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Mixed Ligand Octahedral Co^{3+} β-Diketonates, with Acetylacetone, Benzoylacetone and Dibenzoylmethane. Synthesis, Separation of Isomers and Characterization

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Abstract

Three series of complexes were studied: Co(acetylacetonate)$_n$(dibenzoylmethanato)$_{3-n}$, Co(acetylacetonate)$_n$(benzoylacetonate)$_{3-n}$ and Co(dibenzoylmethanato)$_n$(benzoylacetonate)$_{3-n}$. The product mixtures were separated by thin-layer chromatography. Complete separation of all compounds and stereoisomers was obtained. No attempt was made to separate optical isomers which exist for each single stereoisomer. Characterization was by elemental analyses, NMR spectroscopy and the separation characteristics. Electronic absorption spectra were measured in acetonitrile in the 200–800 nm region. Interpretation of the spectral data is provided in terms of $\Pi \rightarrow \Pi^*$, $d \rightarrow \Pi^*$, $d \rightarrow d^*$ transitions. The influence of geometrical isomerism is discussed.

Introduction

A study of three series of octahedral Co^{3+} β-diketonates is presented. Three β-diketones were used as ligands: 2,4-pentanedione [acetylacetone (acac)], 1-phenyl-1,3-butanedione [1-benzoylacetone (bzac)] and 1,3-diphenyl-1,3-propanedione [dibenzoylmethane (dbzm)].

Two types of complexes were obtained: M(AA)$_n$(BB)$_{3-n}$ and M(AA)$_n$(CD)$_{3-n}$, where M is the metal atom, AA and BB are symmetric bidentate ligands (acac, dbzm), and CD is an unsymmetric bidentate ligand (bzac). The former type is represented by the series Co(acac)$_n$(dbzm)$_{3-n}$ (four complexes $n = 0, 1, 2, 3$), and the latter includes the two series Co(acac)$_n$(bzac)$_{3-n}$ and Co(dbzm)$_n$(bzac)$_{3-n}$. In these two series when $n = 0$ there are two geometric isomers, and three geometric isomers for $n = 1$. The nomenclature is that proposed by Fay [1].

As was done in previous work [2], the method of separation was thin-layer chromatography, which allowed good separation of all compounds and their stereoisomers. NMR spectroscopy was used as the main characterization technique. The methyl region of the spectra was used to identify the various compounds [2].

Electronic absorption spectra of Co^{3+} were reported in the past [3]. Most of the work done was on γ-substituted derivatives. The effect of stereoisomerism on the absorption spectra, in acetonitrile, is examined here.

Experimental

Syntheses

All reagents used were of commercial grade. 2,4-Pentanedione (Aldrich) was distilled as described elsewhere [2]. 1-Phenyl-1,3-butanedione, 1,3-diphenyl-1,3-propanedione and CoCO$_3$ (all from Aldrich) were used as received without further purification. The three series of complexes were obtained by using a mixture of two β-diketones in the known method of synthesis for Co(acac)$_3$ [4]. The elemental analyses and melting points of the newly prepared compounds are reported. Data regarding known compounds were in very good agreement with those reported in the literature.

Chromatography

Separation of all mixtures was done on silica plates from Merck (PF^{256}). About 40 mg of mixture were dissolved in 0.5 ml of dry ether and applied on a single preactivated plate (1 h at 70 °C). Development was with chloroform, and after 2–4 h, complete separation of all compounds and their isomers was achieved. The dry silica bands were removed and washed thoroughly with ether. The ether was filtered and evaporated. No attempt was made to separate the pairs of optical isomers existing for each compound.

NMR data were recorded on a Varian EM-390 in CDCl$_3$ with tetramethylsilane as an internal standard. UV + visible spectra were done on a Perkin-Elmer 330 spectrophotometer, in acetonitrile (1 cm quartz cell).

Two compounds were not synthesized – the *cis* and *trans* isomers of Co(dbzm)(bzac)(acac) – since

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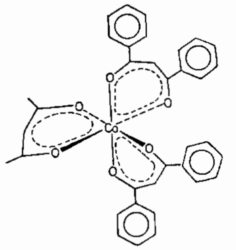

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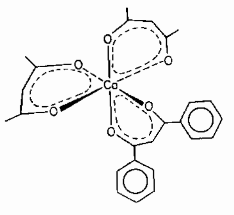

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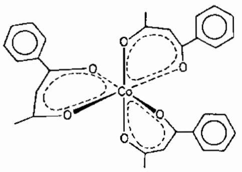

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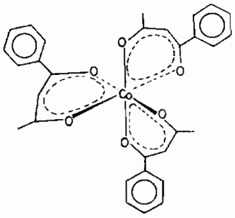

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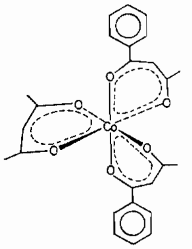

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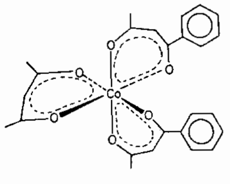

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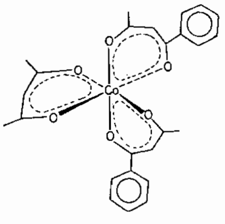

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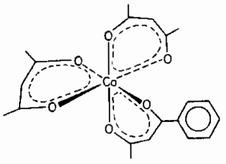

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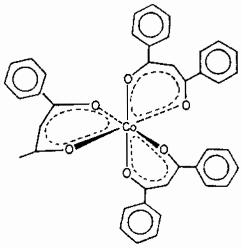

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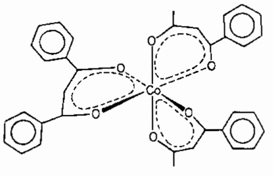

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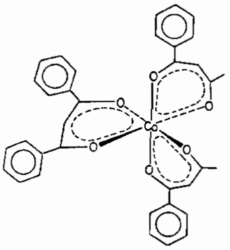

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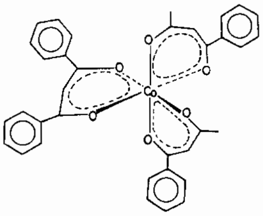

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Fig. 1. Compounds and their isomers studied [not presented Co(dbzm)$_3$, Co(acac)$_3$]. First series: Co(dbzm)$_3$, Co(dbzm)$_2$(acac) **1**, Co(dbzm)(acac)$_2$ **2**, Co(acac)$_3$. Second series: *trans*-Co(bzac)$_3$ **3**, *cis*-Co(bzac)$_3$ **4**, *trans–cis*-Co(acac)(bzac)$_2$ **5**, *cis–trans*-Co(acac)(bzac)$_2$ **6**, *cis–cis*-Co(acac)(bzac)$_2$ **7**, Co(acac)$_2$(bzac) **8**, Co(acac)$_3$. Third series: Co(dbzm)$_3$, Co(dbzm)$_2$(bzac) **9**, *cis–trans*-Co(dbzm)(bzac)$_2$ **10**, *trans–cis*-Co(dbzm)(bzac)$_2$ **11**, *cis–cis*-Co(dbzm)(bzac)$_2$ **12**, *cis*-Co(bzac)$_3$ **4**, *trans*-Co(bzac)$_3$ **3**.

the preparation of these two isomers involves separation and identification of all the other 14 compounds synthesized for this study.

Results and Discussion

Relative Yield

All three series of complexes were prepared by allowing a mixture of two ligands to react with CoCO$_3$ (see Fig. 1 and Table 1 for structure and analytical data). Of particular interest is the relative yield of the isomers in the two series Co(acac)$_n$(bzac)$_{3-n}$ and Co(dbzm)$_n$(bzac)$_{3-n}$, for $n = 0, 1$. When $n = 0$, there are two possible geometric isomers: *cis* and *trans*. Statistically, the yield should be 1:3 in favor of the *trans* isomer, but as was pointed out in the past [5,6] there is a slight stability preference for the *trans* isomer over the *cis* one, resulting in a higher yield of the *trans* isomer (76–77%) and a slightly lower yield of the *cis* isomer (23–24%).

Compared to results obtained in this laboratory [2], with a bromo-substituted benzoylacetone there is a change in the relative yield. The presence of the bromine in the phenyl ring of bzac counteracts the stability preference of the *trans* isomers, and results in a pure statistical yield for these isomers. For $n = 1$ the yield was statistical, indicating that there is no stability preference for any one of the three isomers.

Chromatography and Characterization

Preparative thin-layer chromatography was used to separate the product mixtures. Generally the elution order was according to the number of phenyl groups present in the complexes [2]. Of significant importance is the geometry of the complex. Whenever there are phenyl groups in a relative *trans* position, it results in a higher R_f value. Thus the *trans*-Co(bzac)$_3$ is eluted before the *cis*-Co(bzac)$_3$. Even the *trans–cis*-Co(acac)(bzac)$_2$ is eluted before the *cis*-Co(bzac)$_3$. In the series Co(dbzm)$_n$(bzac)$_{3-n}$, the *trans–cis*-Co(dbzm)(bzac)$_2$ is eluted before the other geometric isomers (*cis–trans* and *cis–cis*), and also before the *cis*-Co(bzac)$_3$. A similar *trans* effect in elution order was obtained in a previous report from this laboratory [2].

Characterization of the compounds was mainly by NMR spectroscopy, using the methyl region of the spectra (Table II).

TABLE I. Analytical Data and Melting Points (All the compounds are presented according to their elution order in the separation.)

		Calculated			Found			Melting point (°C)
		C	H	O	C	H	O	
Co(dbzm)$_3$		74.07	4.56	13.16	74.14	4.62	13.10	–
Co(dbzm)$_2$(acac)	(1)	69.42	4.83	15.85	69.56	4.91	15.81	217–218[a]
Co(dbzm)(acac)$_2$	(2)	62.37	5.23	19.94	62.31	5.29	20.09	182–183
Co(acac)$_3$		50.43	5.92	26.87	50.62	6.12	26.59	–
trans-Co(bzac)$_3$	(3)	66.30	5.01	17.66	66.62	5.35	17.27	–
trans–cis-Co(bzac)$_2$(acac)	(5)	62.37	5.23	19.94	62.43	5.31	19.81	153–154
cis-Co(bzac)$_3$	(4)	66.30	5.01	17.66	66.28	5.17	17.39	–
cis-trans-Co(bzac)$_2$(acac)	(6)	62.37	5.23	19.94	62.13	5.37	20.15	171–172
cis–cis-Co(bzac)$_2$(acac)	(7)	62.37	5.23	19.94	61.98	5.04	20.20	175–176
Co(bzac)(acac)$_2$	(8)	57.29	5.53	22.89	57.01	5.33	22.97	192–193[a]
Co(acac)$_3$		50.43	5.92	26.87	50.61	5.79	26.83	–
Co(dbzm)$_3$		74.07	4.56	13.16	74.20	4.72	13.05	–
Co(dbzm)$_2$(bzac)	(9)	71.96	4.68	14.38	72.21	4.82	14.17	208–209
trans–cis-Co(dbzm)(bzac)$_2$	(11)	69.42	4.83	15.85	69.95	4.98	15.51	204–206
trans-Co(bzac)$_3$	(3)	66.30	5.01	17.66	66.61	4.79	17.92	–
cis–trans-Co(dbzm)(bzac)$_2$	(10)	69.42	4.83	15.85	69.67	5.01	15.80	129–130
cis–cis-Co(dbzm)(bzac)$_2$	(12)	69.42	4.83	15.85	69.52	4.67	15.71	124–126
cis-Co(bzac)$_3$	(4)	66.30	5.01	17.66	66.57	4.85	17.83	–

[a] Decomposition.

TABLE II. Methyl Region, NMR Resonances (Hz), Relative to Tetramethylsilane (CDCl$_3$)

	Methyl resonances	
	dbzm and bzac	acac
Co(dbzm)$_3$	–	–
Co(dbzm)$_2$(acac)	–	–134.9
Co(dbzm)(acac)$_2$	–	–132.6, –134.8
Co(acac)$_3$	–	–132.0
trans-Co(bzac)$_3$	–142.3, –141.9(broad)	–
trans–cis-Co(bzac)$_2$(acac)	–140.3	–133.3
cis-Co(bzac)$_3$	–139.8	–
cis–trans-Co(bzac)$_2$(acac)	–141.2	–133.3
cis–cis-Co(bzac)$_2$(acac)	–141.3, –138.2	–134.2, –132.5
Co(bzac)(acac)$_2$	–138.0	–133.4, –132.6, –131.0, –129.3
Co(acac)$_3$	–	–132.0
Co(dbzm)$_3$	–	–
Co(dbzm)$_2$(bzac)	–144.3	–
trans–cis-Co(dbzm)(bzac)$_2$	–142.5	–
trans-Co(bzac)$_3$	–142.3, –141.9(broad)	–
cis–trans-Co(dbzm)(bzac)$_2$	–143.3	–
cis–cis-Co(dbzm)(bzac)$_2$	–141.9, –138.7	–
cis-Co(bzac)$_3$	–139.8	–

The first series Co(acac)$_n$(dbzm)$_{3-n}$ has four compounds. When $n = 0$, there are no methyl resonances (Table II). For $n = 1$, there is a single methyl at –134.9 Hz. For $n = 2$, two methyl resonances are observed. A single methyl is observed for Co(acac)$_3$. It has no dbzm groups compared to the single methyl resonance of Co(acac)(dbzm)$_2$.

In the second series Co(acac)$_n$(bzac)$_{3-n}$, there are two types of methyl resonances: the acac methyls which resonate at –132 ± 2 Hz and the bzac methyls which resonate at –140 ± 2 Hz.

The first complex to be eluted is the *trans*-Co(bzac), which has three different methyls, which are not completely resolved, resulting in a broad resonance at −141.9 Hz. The second band in chromatography contained the *trans–cis*-Co(bzac)$_2$-acac. It has two methyl resonances, the same as the *cis–trans*-Co(bzac)$_2$acac (fourth band in elution). There is a slight shift of the bzac methyl between these two isomers (~1 Hz). This shift and the elution order confirm the identification of these two isomers, based upon results obtained in this laboratory in the past [2, 7].

The *cis*-Co(bzac)$_3$ has a single methyl resonance at −139.8 Hz, since all three methyls are equivalent.

The *cis–cis*-Co(bzac)$_2$acac has four different methyls, the Co(bzac)(acac)$_2$ has five methyl resonances, and the seventh band is the Co(acac)$_3$.

The third series Co(dbzm)$_n$(bzac)$_{3-n}$ has only bzac methyls. All compounds are distinguishable according to their NMR spectra, elution order and elemental analysis. The *trans–cis*-Co(dbzm)(bzac)$_2$ and the *cis–trans*-Co(dbzm)(bzac)$_2$ were identified according to their elution order (*trans* effect), since they are practically identical in the NMR spectrum.

Spectroscopic Observations

Electronic spectral studies of metal β-diketonates were made in the past by several groups [3, 8–11]. The main effort was to determine the effect of various γ-substituents on the electronic structure of quasi-aromatic chelate rings [3, 8, 11]. Geometrical effects were not studied, although compounds which have geometrical isomers were examined [11].

Ligand Field Transitions

Examining the first series Co(acac)$_n$(dbzm)$_{3-n}$ (Table III), it can be noticed that there is a slight change in the absorption band, shifting to a longer wavelength with the growing number of phenyl groups in the complex. This indicates, as was already stated elsewhere [3], a weak inductive effect of the phenyl ring, predominated by the resonance effect.

This effect is also holding for the other two series. There is no influence of different geometrical configuration on the $d \rightarrow d^*$ transition.

Electron Transfer Transitions

In these bands it is difficult to find direct evidence for the influence of geometric structure on the electron transfer.

There is a shift of the bands to higher energy when one of the acac ligands is replaced by a dbzm or a bzac ligand. The electron transfer for Co(acac)$_3$ has the longest wavelength (390 nm), while Co(dbzm)$_3$ has 381 nm for this transition and Co(bzac)(acac)$_2$ has the transition at 358 nm. This lack of direct correlation between the number of bzac or dbzm ligands in the complex and the absorption wavelength may suggest that there may be an influence of the geometric structure of the diketonate on the energy of the transition.

TABLE III. UV and Visible Absorption Bands [λ max (nm)]

	$d \rightarrow d^*$	$d \rightarrow \Pi^*$	$\Pi \rightarrow \Pi^*$
Co(dbzm)$_3$	601.2	381	284
Co(dbzm)$_2$(acac)	598.3	383	271
Co(dbzm)(acac)$_2$	594.3	382	263
Co(acac)$_3$	591.0	390	246
trans-Co(bzac)$_3$	596.5	368	262
trans–cis-Co(bzac)$_2$(acac)	594.2	352	272
cis-Co(bzac)$_3$	596.3	367	260
cis–trans-Co(bzac)$_2$(acac)	594.2	351	274
cis–cis-Co(bzac)$_2$(acac)	594.3	352	268
Co(bzac)(acac)$_2$	592.3	358	257
Co(acac)$_3$	591.0	390	246
Co(dbzm)$_3$	601.2	381	284
Co(dbzm)$_2$(bzac)	600.1	375	282
trans–cis-Co(dbzm)(bzac)$_2$	598.2	365	262
trans-Co(bzac)$_3$	596.5	368	262
cis–trans-Co(dbzm)(bzac)$_2$	598.3	360	268
cis–cis-Co(dbzm)(bzac)$_2$	598.2	364	260
cis-Co(bzac)$_3$	596.3	367	260

Ligand Transitions

From the UV absorption bands of the first series, it is evident that replacement of an acac ligand by a dbzm ligand shifts the absorption band to longer wavelengths [246 nm for Co(acac)$_3$ and 284 nm for Co(dbzm)$_3$]. In the second series the same trend is observed with the bzac and acac ligands. It is interesting to note that there are slight changes among geometric isomers. This shift is probably due to the inductive effect caused by the phenyl groups which are arranged in various relative positions [compare 262 nm for *trans*-Co(bzac)$_3$ and 260 nm for *cis*-Co(bzac)$_3$, or 272 nm, 274 nm and 268 nm for the *trans–cis*, *cis–trans* and *cis–cis* isomers of Co(bzac)$_2$-(acac), respectively].

The same phenomena are noticed with the third series Co(dbzm)$_n$(bzac)$_{3-n}$, indicating a connection between the geometric configuration of the complex and the ligand transitions.

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