	4.687(1)	4.748(1)	5.148(2)
c (Å)	11.296(2)	11.323(3)	11.445(4)	10.835(7)
α (deg)	90	90	90	90
β (deg)	92.22(2)	92.263(5)	91.60(3)	93.3(2)
γ (deg)	90	90	90	90
V (Å^3)	542.5(2)	547.0(3)	560.9(6)	535.0(1)
temp (K)	190(2)	190(2)	295	295
R1, wR2	0.052, 0.140	0.034, 0.088	0.099	0.129
color	green	blue/green	yellow	orange
M−O (Å)	1.92	1.91	1.98	1.96
M···C[b] (Å)	3.04	3.02	3.05	3.37

[a] This work. [b] Intermolecular interactions.

Similar to the high-temperature solid-state/gas-phase experiments, no traces of mononuclear **1** have been found for the crystals obtained from noncoordinating solvents at lower temperatures. No impurities were detected visually or by powder XRD analysis of the bulk products. We also confirmed that it seems impossible to crystallize **1** from coordinating solvents in the unsolvated form, free of cobalt coordination to basic donor atoms.

Analysis of Reported Mononuclear Square-Planar 1. The monomeric square-planar arrangement is known for three unsolvated divalent metal acetylacetonate compounds: $Cu(acac)_2$,[21] $Cr(acac)_2$,[22] and $Pd(acac)_2$.[23] The reported[7] **1** is isomorphous to all of those (Table 2) and exhibits the same type of planar unit stacking in the solid-state structure. One should note that $Pd(acac)_2$ is significantly different from the latter because of its atomic number, color, unit cell parameters, and length of intermolecular interactions. $Cr(acac)_2$ is only slightly different from the cobalt analogue in terms of its unit cell and M−O bond length. However, the latter has a distinct yellow color and is very air-sensitive, oxidizing instantly to chromium(III) species.

On the other hand, $Cu(acac)_2$ (**4**) has very similar characteristics to those reported[7] for **1**. Those include unit cell parameters, M−O bonds, and the length of the stacking interactions. In addition, copper(II) diketonates are known for their low affinity toward neutral donor ligands. Regarding the color, while the crystals of **4** obtained by sublimation look like large blue blocks, the smaller crystals grown from an ethanol solution appear as dichroic: green in the [001] direction and bluish-green in the directions at right angles to it. To further confirm the similarity between the two structures, we did a refinement of the data collected in ref 7 by inserting a Cu atom instead of a Co atom. As was expected for the sites with close atomic numbers, this resulted in only marginal changes, such as a small drop in the R values. We also performed data collection on the $Cu(acac)_2$ (**4**) crystal of similar size using the same data collection parameters (temperature,

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θ range, number of reflections for unit cell determination, etc.) as reported in ref 7. The results of refinement (Table 2) are within a stunning 0.4% difference from the structural parameters reported for **1**.

Taking into account the observations made in this work and the fact that mononuclear square-planar **1** was isolated[7] as just "several green crystals" and apparently did not experience a high affinity to the donor solvent molecules, we thus conclude that the crystal taken for data collection in ref 7 was likely **4**. The latter possibly appeared as a result of impurities in the starting materials or contaminated glassware.

Conclusions

We found no evidence for the existence of an unsolvated mononuclear form of **1** in all samples that can be obtained by using a variety of preparative techniques and crystallization conditions. It was confirmed that the structure of tetramer $Co_4(acac)_8$, reported back in 1964 by Cotton and Elder, is correct, the synthesis is reproducible, and the bulk material corresponds to single-crystal data. Additionally, the title compound can be isolated in tetranuclear form by reducing cobalt(III) acetylacetonate with cobalt metal in solvent-free conditions or by crystallization from a hexanes solution. On the other hand, from noncoordinating halogenated solvents, **1** crystallizes in the form of solvates as a trinuclear core molecule, in which all Co atoms exhibit octahedral coordination. From coordinating solvents such as ethanol, **1** was found to appear in the form of its bis-adduct $Co(acac)_2(EtOH)_2$. On the basis of observations made in this work and the details presented in the original paper, we suggest that the reported[7] mononuclear structure of square-planar acetylacetonate should likely contain copper instead of cobalt.

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Supporting Information Available: Details on synthesis and crystal growth, powder XRD patterns for the bulk products of **1** and its adducts, ATR-IR spectra, additional details on the XRD procedures, interatomic distances and angles, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.