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Stereochemistry of β-diketone Complexes of Cobalt(III). VIII. Optical Activity of (β-diketonato)bisethylenediaminecobalt(III) Cations

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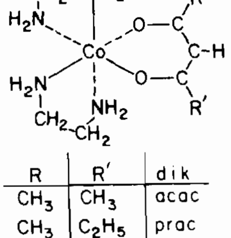
The complexes, $[Coen_2dik]^{2+}$, where dik equals the anion of 2,4-pentanedione, 2,4-hexanedione, 1-trifluomethyl-1,4-butanedione, 1-carboxyethyl-2-propanone, and 1-carboxyethyl-acetophenone, were resolved using sodium(+)-arsenyltartrate. The absorption, ORD and CD spectra of $(+)[Coen_2dik]^{2+}$ were recorded in the ultraviolet and visible region and the electronic transitions assigned. The absolute configuration of the complexes is assigned as Λ. The origin of the ultraviolet absorption of β-diketone complexes of cobalt(III) is discussed and a new assignment scheme is proposed.

Introduction

A continuing interest in the electronic structure of β-diketone complexes of cobalt(III) has prompted the examination of the visible and electronic spectra of a number of mono,[1] bis,[2] and tris[3] β–diketonato complexes. Optical rotatory dispersion and circular dichroism spectra of these complexes are also useful in this context. Detailed reports on the optical activity of the tris[4] and bis[2] complexes have appeared, while only brief mention has been made of the mono chelated compounds.[5] We wish to report here the spectral properties of several compounds of the form $[Coen_2dik]^{2+}$. A structural representation of the materials studied is given in Figure 1.



R	R'	dik
CH_3	CH_3	acac
CH_3	C_2H_5	prac
CH_3	CF_3	tfac
CH_3	OC_2H_5	etoac
C_6H_5	OC_2H_5	bzoac

Figure 1. Structural representation of $[Co\ en_2dik]^{2+}$.

Experimental Section

Materials. The complexes, $[Coen_2dik]I_2$,[1] *cis*$[Coacac_2(NH_3)Cl]$,[2] $[Coacac_3]$[6] and $[Coacac(NH_3)_4]Cl$,[7] were prepared according to previously reported procedures. Purity was confirmed by elemental analyses and spectral measurements. Sodium(+)-artenyltartrate was prepared by the method of Henderson and Ewing.[8]

$(+)[Coen_2dik]I_2$. A mixture of 0.005 moles of the complex and 1.67 g (0.01 moles) of silver acetate in 10 ml of water was ground in a mortar for ten minutes. The mixture was filtered, the residue washed with 5 ml of water, and the washings added to the filtrate. A solution of 2.62 g (0.01 moles) of sodium-(+)-arsenyltartrate in 5 ml of water was then added to the filtrate and the resulting solution allowed to stand at room temperature for several days. During this time the solid diastereoisomer formed. The solid was collected and suspended in a solution of 3.0 g of potassium iodide in 5 ml of 0.4 *M* potassium hydroxide. The resulting mass was isolated on a filter and extracted with methanol. The methanolic filtrate was evaporated to dryness in an air stream and the residue reprecipitated from water by the addition of powdered potassium iodide. The pure dextro isomer was collected on a filter and washed with a little ethanol, ether an dair dried. Yield was ~60% of the pure optical isomer. The corresponding chloride salts were prepared by grinding 0.28 g (0.002 moles) of silver chloride with 10 ml of aqueous solution of 0.001 moles of $(+)[Coen_2dik]I_2$. The silver iodide was filtered off and the filtrate evaporated to dryness. The residue was taken up in methanol, filtered and flooded with diethylether. The resulting precipitate $(+)[Coen_2dik]Cl_2$ was isolated and air dried.

Spectral Measurements. Absorption spectra were recorded on a Cary Model 14 spectrophotometer while ORD and CD curves were recorded on a Durham-

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Table I. Elemental Analysis[a] of $(+)[Co\ en_2dik]I_2$.

dik	$[\alpha]_D$	Found % C	Found % H	Found % N	Calculated % C	Calculated % H	Calculated % N
acac	+406	19.65[b]	4.58	10.19	19.67	4.74	10.06
prac	+406	21.28[b]	4.86	9.93	21.29	4.71	9.85
tfac	+416	18.53	3.46	9.59	18.42	3.42	9.38
etoac	+371	21.15	4.46	9.92	21.43	4.56	9.77
bzoac	+332	27.27[c]	4.72	8.48	27.18	4.46	8.56

[a] Microanalyses by Nemeth, University of Illinois. [b] Assuming one water of crystallization. [c] Assuming two waters of crystallization.

Table II. Absorption and Circular Dichroism Maxima (kK) for $(+)[Co\ en_2dik]^{2+}$ in Water.

acac			prac			tfac			etoac			bzoac			
ν	ν	$\Delta\varepsilon$	ν	ν	$\Delta\varepsilon$	ν	ν	$\Delta\varepsilon$	ν	ν	$\Delta\varepsilon$	ν	ν	$\Delta\varepsilon$	Assignment
20.1(2.14)[a]	20.2	+ 2.4	20.1(2.16)	20.2	+ 2.4	20.3(2.12)	20.5	+ 2.5	20.0(2.16)	18.9	+ 1.8	20.0(2.02)	19.0	+1.9	$^1A_1 \rightarrow {}^1A_2 + {}^1B_2 + {}^1B_1$
~26	26.8	— 1.3	~26	26.7	— 1.3	~26	~26		~26	26.5	— 0.7	~25	~26		$^1A_1 \rightarrow {}^1A_1 + {}^1A_2 + {}^1B_2$
39.0(3.62)	31.0	—10	30.9(3.61)	30.9	—10	30.1(3.42)	29.9	— 5.8	34.1(3.84)	34.0	—14	31.1(3.82)	31.3	—8	$t_{2g} \rightarrow \pi^*$
~37	35.7	— 3	~37	35.6	— 3	~37	~36		~38	38.0	— 5		~33		$\pi \rightarrow e_g$
~42	40.8	—11	~42	40.0	—11	~41	40.0	—13	~43	43.5	—12	40.3(4.19)	38.5	—6	$\sigma_L \rightarrow e_g$

[a] log ε_{max}

Jasco ORD/UV/CD/5 instrument. Specific rotations were determined at the Na_D line using 0.1% aqueous solution with a ETL-NPL Bendix automatic polarimeter (Type 143A). All measurements were made at room temperature.

Results and Discussion

Optically active complexes of $[Coen_2dik]^{2+}$ were first obtained via the reaction[9] of acac and prac with optically active $[Coen_2ClH_2O]^{2+}$. The first direct resolution of one of the complexes of this type was accomplished for $[Coen_2acac]^{2+}$ using sodium(+)-arsenyltartrate as a resolving agent.[10] The resolution of all the complexes reported here was performed using a simple modification of that method. Attempts to resolve complexes of benzoylacetone and thenoyltrifluoroacetone were unsuccessful. Elemental analyses and specific rotation of the resolved materials are given in Table I.

Electronic Spectra. The frequencies of the absorption maxima in the uv and visible spectra of $[Coen_2dik]I_2$ are collected in Table II with the respective extinction coefficients. Typical spectra are shown in Figures 2 and 3. Measurements in the 36-46 kK range were made with the chloride salts.

The spectra show a low intensity band in the visible region at ~20 kK which arises from a cobalt(III) d→d transition, *i.e.*, the first octahedral band $^1A_{1g} \rightarrow {}^1T_{1g}$. The actual symmetry of the complexes is C_2 and, for this low symmetry case, three absorption bands are expected $^1A_1 \rightarrow {}^1B_1 + {}^1A_2 + {}^1B_2$. The overlap of these absorptions gives rise to the observed unresolved single absorption. Since the splittings of the first band are apparently small, the complexes are considered to be pseudo-octahedral. The position of the visible absorption band of $[Coen_2dik]^{2+}$ is only slightly dependent on the substituent on the β-diketone, varying from 20.0 to 20.3 kK. The frequency variation is small enough to support the assumption that the ligand field about the metal is constant and is determined by the ethylenediamine ligands and the oxygen atoms of the β-diketone ligand. The second octahedral Co^{III} absorption $^1A_{1g} \rightarrow {}^1T_{2g}$ is seen in the

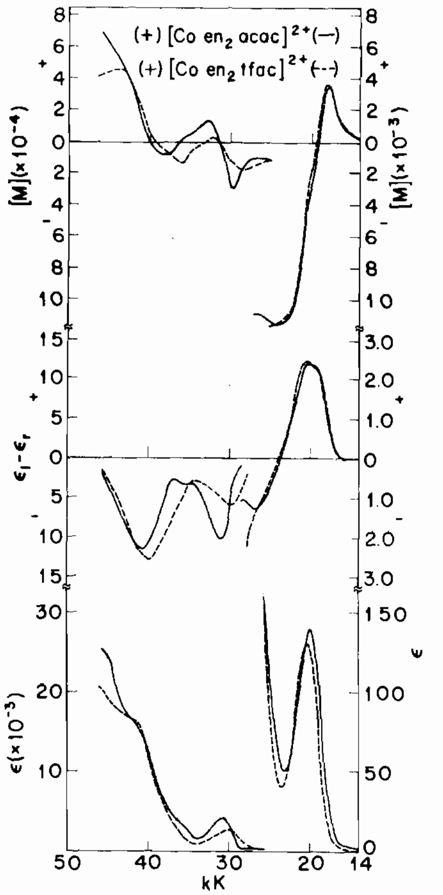

Figure 2. The optical rotatory dispersion (top), circular dichroism (middle) and absorption spectra (bottom) of (+) $[Co\ en_2dik]^{2+}$, dik=acac, tfac, in water.

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spectra as a poorly resolved shoulder around 26 kK.

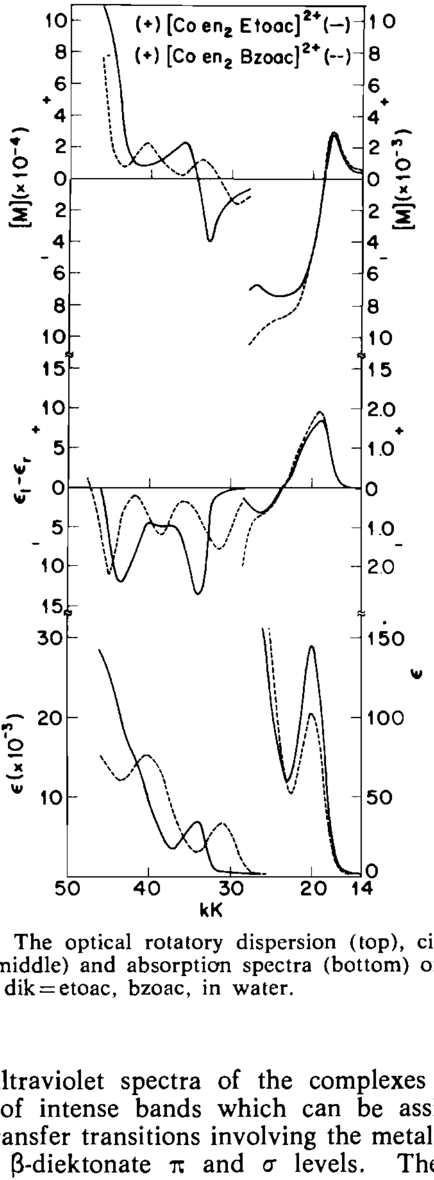

Figure 3. The optical rotatory dispersion (top), circular dichroism (middle) and absorption spectra (bottom) of (+)[Co en$_2$dik]$^{2+}$, dik = etoac, bzoac, in water.

The ultraviolet spectra of the complexes show a number of intense bands which can be assigned to charge transfer transitions involving the metal d levels and the β-diektonate π and σ levels. The lowest energy band, 30-34 kK, has been previously assigned to $t_{2g}\rightarrow\pi^*$, metal-to-ligand charge transfer.[11] The next higher energy absorption appears as a weak shoulder in the 33-38 kK region and can be assigned to a $\pi\rightarrow e_g$ ligand-to-metal charge transfer.[12] The highest energy absorption is seen as a prominent shoulder in 38-41 kK. By analogy with other metal β-diektonates, this band can be assigned to a $\sigma_L\rightarrow e_g$ ligand-to-metal charge transfer.[13] The maxima of the charge transfer bands are clearly shown in the CD spectra and the energy of the transitions can be obtained from these spectra. Since the d orbital energies remain approximately constant, the frequency changes in the charge transfer bands mainly correspond to changes in the energy levels of the β-diketone which are caused by the variation in β substituent. For example, substituting the methyl by trifluoromethyl gives rise to a stabilization of the π* level. This results in a red shift of $t_{2g}\rightarrow\pi^*$ charge transfer band. On the other hand, replacing methyl by ethoxy destabilizes the π* level and stabilizes the π level. In this case, charge transfer bands are all blue shifted. Lastly, substituting phenyl for methyl stabilizes the π* and destabilizes the π levels through a conjugative effect. The resulting spectrum then shows a red shift for all the charge transfer bands. The effect of the β substituent on the π, π* levels of the β-diketonate ligand observed here is in general agreement with previous work on [Fe(dik)$_3$].[15] The splitting of the t_{2g} and e_g levels is assumed to be constant at 22 kK. The average ligand field parameter for [Coen$_2$acac]$^{2+}$ is computed using[14]

$$\Delta=\frac{2\Delta_{acac}+\Delta_{en}}{6}$$

with Δ_{en} = 23.2 kK[18] and Δ_{acac} = 20.0. The latter quantity is obtained from Jorgensen's expression

$$\Delta_{acac}=(acac)\cdot g(Co^{III})$$

with g = 19.0 kK[14] and f = 1.05.[15] With Δ and the energies of the charge transfer bands, the ligand $\pi\rightarrow\pi^*$ transition can be computed.

$$(\pi\rightarrow\pi^*)=(\pi\rightarrow e_g)+(t_{2g}\rightarrow\pi^*)-(t_{2g}\rightarrow e_g)$$

The values are: acac (44.7 kK), prac (44.5 kK), tfac (43.9 kK), etoac (50.0 kK), bzoac (42.3 kK). Unfortunately, the $\pi\rightarrow\pi^*$ absorptions for [Coen$_2$dik]$^{2+}$ are obscured by the tail of the intense ethylenediaminecobalt(III) $\sigma_L\rightarrow e_g$ charge transfer band at ~47 kK.[16] The values for acac and tfac agree reasonably well with those from the spectra of [Co(dik)$_3$]; *i.e.*, for acac $\pi\rightarrow\pi^*$ is seen at 44 kK (see Figure 5) and for tfac $\pi\rightarrow\pi^*$ is seen at ~43 kK.[17] Spectra of the tris etoac and bzoac complexes have not been reported. It has been observed, however, that the $\pi\rightarrow\pi^*$ transition of etoac is about 4 kK higher in energy than for acac in the complexes Cu(dik)$_2$.[18] The internal consistency of the assignment scheme lends support to the proposal.

The assignments presented here for the ultraviolet bands should be applicable to the spectra of [Co(dik)$_3$] and [Co(dik)$_2$L$_2$]$^{n+}$. Typical spectra for these complexese are shown in Figure 4. Although the frequencies of the absorptions differ, the overall spectral pattern is the same for mono, bis and tris chelated complexes. As the rule of average environment predicts, the ligand field bands move to higher energy as the oxygen donors are replaced by nitrogen donors. Conversely, the first charge transfer band $t_{2g}\rightarrow\pi^*$ remains at approximately the same frequency for the three complexes. This is consistent with the notion that the t_{2g} level is essentially non-bonding and that the energy of the π* is invariant in these complexes. An obvious conclusion that can be drawn here is that

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the t_{2g}, π bonding effects must be nearly the same for the three types of complexes. If this is true, then then π → π* transition should be at the same frequency foı the three complexes Unfortuantely, the severe overlap of the bands in this region makes a direct test of this prediction difficult. It is evident that ligand field splitting in these complexes is almost solely determined by the sigma bonding of the ligands. The variation in energy of the e_g levels should give rise to a blue shift in both the π → e_g and σ_L → e_g charge transfer bands when going from [Co $acac_3$] to [Co acac $(NH_3)_4]^{2+}$. The bands near 35 kK and 40 kK do show the expected behavior.

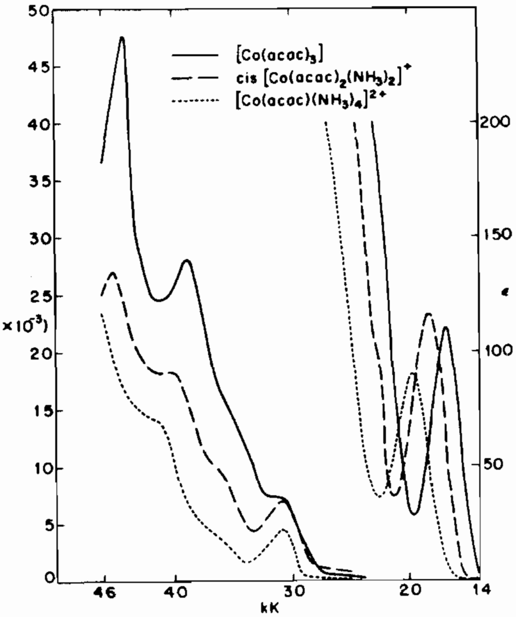

Figure 4. Absorption spectrum of [Co $acac_3$] (———), cis[Co $acac_2(NH_3)_2$]Cl (— —) and Co[$acac(NH_3)_4$]Cl_2 (- - -) in methanol.

Based on molecular orbital calculations the bands at 30.6, ~ 35 and 38.8 kK in the spectrum of [Co $acac_3$] have been recently assigned to charge transfer transitions of the type t_{g2} → π*.[19] The first two bands are thought to arise from the splitting of the triply degenerate t_{2g} → π* transition in D_3 symmetry. The work presented here indicates that the second band is due to a different charge transfer, π → e_g, while the high energy band is most probably σ_l→e_g. The large quantum yield for photoreduction of [Co $acac_3$] at 37.7 kK is indicative of the presence of a ligand-to-metal absorption in this region.[20]

Optical Rotatory iDspersion and Circular Dichroism. Typical ORD and CD curves are displayed in Figures 2 and 3 . The general pattern is the same for all the complexes and spectra for prac and acac derivatives are superimposable within experimental error. The ORD curves show a positive Cotton effect at the first octahedral cobalt(III) band and a number of overlapping Cotton effects at the charge transfer bands in the ultraviolet region. There also appears to be tail of a strong positive Cotton effect at > 46 kK. The CD spectra more clearly show the correspondence of the Cotton effects and the absorption maxima. The frequencies, intensities and signs of the CD maxima are collected in Table II. The CD spectra show two Cotton effects in the region of the d-d electronic transitions: a positive one at ~ 20 kK and a negative one at ~ 26 kK. The CD maxima correspond to the first and second octahedral cobalt(III) bands. The single maxima result from the overlap of the expected low symmetry components. The shapes of the CD Curves of (+)[Co $en_2dik]^{2+}$ are almost identical and possess the same sign. For such similar complexes it is safe to assign them the same relative optical configuration. It has been proposed that the configuration of the C_2 cobalt(III) complexes like [Co $en_2L_2]^{n+}$ can be related to the known configuration of $(+)[Co(en)_3]^{3+}$, Λ.[5] The relative configuration of (+)[Co $en_2acac]^{+2}$ has been assigned the same as Λ[Co $en_3]^{3+}$. Thus the absolute configurations of all (+)[Co en_2dik] can be assigned as Λ. The ultraviolet CD spectra show moderate intensity negative Cotton effects for the three charge transfer bands. As expected, the β-diketone π → π* transition does not appear to be optically active. Of course, accurate measurements in this region are difficult for highly absorbing solutions.

The spectral properties of one other optically active mono acetylacetone complex $(-)_{546}$[Co $ox_2acac]^{2-}$ have been determined. The ultraviolet CD spectrum shows negative Cotton effects for the absorption at 30.5 kK, 40 kK, and at 36kK (shoulder). The high energy band can be assigned to an oxalate dependent charge transfer band. The bands at 30.5 kK and 36 kK can be assigned to the charge transfer transitions t_{2g} → π* and σ_L → e_g. As expected the first band is at about the same frequencies as for [Co $en_2acac]^{2+}$. This is due to the non-bonding nature of the t_{2g} level and the essentailly unperturbed energy π* level of the acac ligand. On the other hand, the σ_L → e_g band is at considerably lower energy in [Co $ox_2acac]^-$ than in [Co $en_2acac]^{2+}$. This is related to the stabilization of the e_g level in the former complex because of the weaker σ donor strength of the oxalate ligand in comparison to ethylenediamine.

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