Contribution from the Department of Chemistry,
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

Stereochemistry of β-Diketone Complexes of Cobalt(III). IV. Optical Activity of *cis*-Diaminebis(acetylacetonato)cobalt(III) Cations

By L. J. BOUCHER

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The resolution of *cis*-$[\mathrm{Co(acac)_2(NH_3)_2}]\mathrm{I}$ and $[\mathrm{Co(acac)_2en}]\mathrm{I}$ by formation of diastereoisomeric salts is reported. Aqueous solutions of $(+)_{546}[\mathrm{Co(acac)_2en}]\mathrm{I}$ are optically stable at $\sim$100° for many hours while those of $(+)_{546}$-*cis*-$[\mathrm{Co(acac)_2(NH_3)_2}]\mathrm{I}$ lose optical activity with decomposition of the complex. Optical rotatory dispersion, circular dichroism, and absorption spectra of the ions are presented and assignments of the bands are made. The absolute configuration of $(+)_{546}[\mathrm{Co(acac)_2en}]\mathrm{I}$ and $(+)_{546}[\mathrm{Co(acac)_2(NH_3)_2}]\mathrm{I}$, based on the positive sign of the dominant CD band ($A_2 + B_2$) in the region of the first octahedral transition of cobalt(III), is assigned as $\Delta(C_2)$. The ultraviolet CD spectrum is discussed in terms of cobalt–ligand-$d\pi \rightarrow \pi^*$ transitions and $\pi \rightarrow \pi^*$ transitions of the acetylacetonate anion.

Although studies of the stereochemical transformations of complexes of cobalt(III) containing two β-diketone ligands have been initiated,[1] the bulk of work has dealt with the syntheses, separation of isomers, and structural characterization of these materials.[2,3] The *cis* isomer of this type of complex can, in principle, be resolved into optical isomers. The optically active complexes would be useful not only for spectroscopic reasons but, more importantly, also for stereochemical studies.[4] We have now successfully resolved the two ions[5] $\mathrm{Co(acac)_2en^+}$ and *cis*-$\mathrm{Co(acac)_2(NH_3)_2^+}$ (see Figure 1) and measured their ORD and CD spectra as well as determined their optical stability. Previously one other ion of this type, $\mathrm{Co(acac)_2ox^-}$, had been resolved.[6] In addition, the optically active complexes $\mathrm{Co(acac)_2}$(L-AA) have been prepared with L-amino acids.[7]

Experimental Section

Materials.—All complexes were prepared according to previously reported procedures.[1,3] Purity was confirmed by elemental analyses and spectral measurements. Sodium (+)-arsenyltartrate was prepared by the method of Henderson and Ewing,[8] and ammonium α-bromocamphor-π-sulfonate was obtained from K & K Laboratories.

(+)$[\mathrm{Co(acac)_2en}]\mathrm{I}$.—The racemic iodide (8.9 g, 0.02 mol) was dissolved in 50 ml of hot distilled water and shaken with silver chloride (2.9 g, 0.02 mol) for 10 min. The silver iodide was filtered off and washed with water (25 ml). The combined filtrate was reduced to a volume of $\sim$25 ml. Sodium (+)-arsenyltartrate (5.2 g, 0.02 mol), in 15 ml of water, was added and the solution was allowed to stand for 48 hr at room temperature. The solution was filtered to remove any undissolved resolving agent and the filtrate was slowly evaporated to a volume of 10 ml. Purple crystals of the diastereoisomer were filtered off and washed with a little cold water and air dried; yield 3.3 g (0.006 mol), 60%. A 0.07% aqueous solution in a 1-dm tube gave α_{546} +0.470°, $[\alpha]_{546}$ +670°. *Anal.*[9] Calcd for $(+)[\mathrm{Co(C_5H_7O_2)_2(C_2H_8N_2)}](+)[\mathrm{C_4H_4O_6AsO}]$: C, 34.55; H, 4.71; N, 5.04. Found: C, 35.33; H, 4.93; N, 5.03.

The diastereoisomer was suspended in 25 ml of 0.1 *N* sodium hydroxide and 25 g potassium iodide was added. The mixed purple and white precipitate was filtered and extracted repeatedly with methanol. The dextro complex iodide was precipitated from methanol solution with ether. The purple precipitate was stirred in 100 ml chloroform for a few minutes and the mixture was filtered. The chloroform filtrate was evaporated to dryness and the residue was collected, washed with ether, and dried *in vacuo* at 110°; yield 1.1 g (25%). A 0.065% aqueous solution in a 1-dm tube gave α_{546} +0.770, $[\alpha]_{546}$ +1190°. *Anal.* Calcd for $(+)[\mathrm{Co(C_5H_7O_2)_2(C_2H_8N_2)}]\mathrm{I}$: C, 32.43; H, 5.0; N, 6.31. Found: C, 32.16; H, 4.93; N, 6.13.

Addition of sodium iodide to the original filtrate, after removal of the first diastereoisomer, gave largely racemic crystals. Further isolation of the (−) isomer from the mother liquor was not attempted.

(+)$[\mathrm{Co(acac)_2(NH_3)_2}]\mathrm{I}$.—The racemic iodide (10.0 g, 0.024 mol) was dissolved in 50 ml of distilled water and shaken with 4.0 g (0.024 mol) of silver acetate for 10 min. The silver iodide was filtered off and washed with 25 ml of water. The combined filtrate was reduced to a volume of $\sim$25 ml. Ammonium α-bromocamphor-π-sulfonate (4.1 g, 0.012 mol), in 10 ml of water, was added to the filtrate and the solution was allowed to evaporate slowly to a volume of 10 ml. The purple crystals of the diastereoisomer were filtered off and washed with a little cold water and air dried; yield 6.1 g (0.01 mol), 82%. A 0.04% aqueous solution in a 1-dm tube gave α_{546} +0.672, $[\alpha]_{546}$ +1580°. *Anal.* Calcd for (+)-*cis*-$[\mathrm{Co(C_5H_7O_2)_2(NH_3)_2}][\mathrm{C_{10}H_{10}O_9SBr}]\cdot 2\mathrm{H_2O}$: C, 37.77; H, 5.96; N, 4.40. Found: C, 37.95; H, 5.72; N, 4.41.

The diastereoisomer was dissolved in 25 ml of $\mathrm{H_2O}$ and 10 g of sodium iodide was added. The solution was slowly evaporated to a volume of 10 ml. The purple crystals were collected and air dried. The impure material was then extracted with 100 ml of chloroform. The complex was precipitated from solution by the addition of petroleum ether and then collected on a filter and air dried; yield 1.0 g (20%). A 0.04% aqueous solution in a 1-dm tube gives α_{546} +0.740, $[\alpha]_{546}$ +1900°. *Anal.* Calcd for (+)-*cis*-$[\mathrm{Co(C_5H_7O_2)_2(NH_3)_2}]\mathrm{I}\cdot 0.5\mathrm{H_2O}$: C, 28.10; H, 4.91; N, 6.56. Found: C, 28.06; H, 4.35; N, 6.09. Addition of 10 g of sodium iodide to the original filtrate, after the removal of the first diastereoisomer, yields 3.0 g of the racemic complex iodide. Evaporation of the filtrate to dryness and the extraction of the residue into chloroform gives 1.5 g of (−)-$[\mathrm{Co(acac)_2(NH_3)_2}]\mathrm{I}$; $[\alpha]_{546}$ −1960°.

Spectral Measurements.—Absorption spectra were recorded

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(1) B. P. Cotsoradis and R. D. Archer, *Inorg. Chem.*, **6**, 800 (1967).

(2) L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965); L. J. Boucher, *Inorg. Chem.*, **6**, 2162 (1967); R. J. York, W. D. Bonds, B. P. Cotsoradis, and R. D. Archer, *ibid.*, **8**, 789 (1969).

(3) R. D. Archer and B. D. Cotsoradis, *ibid.*, **4**, 1584 (1965).

(4) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967.

(5) Abbreviations include: acac, enolate anion of 2,4-pentanedione (acetylacetone); en, ethylenediamine; ox, oxalate; L-AA, amino acid; hmc, hydroxymethylenecamphor.

(6) F. P. Dwyer, I. K. Reid, and A. M. Sargeson, *Australian J. Chem.*, **18**, 1919 (1965).

(7) S. H. Laurie, *ibid.*, **21**, 679 (1968).

(8) G. G. Henderson and A. R. Ewing, *J. Chem. Soc.*, 102 (1895).

(9) All elemental analyses by Galbraith Laboratories, Inc., Knoxville, Tenn.

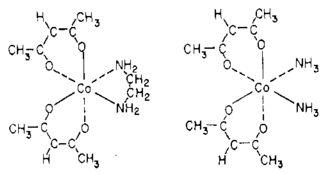

Figure 1.—Absolute configurations of $(+)_{546}$Co(acac)$_2$en$^+$ and $(+)_{546}$Co(acac)$_2$(NH$_3$)$_2$$^+$.

on a Cary Model 14 spectrophotometer using aqueous solutions of the complexes. ORD and CD curves were recorded on a Durrum–Jasco ORD/UV/CD/5 instrument using aqueous solutions of the complex in a 10-mm cell. Optical activity measurements were made at the mercury line, 5461 Å, with a Perkin-Elmer Model 141 photoelectric polarimeter with an accuracy of ±0.002°. The optical rotation at the Na D line is almost zero for the complexes. All measurements were made at room temperature. Reported $[\alpha]_\lambda$, $[M]_\lambda$, and the decadic molar extinction coefficients (M^{-1} cm^{-1}), $\Delta\epsilon$ ($=\epsilon_l - \epsilon_r$), were obtained using the standard expressions[10] and the error limits in each case are no more than ±5%.

Results and Discussion

Optical Activity.—The complex ion Co(acac)$_2$en$^+$ can be easily resolved into its optical isomers, using a modified form of the resolution procedure developed for Co(en)$_2$acac^{2+},[11] with the formation of diastereoisomers with sodium (+)-arsenyltartrate. On the other hand, *cis*-Co(acac)$_2$(NH$_3$)$_2$$^+$ could not be resolved using this procedure. In this case, use of the resolving agent α-bromocamphor-π-sulfonate gave the desired results. Numerous attempts were made to resolve *cis*-Co(acac)$_2$(NO$_2$)$_2$$^-$ using (−)Co(en)$_2$(NO$_2$)$_2$$^+$ as a resolving agent. In each case the first material to crystallize from solution after long standing is the salt of *trans*-Co(acac)$_2$(NO$_2$)$_2$$^-$. This complex slowly forms by the isomerization of the original *cis* isomer. The *cis* isomer is very soluble in water and we have not been able to crystallize it with the resolving agent even with evaporation of water. Evaporation of the solution to dryness yields a mixture of the racemic *cis* and *trans* complex as well as the resolving agent.

The optical stability of the two resolved complexes in aqueous solution was studied. The complex $(+)_{546}$-Co(acac)$_2$(NH$_3$)$_2$$^+$ loses optical activity very slowly at room temperature with a $t_{1/2}$ of ~420 days. The corresponding value for acetone solutions is a $t_{1/2}$ of ~90 days. At higher temperatures loss of optical activity of aqueous solutions is much more rapid with a $t_{1/2}$ of ~30 days at 60° and a $t_{1/2}$ of ~0.1 day at 100°. The loss of optical activity of the complex arises from a decomposition process (to a Co(II) species) and does not appear to involve the formation of the racemic *cis* or *trans* isomers. Spectrophotometric measurements show a loss of absorbance in the visible and near-uv region which closely parallels the decrease in optical rotation. Redox instability appears to be a feature of this type of complex. In contrast to the ammonia complex, $(+)_{546}$Co(acac)$_2$en$^+$ is optically stable in aqueous solution. There is no loss of optical activity after refluxing a solution, ~100°, for 0.5 day. At room temperature, ethanol, acetone, and dimethyl sulfoxide solutions are stable to racemization for days. Aqueous solutions in the pH range 2–12 are also stable for days at room temperature. At higher or lower pH's the complexes lose optical activity slowly, with decomposition.

The stability of the (+)-Co(acac)$_2$en$^+$ may be attributed to its fully chelated structure. It is unlikely that ethylenediamine chelate ring rupture will occur often, even at 100°, to give racemization or decomposition. The great optical stability of cobalt(III)–ethylenediamine complexes is well known.[12] The rate of racemization at 90° of optically active Co(acac)$_3$ in chlorobenzene has been measured and a $t_{1/2}$ of ~0.2 day reported.[13] The favored mechanism for the racemization is one that involves a chelate ring opening with the formation of a symmetric trigonal-bipyramidal intermediate.[13] Since Co(acac)$_2$en$^+$ does not racemize at 100° in aqueous solution in 0.5 day the acetylacetonate chelate ring opening mechanism does not seem accessible to it for racemization (high activation energy). This may be a function of the different solvent. However, a good solvating and a high dielectric solvent like water should favor the chelate ring opening more than would chlorobenzene and consequently racemization should be facilitated in water. The positive charge of $(+)_{546}$Co(acac)$_2$en$^+$ is probably the source of its racemization inertness. It should be less energetically favorable to rupture the chelate ring and remove a negatively charged atom away from a positively charged cobalt complex than for a similar process with a neutral complex.[14] The racemization inertness of the similar but doubly charged complex Co(en)$_2$acac^{2+} (no loss of optical activity of an aqueous solution kept in a steam bath for many hours) is consistent with this notion. In fact, the optical lability[15] of a similar complex, Co(en)(ox)$_2$$^-$, in contrast to the stability of Co(en)$_2$ox$^+$, may be attributed to the overall negative charge on the former complex.

Electronic Spectra.—The frequencies of the absorption maxima in the uv and visible spectra of the complexes are collected in Table I with the respective extinction coefficients. Typical spectra are shown in Figures 2 and 3. The uv spectra were also determined for the chloride salts. The positions of the absorption maxima are the same for the iodide and chloride salts; the extinction coefficient for the high-energy band was ~30% lower for the chloride salt.

The spectra show a broad low-intensity band in the visible region which arises from a cobalt(III) d → d transition. The absorption can be assigned to the first octahedral cobalt(III) band. The actual symmetry of the complexes is C$_2$ and under this symmetry three

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[10] R. D. Gillard in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Interscience Publishers, New York, N. Y., 1968, p 167.

[11] I. K. Reid and A. M. Sargeson, *Inorg. Syn.*, **9**, 167 (1967).

[12] W. G. Gehman and W. C. Fernelius, *J. Inorg. Nucl. Chem.*, **9**, 71 (1959).

[13] U. Klabunde and R. C. Fay, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. INOR 37.

[14] R. G. Pearson, C. P. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

[15] F. P. Dwyer, I. K. Reid, and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 1285 (1961).

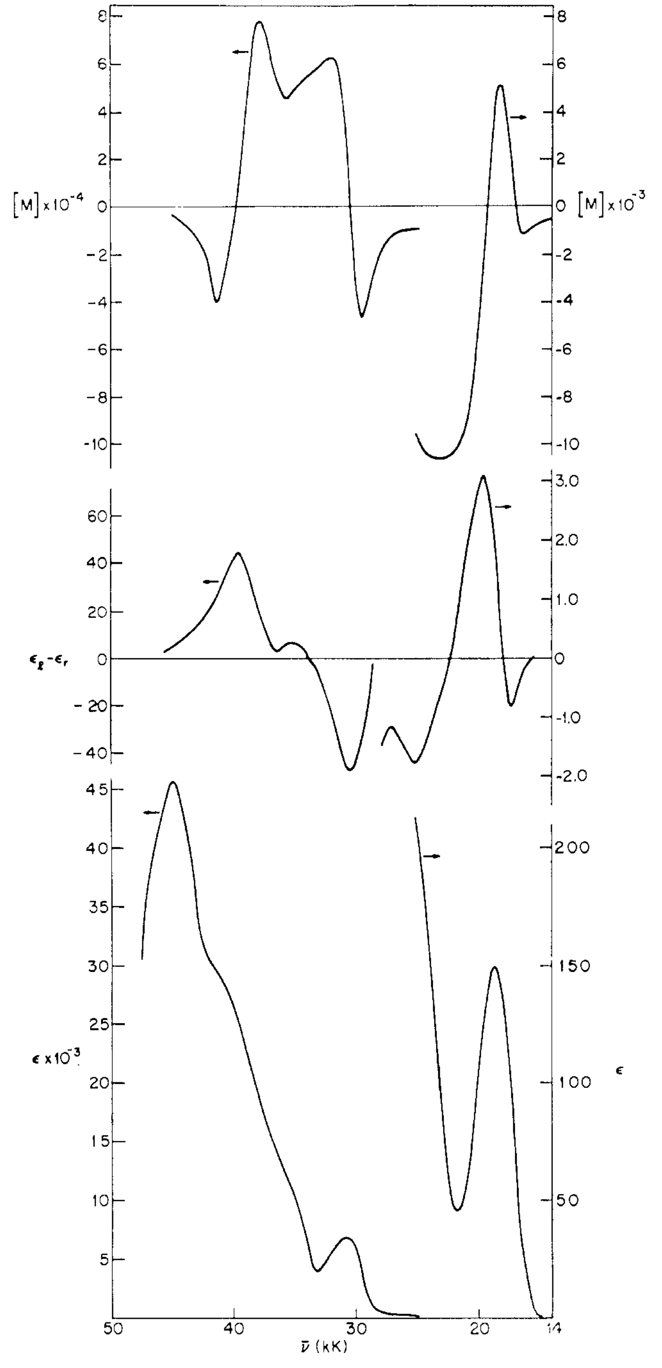

Figure 2.—The optical rotatory dispersion (top), circular dichroism (middle), and absorption spectra (bottom) of $(+)_{546}$[Co(acac)$_2$en]I in aqueous solution.

bands are expected. The overlap of these absorptions gives rise to the observed unresolved single absorption. The second octahedral cobalt(III) absorption is seen as an unresolved shoulder in the ~24-kK region. The positions of the visible absorption bands are at higher energy for the ethylenediamine complex than for the ammonia complex. This is consistent with the greater ligand field of ethylenediamine.[4] The ultraviolet spectra of the two complexes are similar and show a strong absorption at 30.8 kK, two shoulders at ~35 and ~40 kK, and a very strong band at 45.0 kK. The absorptions are at about the same frequencies for both complexes. The spectrum in the uv region is related to the presence of the conjugated acetylacetonate ligand which has accessible $\pi \rightarrow \pi^*$ electronic transitions. In addition to these, metal-to-ligand $d\pi \rightarrow \pi^*$ transitions are allowed. The band near 30 kK has been previously assigned to the charge-transfer band.[16,17] Further, the shoulders at 35 and 40 kK were assigned to $\pi \rightarrow \pi^*$ transitions. More recent calculations for Co(acac)$_3$ make an alternate assignment of these bands to $d\pi \rightarrow \pi^*$ charge-transfer transitions.[18] The strong high-energy band at 45.0 kK is assigned to the $\pi \rightarrow \pi^*$ transition by both groups.[17,18] The multiple $\pi \rightarrow \pi^*$ transitions (and $d\pi \rightarrow \pi^*$ as well) are thought to arise because of the presence of three chelate rings, in the molecular point group D_3, for Co(acac)$_3$. With two acetylacetonate chelate rings, similar splittings of the π and π^* levels are expected and it is not surprising that the spectral pattern observed for Co(acac)$_2$en$^+$ is analogous to that of Co(acac)$_3$. What is surprising is that complexes with one acetylacetonate chelate ring like Co(en)$_2$acac$^+$ also show the same spectral pattern.[19]

Table I

Absorption and Circular Dichroism Data

Absorption spectrum		CD spectrum		
ν, kK	Log ϵ	ν, kK	$\Delta\epsilon$	Assignment
		$(+)_{546}$[Co(acac)$_2$en]I		
18.6	2.17	17.3	−0.8	$A_1 \rightarrow B_1$
		19.5	+3.1	$A_1 \rightarrow A_2 + B_2$
~24		25.2	−1.8	$A_1 \rightarrow A_1 + B_1 + B_2$
30.8	3.84	30.4	−47	$d\pi \rightarrow \pi^*$
~35		35.0	+6	$d\pi \rightarrow \pi^*$
~40		39.5	+44	$d\pi \rightarrow \pi^*$
45.0	4.66	...	...	$\pi \rightarrow \pi^*$
		$(+)_{546}$[Co(acac)$_2$(NH$_3$)$_2$]I		
18.3	2.07	17.0	−1.6	$A_1 \rightarrow B_1$
		19.2	+2.5	$A_1 \rightarrow A_2 + B_2$
~24		25.0	−2.0	$A_1 \rightarrow A_1 + B_1 + B_2$
30.8	3.85	30.2	−54	$d\pi \rightarrow \pi^*$
~36		35.1	+11	$d\pi \rightarrow \pi^*$
~40		39.8	+61	$d\pi \rightarrow \pi^*$
44.9	4.60	...	...	$\pi \rightarrow \pi^*$

Optical Rotatory Dispersion and Circular Dichroism.—Typical ORD and CD curves are displayed in Figures 2 and 3. The general pattern is the same for both complexes. The ORD curve shows an overlap of two Cotton effects, a low-energy negative one and a higher energy positive one, in the region of the visible absorption bands of the complex. The ultraviolet region clearly shows two intense Cotton effects of opposite sign: a negative one at ~30.3 and a positive one at ~39.5 kK. There do not appear to be any strong Cotton effects on the high-energy side of the latter band. Amplitudes of the dominant dispersion curve are about 40% less for $(+)_{546}$Co(acac)$_2$en$^+$ than for $(+)_{546}$-*cis*-Co(acac)$_2$ (NH$_3$)$_2$$^+$.

The CD spectra more clearly show the correspondence of the Cotton effects and the absorption maxima. The frequencies, intensities, and signs of the CD

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(16) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

(17) D. W. Barnum, *ibid.*, **22**, 183 (1961).

(18) I. Hanazaki, F. Hanazaki, and S. Nogakura, *J. Chem. Phys.*, **50**, 265 (1969).

(19) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

maxima are collected in Table I. The CD spectra show three cotton effects in the region of the d–d electronic transitions: a negative one at ~17 kK, a positive one at ~19 kK, and a negative one at ~25 kK. The first two bands correspond to the low-symmetry components of the first octahedral cobalt(III) transition. For the actual symmetry of the complexes, C_2, three components arising from the transitions $A_1 \rightarrow B_1$, B_2, A_2 are expected.[19] The lower energy CD band can be assigned to the $A_1 \rightarrow B_1$ transition, while the next higher energy band can be assigned to the overlap of the two transitions $A_1 \rightarrow B_2$ and $A_1 \rightarrow A_2$.[19] The higher energy visible CD maximum corresponds to the second octahedral cobalt(III) band. The overlap of the three expected components in C_2 symmetry, $A_1 \rightarrow A_1$, B_1, B_2, gives rise to the observed unresolved broad band at 25 kK. One or more of the components may also be buried under the tail of the strong ultraviolet Cotton effect.

The CD band display in the visible region does not resemble that of the similar $Co(O_4N_2)$ chromophore, *e.g.*, $Co(en)(ox)_2^-$. In the latter case all six rhombic components of the CD curve can be resolved.[20] On the other hand, the visible CD spectra of $(+)_{546}Co(acac)_2(NH_3)_2^+$ and $(+)_{546}Co(acac)_2en^+$ closely resemble the spectra for $(-)_{546}Co(acac)_2ox^{2-}$,[6] $Co(acac)_2$(L-AA),[7] and the β-diketone-like complex $(+)Co((+)hmc)_3$.[21] In other words, optically active complexes with two or three β-diketone ligands show two components of opposite sign at the first octahedral cobalt(III) band with the higher energy component dominating and a broad CD band at the second octahedral cobalt(III) band. The situation with one β-diketone chelate ring appears to be different. The visible CD spectrum of $(+)Co(en)_2acac^{2+}$ shows a broad positive band at the first cobalt(III) absorption at ~20 kK and a broad, negative band at the second cobalt(III) absorption. However, when an unsymmetric β-diketone-like trifluoromethylacetylacetone is used, the visible CD maximum at ~20 kK for $(+)Co(en)_2tfac^{2+}$ is partially resolved into a main band which appears at 20.4 kK ($A_2 + B_2$) and a prominent shoulder at 19.5 kK (B_1).[22] It is interesting to note that the $A_2 + B_2$ component for $(+)_{546}Co(acac)_2en^+$ is stronger than for $(+)_{546}$-*cis*-$Co(acac)_2(NH_3)_2^+$. This is consistent with the observation that chelated complexes have greater rotational strength than complexes with monodentate ligands.[23]

Relative and Absolute Configuration.—The shapes of the CD curves of $(+)_{546}Co(acac)_2en^+$ and $(+)_{546}Co(acac)_2(NH_3)_2^+$ are almost superimposable. For such similar complexes it is safe to assign them the same relative optical configuration. It has been proposed[19] that the configurations of C_2 cobalt(III) complexes, particularly $Co(en)_2L_2^{n+}$, can be related to the known absolute configuration of $(+)_{589}Co(en)_3^{3+}$ by determining the sign of the major component, $A_2 + B_2$, of the first octahedral cobalt(III) d → d band. The assignment of the $A_2 + B_2$ component is based on the relative intensities of the $A_2 + B_2$ and B_1 bands and on the displacement of these bands from that of the parent trigonal complex, $Co(en)_3^{3+}$. The $A_2 + B_2$ component is more intense than the B_1 component and the former band is also closer in energy to the $Co(en_3)^{3+}$ Ea component at 21.3 kK. The relative configuration of a complex can be assigned the same as $(+)Co(en)_3^{3+}$, $\Delta(C_2)$,[24] if the sign of the $A_2 + B_2$ band is the same as that of the Ea band of the parent complex, *i.e.*, positive. On this basis the configuration of $(+)Co(en)_2acac^{2+}$ has been

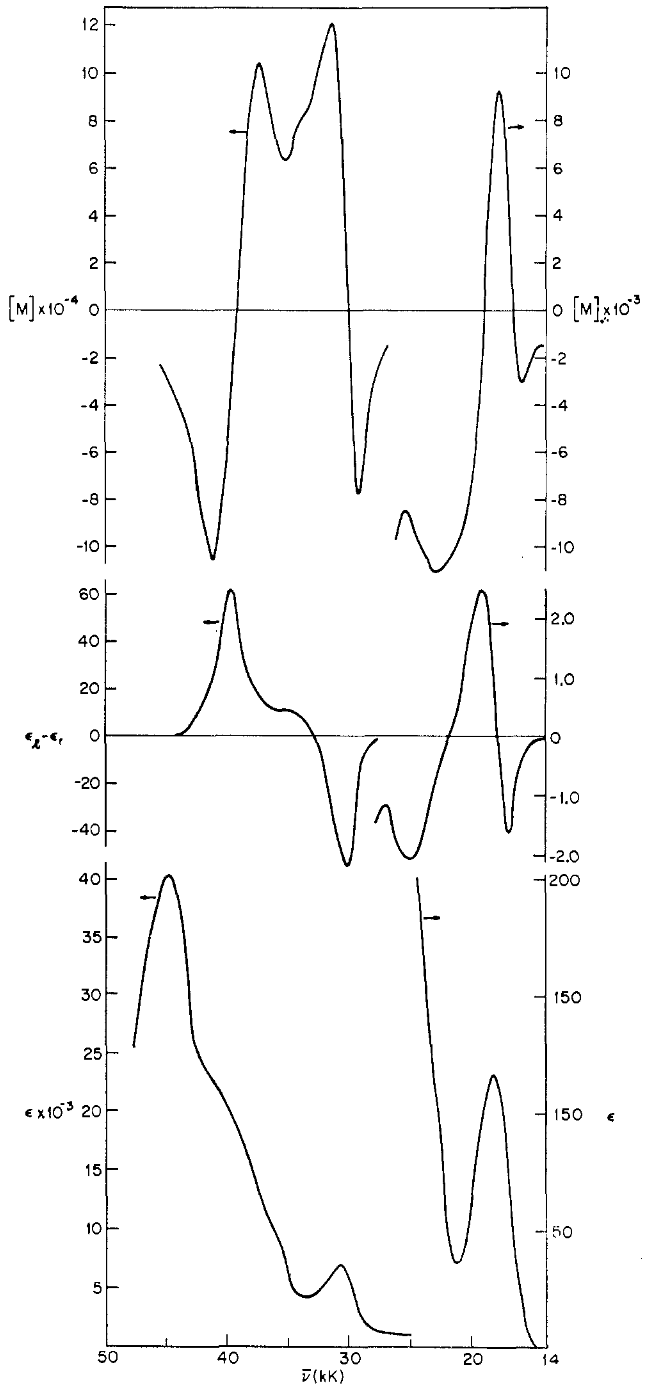

Figure 3.—The optical rotatory dispersion (top), circular dichroism (middle), and absorption spectra (bottom) of $(+)_{546}[Co(acac)_2(NH_3)_2]I$ in aqueous solution.

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(20) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

(21) A. J. McCaffery, S. F. Mason, and R. F. Ballard, *J. Chem. Soc.*, 2883 (1965).

(22) L. J. Boucher, unpublished work.

(23) R. D. Gillard, *J. Inorg. Nucl. Chem.*, **26**, 657 (1964).

(24) J. I. Legg and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 2697 (1966).

assigned as $\Delta(C_2)$.[19] Since the ligand field strength of acetylacetonate ion is less than that of ethylenediamine, the CD components of the first band will be shifted to lower energy. As it turns out, the sign of the two components is the same for this complex and only a broad unresolved CD maximum is observed. For the similar complex $(+)Co(en)_2tfac^{2+}$ the CD band can be resolved into the expected prominent positive $A_2 + B_2$ maximum at higher energy and weaker B_1 maximum at lower energy. Although $Co(acac)_2en^+$ is no longer directly related to the *cis*-$Co(en)_2L_2^{n+}$ series, the ions still have C_2 symmetry and should, at least formally, conform to the general rule. The $A_2 + B_2$ component may be identified as the higher energy band of the two visible CD maxima because it is the more intense of the two. Based on the observation that the $B_2 + A_2$ band has a positive rotational strength, both $(+)_{546}$-*cis*-$Co(acac)_2(NH_3)_2^+$ and $(+)_{546}Co(acac)_2en^+$ can be assigned the $\Delta(C_2)$ configuration. (See Figure 1 for absolute configurations.) The similar $(-)_{546}Co(acac)_2ox^-$ and $(-)_{546}Co(ox)_2acac^{2-}$ can also be assigned the $\Delta(C_2)$ configuration. Only one optically active tris-chelated cobalt(III) which contains a β-diketone-like ligand has been studied, $(+)Co((+)hmc)_3$.[21] This complex has been assigned the $\Delta(C_2)$ configuration based on the criteria given above. If the CD spectrum of this compound is compared with that of $(+)_{546}Co(acac)_2en^+$, it is seen that the pattern of the CD bands is the same and the bands are shifted to higher energy because of the increased ligand field of the latter complex. However, the B_1 component of $(+)_{546}Co(acac)_2en^+$ appears to be closer in energy to the parent Ea band of $(+)Co((+)hmc)_3$ than does the $A_2 + B_2$ band. While it is not always possible to assign relative configurations of cobalt(III) complexes by using the CD absorption in the region of the second cobalt octahedral band, it is interesting to note that $(+)_{546}Co(acac)_2en^+$, $(+)_{546}Co(acac)_2(NH_3)_2^+$, $(-)_{546}Co(acac)_2ox^-$, $(+)_{589}Co(acac)en_2^+$, and $(+)_{589}Co((+)hmc)_3$ all show broad negative CD bands in this region. This is consistent with a common absolute configuration for the ions.

Ultraviolet CD Spectra.—The ultraviolet CD spectra show three features: a strong negative band at ~30 kK, a weaker positive one at ~35 kK, and a strong positive one at ~40 kK. The low-energy ultraviolet band can be assigned to the first metal-to-ligand charge-transfer band, $d\pi \rightarrow \pi^*$. This CD maximum is at a higher energy for the ethylenediamine than for the ammonia complex, in agreement with the increased stability of the filled metal orbitals (π) for this ligand. The weak CD band at 35 kK can be assigned to another $d\pi \rightarrow \pi^*$ transition or to a short axis polarized $\pi \rightarrow \pi^*$ transition.[25] The high-energy band at 40 kK can be assigned to a $d\pi \rightarrow \pi^*$ transition. It is interesting to note that the highest energy band in the absorption spectrum at 45 kK, $\pi \rightarrow \pi^*$, does not give rise to any CD maximum. The CD band at ~40 kK is asymmetric toward the high-energy side so that there may be some small optical activity at the 45-kK band. It must be admitted that measurements in the region are not accurate because of a combination of the great absorption and relatively low optical activity of the complexes. Use of the less absorbing chloride salts of the complex instead of the iodide salts leads to the same CD spectrum in the ultraviolet region.

The ultraviolet CD spectra are similar to those of other cobalt(III) complexes with one and two acetylacetonate chelate rings. Both $Co(en)_2acac^{2+}$ [21] and $Co(ox)_2acac^{2-}$ [6] show negative CD bands at 30–31 kK ($d\pi \rightarrow \pi^*$) and negative CD bands at 40–36 kK ($d\pi \rightarrow \pi^*$). The strong CD bands are of nearly equal magnitude for each complex. On the other hand, $(-)_{546}Co(ox)(acac)_2^-$ [6] shows a strong negative band at ~30 kK ($d\pi \rightarrow \pi^*$) and a strong positive band at ~38 kK ($d\pi \rightarrow \pi^*$). Like $(+)_{546}Co(acac)_2en^+$, the magnitudes of the two bands for $(-)_{546}Co(acac)_2ox^-$ are equal. The presence of two acetylacetonate chelate rings increases the intensity of the $d\pi \rightarrow \pi^*$ CD bands observed for complexes with one acetylacetonate chelate by 3–5 times.

It is in the ultraviolet region that the exciton mechanism of coupling of the acetylacetonate ion $\pi \rightarrow \pi^*$ transitions should be important.[25] The exciton theory of optical activity states that when a disymmetric molecule possesses two or more chelate rings that contain π-electron systems, the long-axis $\pi \rightarrow \pi^*$ transitions couple electrostatically the electric transition dipoles to give two CD bands of equal and opposite magnitude split equally from the uncoupled transition.[25] This is just what is observed for $(-)Si(acac)_3^+$ in the region of the long-axis $\pi \rightarrow \pi^*$ absorption of the acetylacetonate ion at 34 kK.[26] Since the coupling cannot occur in monochelated complexes, optical activity of a single acetylacetonate chelate $\pi \rightarrow \pi^*$ transition should be weak or absent. Accordingly, the CD spectrum of $(+)Co(en)_2acac^+$ shows no CD band at 45 kK for $\pi \rightarrow \pi^*$.[22] It is interesting to note that the ultraviolet CD spectrum of $(+)_{546}Co(acac)_2en^+$ does not show the two expected CD bands of opposite sign near 45 kK in the $\pi \rightarrow \pi^*$ transition. There are several qualifications for the exciton treatment of optical activity to apply to bis- or tris-chelated complexes of unsaturated ligands.[27] First, the absorption bands of the free ligand should be distinguishable in the complex at a frequency close to the value for the free ligand and at an intensity appropriate to the number of ligands in the complex. Second, the CD connected with a given ligand absorption has the characteristic exciton form consisting of two dichroism bands with opposed signs and approximately equal areas. In the case of the cobalt(III) acetylacetonate complexes, the $\pi \rightarrow \pi^*$ absorption is considerably shifted to higher energy and appears to be of higher intensity than for two noncomplexed acetylacetonate ions. In addition, the second criterion is not satisfied. It therefore appears that the exciton treatment cannot be used in the discussion of the ultraviolet CD spectra

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of $(+)_{546}Co(acac)_2en^+$ and $(+)_{546}Co(acac)_2(NH_3)_2^+$. This may be a consequence of the mixing of the charge-transfer and ligand states.

There is an interesting difference in the ultraviolet CD between cobalt(III) complexes of the same absolute configuration with one acetylacetonate chelate and those containing two chelates. It appears that the sign of the $d\pi \rightarrow \pi^*$ CD found at ~30 kK is negative for all the $\Delta(C_2)$ complexes with one, two, or even three β-diketone chelates. Conversely, the charge-transfer CD band, at 40 kK, shows a reversal of sign, negative to positive, in going from $(+)Co(en)_2acac^+$ to $(+)_{546}Co(acac)_2en^+$. The ultraviolet CD spectra of mixed complexes of acetylacetone and ethylenediamine could also be complicated by the presence of ethylenediamine chelate charge-transfer bands in the 40–45-kK region.[28] However, the similarity of the ultraviolet CD spectra for $(+)_{546}Co(acac)_2(NH_3)_2^+$ and $(+)_{546}Co(acac)_2en^+$ indicates that the spectral difference noted above is mainly a function of the presence of two acetylacetonate chelate rings.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
THE UNIVERSITY OF ARIZONA, TUCSON, ARIZONA 85721

The Spectra of Bis(tertiary arsine) Complexes. II. Spin-Paired Iron(III)[1a]

BY ROBERT D. FELTHAM AND W. SILVERTHORN[1b]

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New spin-paired compounds of iron(III) have been prepared and their visible spectra and magnetic properties examined. The spectral properties of the complexes tris[*cis*-1,2-bis(dimethylarsino)ethylene]iron(III), tris[*o*-phenylenebis(dimethylarsine)]iron(III), and tris(8-dimethylarsinoquinoline)iron(III) were compared with those of the corresponding complexes of α,α'-bipyridyl and *o*-phenanthroline. All of the compounds examined have one unpaired electron per iron(III) and their visible spectra can be interpreted on the basis of a ligand field model.

Introduction

The iron complexes with *o*-phenylenebis(dimethylarsine) (das) have been the subject of several previous studies.[2-4] The magnetic properties of the iron(III) complexes have received particular attention because they are all spin paired with $^2T_2$ ground states. The only other common spin-paired complexes of iron(III) are formed with strong-field ligands including cyanide, *o*-phenanthroline,[5] α,α'-bipyridyl,[6] dithiocarbamates,[7] etc. Of these iron(III) complexes, only the cyanide[8] and, more recently, the ethylenediamine complexes[9] have had their spectral properties examined in any detail. Since the ligand field spectra of many complexes of *o*-phenylenebis(dimethylarsine) and *cis*-1,2-bis(dimethylarsine)ethylene (edas) are by now rather well understood,[1a,10,11] it was of interest to examine the d–d transitions of the iron(III) complexes with these ligands. The results of these investigations are outlined below.

Experimental Section

Materials.—The ligands *o*-phenylenebis(dimethylarsine) and *cis*-bis(dimethylarsino)ethylene were prepared according to the methods described in the literature.[11,12] The compounds *o*-phenanthroline and α,α'-bipyridyl purchased from G. F. Smith and Co. were used without further purification. The perchlorate salts of the iron(III) complexes of *o*-phenanthroline and α,α'-bipyridyl, were prepared directly from these ligands using well-known procedures.[2,13]

Tris[*o*-phenylenebis(dimethylarsine)]iron(III) Perchlorate.—This complex was prepared from $Fe(das)_3^{2+}$ by oxidation[10] in concentrated nitric acid. Numerous attempts were made to prepare the pure solid. Although the complex is readily prepared in solution, it proved difficult to obtain this solid compound in reproducible yields. The following procedure represents the best preparation thus far found.

The ferrous complex $[Fe(das)_3][ClO_4]_2$ (1 g) was dissolved in a minimum (25 ml) of concentrated nitric acid. The resultant

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