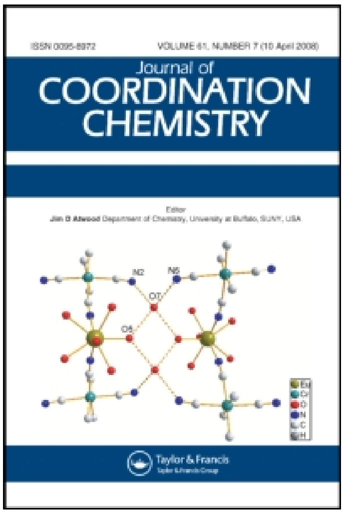

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

CIRCULAR DICHROISM STUDY OF SOME BICYCLIC 1,3-DIKETONE IRON(III) AND COPPER(II) COMPLEXES

Michael P. Granchi[a]; Bodie E. Douglas[b]
[a] Contribution from the University of Pittsburgh, Pittsburgh, PA [b] Mobil Research and Development Corporation, Paulsboro, New Jersey

To cite this Article Granchi, Michael P. and Douglas, Bodie E.(1978) 'CIRCULAR DICHROISM STUDY OF SOME BICYCLIC 1,3-DIKETONE IRON(III) AND COPPER(II) COMPLEXES', Journal of Coordination Chemistry, 8: 3, 149 — 155

To link to this Article: DOI: 10.1080/00958977808073088

URL: http://dx.doi.org/10.1080/00958977808073088

J. Coord. Chem.
1978, Vol. 8, pp. 149–155

CIRCULAR DICHROISM STUDY OF SOME BICYCLIC 1,3-DIKETONE IRON(III) AND COPPER(II) COMPLEXES

MICHAEL P. GRANCHI[1] and BODIE E. DOUGLAS[2]

Contribution from the University of Pittsburgh, Pittsburgh, PA 15260

(*Received February 21, 1978*)

The absorption and circular dichroism (CD) spectra are reported for the free ligands and the Cu(II) and Fe(III) complexes of chiral 1,3-diketones (+)-3-hydroxymethylenecamphor ((+)-hmcH), (+)-3-acetylcamphor ((+)-3-acH), and the newly synthesized (+)-3-propionylcamphor ((+)-3-pcH). Only one diastereoisomer of the tris(1,3-diketonate) Fe(III) complexes seemed to be formed. The CD spectra give preference to one of two conflicting earlier assignments of transitions of Fe(III) 1,3-diketonate complexes. The absorption spectra for the bis(1,3-diketonate)Cu(II) complexes could be interpreted based on earlier work on Cu(II) 1,3-diketonates.

INTRODUCTION

Metal complexes of 1,3-diketones have been known for many years.[3] Complexes of this type have been reported for all of the nonradioactive metals and metalloids in the periodic table. Complexes of 1,3-diketones derived from camphor were investigated quite early, primarily by Lifschitz.[4,5] He reported studies of cobalt, nickel, and copper ions with optically active 3-hydroxymethylenecamphor (hmcH), see Figure 1. More recent studies of the metal complexes of optically active hmcH have been carried out with cobalt, chromium, and rhodium.[6,7] These complexes were not separated completely into the four possible isomers.

Complexes of a similar ligand, (+)-3-acetylcamphor ((+)3-acH) have been studied also. All four diastereoisomers of the (+)3-acH complex have been isolated and identified for cobalt(III), chromium(III), rhodium(III), and ruthenium(III).[8-11] Copper(II) complexes of both (-)-hmcH and (-)-3-acH have been reported along with their absorption spectra, but details of the spectra and discussion of the results were not presented.[12,13]

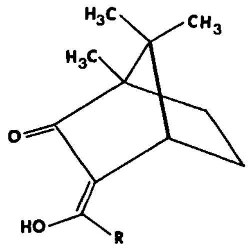

FIGURE 1 Structures of the $(+)_{589}$-isomers of 3-acetylmethylenecamphor (hmcH, R = H), 3-acetylcamphor (3-acH, R = CH_3), and 3-propionylcamphor (3-pcH, R = C_2H_5).

In this paper 1,3-diketone complexes of the labile iron(III) and copper(II) ions are studied by absorption and circular dichroism spectroscopy. The new ligand (+)-3-propionylcamphor ((+)-3-pcH) is reported.

EXPERIMENTAL

Preparation of (+)-3-hydroxymethylenecamphor, $C_{11}H_{16}O_2$, *(+)-hmcH.* The preparation follows that of Lintvedt and Fatta[14] for racemic hmcH. m.p. 70°, $[\alpha]_D^{21} = +152°$.

Preparation of (+)-3-acetylcamphor, $C_{12}H_{18}O_2$, *(+)-3-acH.* This ligand was prepared by a method similar to the preparation of (+)-3-acH by Brühl.[15] Purification was by triple vacuum distillation. b.p. 74–79° at 0.44 torr, $[\alpha]_D^{25} = +50.9°$.

Preparation of (+)-3-propionylcamphor, $C_{13}H_{20}O_2$, *(+)-3-pcH.* The compound was prepared by a method similar to the preparation of (+)-3-acH except ethyl propionate was used instead of ethyl acetate. Purification was by vacuum distillation. b.p. 125–127° at 9.5 torr $[\alpha]_D^{25} = +59.1°$.

Preparation of Tris((+)-3-hydroxymethylenecamphorato)iron(III), Fe((+)-hmc)$_3$. The product was prepared by a modification of a published procedure.[14] A solution of 2.70 g (0.01 mole) of $FeCl_3 \cdot 6H_2O$ in 150 ml of water was added to a solution of 5.4 g (0.03 mole) of (+)-hmcH in 50 ml of methanol. The resulting solution was stirred for 15 min and then extracted with two 20-ml portions of diethyl ether. The deep red ether layers were combined and evaporated to dryness with an air stream. Acetone was added to the resulting red glassy layer (200 ml), followed by water until a slightly turbid solution was achieved. The solution was refrigerated and the crude product crystallized overnight. One-fourth of the filtered red product was dissolved in 150 ml of acetone and water was added slowly until the point of visible turbidity, and then a small amount of acetone was added in order to just regain a transparent red solution. The shiny red plate crystals, which separated while the solution was refrigerated for approximately one week, were filtered and air dried. Yield, 0.5 g, m.p. 210–212°. *Anal.* Calcd for $FeC_{33}H_{45}O_6$: C, 66.78; H, 7.64. Found: C, 66.28; H, 7.68.

Preparation of Tris((+)-3-acetylcamphorato)iron(III), Fe((+)-3-ac)₃. A solution of 0.92 g (3.43 mmole) of $FeCl_3 \cdot 6H_2O$ in 15 ml of 95% ethanol and a solution of 2.00 g (10.3 mmole) of (+)-3-acH in 5 ml of 95% ethanol were combined and stirred for 15 min. After the addition of 15 ml of water, the mixture was extracted with four 15-ml portions of *n*-heptane. The combined *n*-heptane layers were evaporated to dryness under an air stream. Two hundred milliliters of acetone was added to the red glass-like solid and the solution was heated to 35°. During the heating process water (100 ml) was added to the solution. When the solution reached 35° it was removed from the heat, covered, and refrigerated for eight days. The deep red needle crystals that formed were filtered and air dried. Yield, 0.53 g, m.p. 167–168°. *Anal.* Calcd. for $FeC_{36}H_{51}O_6$: C, 68.02; H, 8.09. Found: C, 67.74; H, 7.91.

Preparation of Tris((+)-3-propionylcamphorato)-iron(III), Fe((+)-3-pc)₃. A solution of 2.27 g (10.2 mmole) of (+)-3-propionylcamphor in 5 ml of 95% ethanol was stirred with a solution of 0.92 g (3.4 mmole) of $FeCl_3 \cdot 6H_2O$ in 15 ml of 95% ethanol for 15 min. Water (15 ml) and *n*-heptane (10 ml) were added to the reaction solution in a separatory funnel. After shaking, the layers were separated and the blue aqueous layer was extracted with 10-ml portions of *n*-heptane until only a transparent heptane layer was obtained. The combined heptane fractions were evaporated to dryness by an air jet. Various combinations of organic solvents, water, and the crude product were combined and cooled in order to obtain pure crystals. The best crystals were obtained by dissolving 0.14 g of the glass-like crude product in enough acetone to make the solution just transparent to daylight. Water (and then acetone) were added to bring the solution almost to the point of turbidity. Cooling in a freezer (−15°) for one week yielded fine red crystals which were filtered and air dried. Yield, 0.045 g, m.p. 112°. *Anal.* Calcd. for $FeC_{39}H_{57}O_6$: C, 69.12; H, 8.48. Found: C, 68.94; H, 8.68.

Preparation of Bis((+)-3-hydroxymethylenecamphorato)copper(II), Co((+)-hmc)₂. The complex was prepared as reported in the literature[14] but a modification was necessary in the purification step in order to obtain a pure crystalline product.

Ammonium hydroxide was added to a mixture of 3.0 g (17 mmole) of (+)-3-hydroxymethylenecamphor in 100 ml of water with vigorous stirring until all of the ligand dissolved. A solution of 2.0 g (8.3 mmole) of $Cu(NO_3)_2 \cdot 6H_2O$ in 50 ml of water combined with the ligand solution was refluxed for 1 hr. The mixture was cooled, filtered, washed with water, and the crude product (3.4 g) dried at 110°. The crude product was recrystallized twice from warm *n*-heptane and then from *n*-octane to give shiny plate crystals. Yield, 0.02 g, m.p. 167°. *Anal.* Calcd. for $CuC_{22}H_{30}O_4$: C, 62.61; H, 7.17. Found: C, 62.81; H, 7.51.

Preparation of Bis((+)-3-acetylcamphorato)copper(II), Cu((+)-3-ac)₂. A solution of (+)-3-acetylcamphor in water was prepared by adding 2.0 g (10.3 mmole) of (+)-3-acH to 60 ml of water and adding concentrated ammonium hydroxide dropwise, with stirring, to pH 11. The solution was filtered and to the filtrate was added a solution of 1.24 g (5.15 mmole) of $Cu(NO_3)_2 \cdot 3H_2O$ in 30 ml of water. A green precipitate formed immediately. After stirring for 2 hr the mixture was added to a round-bottomed flask and refluxed for 1 hr. Filtration yielded 1.5 g of crude product which was washed with two portions of water. The product (dried in a vacuum desiccator over $CaCl_2$) was recrystallized twice from *n*-heptane to give shiny olive-green crystals. Yield, 0.1 g, m.p. 205–206°. *Anal.* Calcd. for $CuC_{24}H_{34}O_4$: C, 64.05; H, 7.61. Found: C, 63.78; H, 7.66.

Preparation of Bis((+)-3-propionylcamphorato)-copper(II), Cu((+)-3-pc)₂. To 40 ml of water was added 1.2 g (5.76 mmole) of (+)-3-propionylcamphor and enough concentrated ammonium hydroxide to raise the pH to eleven. After stirring overnight the solution was filtered and then stirred for 4 hr with a solution of 0.70 g (2.88 mmole) of $Cu(NO_3)_2 \cdot 3H_2O$ in 20 ml of water. The mixture was transferred to a round-bottomed flask and refluxed for 1 hr. The cooled reaction mixture was extracted twice with a volume of diethyl ether equal to that of the reaction solution. The combined ether layers were evaporated to dryness by an air stream and the crude product was dried over $CaCl_2$ in a vacuum desiccator. The crude product was recrystallized from *n*-heptane and air dried. Yield, 0.60 g, m.p. 123–125°. *Anal.* Calcd. for $CuC_{26}H_{38}O_4$: C, 65.31; H, 8.01. Found: C, 64.99; H, 8.17.

The visible absorption spectra were recorded on a Cary Recording Spectrophotomer Model 14 using a tungsten lamp, the ultraviolet spectra were recorded on the same instrument using a deuterium discharge lamp. Spectra were measured in 1 cm quartz cells at room temperature. Sample concentrations ranged from 10^{-3} to 10^{-6} M.

Circular dichroism spectra were recorded on a Cary Model 61 CD Spectropolarimeter using a xenon arc source. Concentrations of 10^{-3} to 10^{-6} M in 1 cm quartz cells were used.

RESULTS AND DISCUSSION

The spectra of (+)-hmcH, (+)-3-acH, and (+)-3-pcH in ethanol are shown in Figure 2. The spectral data for the neutral ligands in ethanol solution and the anionic ligands in ethanol containing 0.025 M sodium ethoxide are given in Table 1. The single absorption band for each of the ligands is attributed to a $\pi \rightarrow \pi^*$ $(\pi_3 \rightarrow \pi_4)$[16, 17] transition.

These bands have about the same intensities for (+)-3-acH and (+)-3-pcH, but almost three times greater intensity for (+)-hmcH. The intensities for $\pi \rightarrow \pi^*$ transitions increase with increasing enol concentration;[18] this suggests that (+)-hmcH perhaps exists in solution mainly in the enol form with the other ligands in the keto form. However, these three bands are very similar in position and *relative* intensities for the free ligands (Figure 2) and for the Fe(III) complexes (Figure 3). Since the keto–enol equilibrium is not involved for the complexes this explanation is not plausible.

The explanation for the spectral differences among the three ligands is probably structural. Two of the ligands are diketones while (+)-hmcH has one aldehyde group. There is considerable difference in the electron-releasing ability of an alkyl group compared

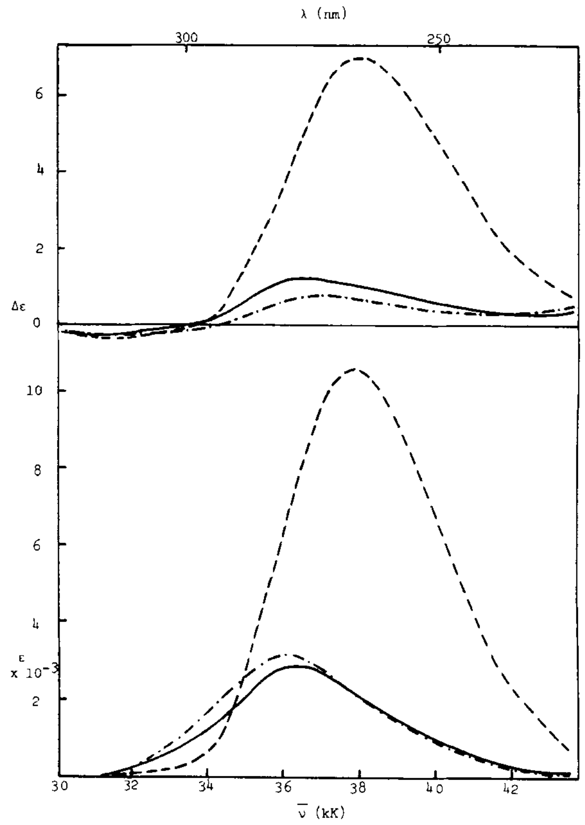

FIGURE 2 Absorption and circular dichroism spectra of (+)-hmcH (– – –), (+)-3-acH (——), and (+)-3-pcH (–.–.) in 95% ethanol.

TABLE I
Absorption and circular dichroism data for (+)-hmcH, (+)-3-acH, and (+)-3-pcH in 95% ethanol and for the anions in ethanol containing 0.025 M sodium ethoxide

	Absorption		CD	
Compound	kK	log ε	kK	Δε
(+)-hmcH	37.88	4.02	31.25	−0.41
			37.88	7.01
(+)-hmc⁻	32.89	4.26	29.59	−0.26
			32.68	2.49
			39.22	8.73
(+)-3-acH	36.50	3.45	30.86	−0.28
			36.50	1.26
(+)-3-ac⁻	32.47	4.13	30.12	−0.32
			34.13	3.62
			38.46	4.42
(+)-3-pcH	36.10	3.49	30.96	−0.33
			36.90	0.76
(+)-3-pc⁻	32.15	4.27	30.77	−0.62
			33.90	3.67
			38.02	6.44

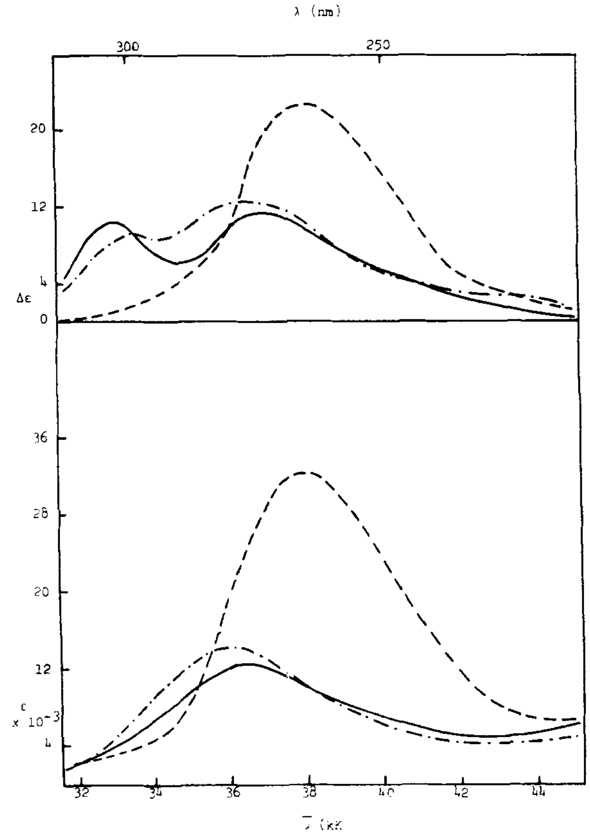

FIGURE 3 Ultraviolet absorption and circular dichroism spectra of Fe((+)-hmc)$_3$ (– – –), Fe((+)-3-ac)$_3$ (——), and Fe((+)-3-pc)$_3$ (–·–·) in 95% ethanol.

to a hydrogen. The $\pi\rightarrow\pi^*$ transition energy undergoes a bathochromic shift as the H is replaced by a methyl and then an ethyl group. The methyl and ethyl groups have nearly the same electron-releasing ability.

The absorption bands are shifted to about 32.5 kK for the anionic ligands (Table I) and the band for (+)-hmc$^-$ has about the same intensity as for (+)-3-pc$^-$. Each band has a long tail on the higher energy side. The similarity among the anions but not the neutral ligands would be expected if the differences among the neutral ligands were caused by shifts in the keto-enol equilibrium. However, the great similarities between the absorption spectra for the neutral ligands and the Fe(III) complexes argue against this.

In neutral solution the ligands exhibit two CD bands of opposite sign, with the negative peak very weak (Figure 2). The great intensity for (+)-hmcH compared to the other two ligands is even more striking than for the absorption bands. In basic solution there are still two CD peaks of opposite sign for each ligand, but the intensities are about the same for each ligand (Table I). There is a high intensity positive CD peak at about 38–39 kK for each ligand. The absorption in this region has very low intensity. Presumably this is the $\pi_3\rightarrow\pi_5$ transition.[16,17]

Iron(III) complexes. The iron(III) complexes of (+)-hmcH, (+)-3-acH, and (+)-3-pcH have four isomeric possibilities, Λ-*cis*, Δ-*cis*, Λ-*trans*, and Δ-*trans*. Only one crystalline form of each complex could be isolated. Various TLC and column chromatographic separation methods utilizing different solvents and supports did not yield separation. The iron(III) complexes of these bulky bicyclic 1,3-diketones are quite labile.

The absorption and circular dichroism spectra of Fe((+)-hmc)$_3$, Fe((+)-3-ac)$_3$, and Fe((+)-3-pc)$_3$ in 95% ethanol are shown in Figures 3 and 4 and in Table II. The visible absorption spectra of the three

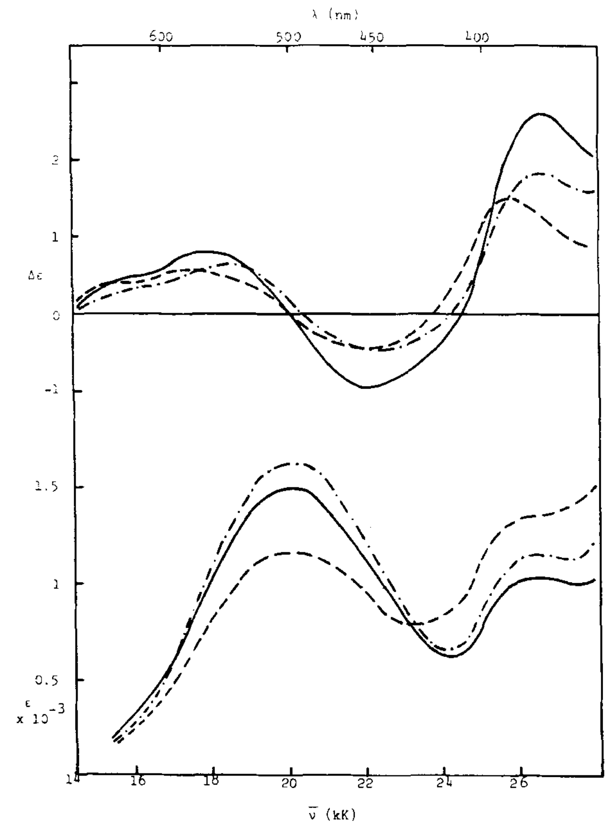

FIGURE 4 Visible region absorption and circular dichroism spectra of Fe((+)-hmc)$_3$ (– – –), Fe((+)-3-ac)$_3$ (——), and Fe((+)-3-pc)$_3$ (–·–·) in 95% ethanol.

TABLE II
Absorption and circular dichroism data for Fe((+)-hmc)$_3$ Fe((+)-3-ac)$_3$, and Fe((+)-3-pc)$_3$ in 95% ethanol

	Absorption		CD	
Compound	kK	log ϵ	kK	$\Delta\epsilon$
Fe((+)-hmc)$_3$	20.00	3.06	15.50	sh
	26.18	sh	17.04	0.64
	38.02	4.51	21.74	−0.45
			25.71	1.43
			37.88	22.9
Fe((+)-3-ac)$_3$	20.08	3.18	16.10	sh
	26.67	3.01	17.95	0.80
	36.36	4.09	21.98	−0.92
			26.53	2.63
			32.89	11.2
			36.90	11.3
Fe((+)-3-pc)$_3$	20.00	3.21	16.38	sh
	26.32	3.07	18.35	0.65
	36.23	4.16	22.12	−0.45
			26.53	1.82
			33.44	9.25
			36.36	12.4

complexes reveal the presence of two bands, a symmetrical intense band at lower energy followed by a weaker peak at high energy. The second peak merges with an extremely strong band in the ultraviolet region. Similarities between the three iron(III) complexes are obvious in the visible region, but in the uv region Fe((+)-hmc)$_3$ has a band which is nearly three times as intense as those of the other two complexes. The spectra of the complexes in the uv region are very similar to those of the free ligands in ethanol (Figure 2, Table I) except for intensities. The intensities are greater for the complexes, but still in about the same ratios as for the free ligands.

The spectra of the iron(III) complexes are very similar to that of tris(acetylacetonato)iron(III). Barnum's assignments[16,17] (Table III) were based on LCAO–MO calculations for a series of transition metal acetylacetonato complexes. Jørgensen's assignments[19] (Table III) disagree with two of those given by Barnum. Both agree on the assignment of the highest energy band as $\pi_3 \rightarrow \pi_4$ ($\pi \rightarrow \pi^*$). The striking similarities for the free ligands and the complexes makes it apparent that this is a ligand $\pi \rightarrow \pi^*$ transition. Barnum considered the possible splitting of the O_h levels into D_3 components, but did not expect that these components would be separated for the $\pi \rightarrow \pi^*$ band.

For the high-spin Fe(III) complexes the spin-forbidden *d–d* transitions are not expected to appear, so the other two bands should involve charge transfer. Barnum assigned these as D_3 components of $t_{2g} \rightarrow \pi_4$. Only three components are expected to appear since $a_1 \rightarrow a_1$ is forbidden. He expected the $a_1 \rightarrow e$ and $e \rightarrow a_1$ transitions to be unresolved (*ca.* 26.5 kK here) but the $e \rightarrow e$ to occur at much lower energy (*ca.* 20 kK here). Barnum considered the assignment of the lowest energy band to be uncertain. Jørgensen assigned the $\sim$26.5 kK band as $e_g \rightarrow \pi$ and the 20 kK band as $\pi_3 \rightarrow t_{2g}$, using O_h symmetry.

The circular dichroism spectra help clarify the assignments. In the $\pi_3 \rightarrow \pi_4$ absorption region Fe((+)-3-ac)$_3$ and Fe((+)-3-pc)$_3$ show two positive CD peaks – perhaps the D_3 components expected by Barnum. Only one very intense peak appears for Fe((+)-hmc)$_3$. This peak is unsymmetrical, so presumably the second component is unresolved. Since these are pure ligand transitions, the sign of the dominant CD peak (at higher energy for two of the complexes) is determined by the absolute configuration of the ligand. In benzene the three complexes show absorption bands at about the same energy (34.1 – 34.7 kK) and of comparable intensities (log ϵ 4.33 – 4.42). Only one CD peak appears for each complex also (32.4 – 32.9 kK, $\Delta\epsilon$ 15.9 – 16.9).

In the region of the 26 kK absorption band only one CD peak appears. If one of the D_3 components were to appear as low as 20 kK, one might expect to see evidence for separation of the other two D_3 CD components, but this is not the case. Within the manifold of the 20 kK band there are three CD peaks.

TABLE III
Transition energies and assignments for Iron(III) 1,3-diketonate complexes. Energies are given in kK

Assignments of transitions		Fe((+)-hmc)$_3$	Fe((+)-3-ac)$_3$	Fe((+)-3-pc)$_3$
Jørgensen[19]	Barnum[16,17]			
$\pi_3 \rightarrow \pi_4$	$\pi_3(e) \rightarrow \pi_4(e)$	38.0	36.4	36.2
	$\pi_3(a_2) \rightarrow \pi_4(a_1)$			
	$t_2g(a_1) \rightarrow \pi_4(e)$	26.2	26.7	26.3
$e_g \rightarrow \pi_4$	$t_2g(e) \rightarrow \pi_4(a_1)$			
$\pi_3 \rightarrow t_2g$	$t_2g(e) \rightarrow \pi_4(e)$	20.0	20.1	20.0

Only one is expected from Barnum's assignment, but these could be the expected three D_3 components of $\pi_3 \rightarrow t_{2g}$. The CD spectra are consistent with the assignments of Jϕrgensen and disagree with those of Barnum. In benzene only one CD peak appears in the region of the 26.5 kK absorption band. The low energy shoulder (*ca.* 16 kK, Figure 4), is less apparent in benzene solution.

The possibility exists for the stereoselective formation of one disastereoisomer of the labile Fe(III) complexes or for an equilibrium mixture. The CD intensities are much higher than would be expected for an active racemate. Since the ratios of the intensities of the highest energy CD peak are so very nearly the same for free ligands and for the complexes, it is likely that only one disastereoisomer was formed in each case. It would be very unlikely that the same equilibrium mixture would result for each complex.

Copper(II) complexes. The absorption and CD spectra of $Cu((+)\text{-hmc})_2$, $Cu((+)\text{-3-ac})_2$, and $Cu((+)\text{-3-pc})_2$ are illustrated in Figures 5 and 6. The lowest energy absorption band for the three complexes occur at approximately 15 kK. There is not just a single band in this region; at about 17.5 kK there appears to be a shoulder of another absorption band of similar intensity to the first band. The second band is obscured because of the overlap with another more intense band which appears as a shoulder at about 24 kK for the copper complex series. Following this shoulder appears an intense band ($> 10^4$ ϵ) in the uv region. This band is unsymmetrical with a weak splitting appearing on the lower energy side of the band. One more band is obvious in the uv region, this one is a symmetrical peak occurring at approximately 38 kK with an ϵ value of about 14,000.

An interpretation of the absorption spectra of the copper chelates is based on the work of Cotton and Wise.[20] They performed LCAO–MO calculations on a model copper 1,3-diketonate complex followed by a single crystal spectral study of the same complex.[21] The model 1,3-diketone of the studies was dipivaloylmethane, DPM, 2,2,6,6-tetramethylheptane-3,5-dione.

The copper complexes of (+)-hmcH, (+)-3-acH, and (+)-3-pcH can be considered similar to $Cu(DPM)_2$ if the chelate rings are given the most important consideration. The similarity is more obvious if the spectrum of $Cu(DPM)_2$ is compared to the spectra of $Cu((+)\text{-hmc})_2$, $Cu((+)\text{-3-ac})_2$, and $Cu((+)\text{-3-pc})_2$. There exists nearly a peak-to-peak correspondence. The assignment of absorption bands is given in Table IV.

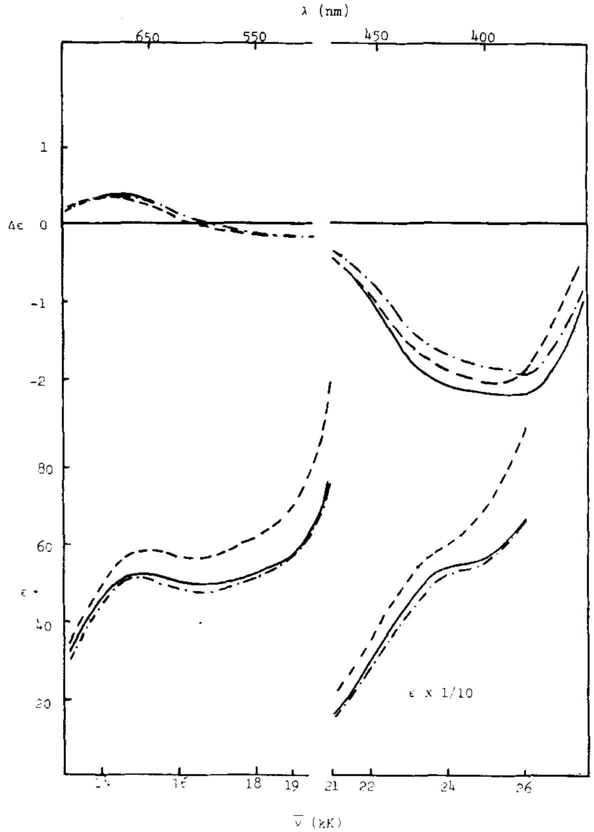

FIGURE 5 Visible region absorption and circular dichroism spectra of $Cu((+)\text{-hmc})_2$ (– – –), $Cu((+)\text{-3-ac})_2$ (——), and $Cu((+)\text{-3-pc})_2$ (–·–·) in cyclohexane.

The bands in the visible region centred at ∿16.5 kK are the *d–d* transitions expected. Four transitions of this type are predicted, but since they are all close in energy, resolution into individual transitions cannot be expected in the absorption spectrum.

In the circular dichroism spectra of the copper complexes the region of *d–d* transitions shows a positive low energy band followed by a less intense negative component for which the position of its maximum is obscured by the more intense negative band which follows. The CD in the *d–d* transition region is of low intensity as would be expected since it is due to the vicinal effect of the chiral ligands. A negative broad unsymmetrical CD band, which follows at higher energy (*ca.* 24 kK), corresponds to the $d \rightarrow \pi^*$ absorption band. Absorptions at ∿32 kK assigned to $\pi \rightarrow \pi^*$ transitions show a rather broad positive CD band with two maxima close in energy. The $\pi \rightarrow \pi^*$ absorption bands for the complexes are similar in energy and shape to those of the anionic ligands. The highest energy $\sigma \rightarrow d_{xy}$ transition is split

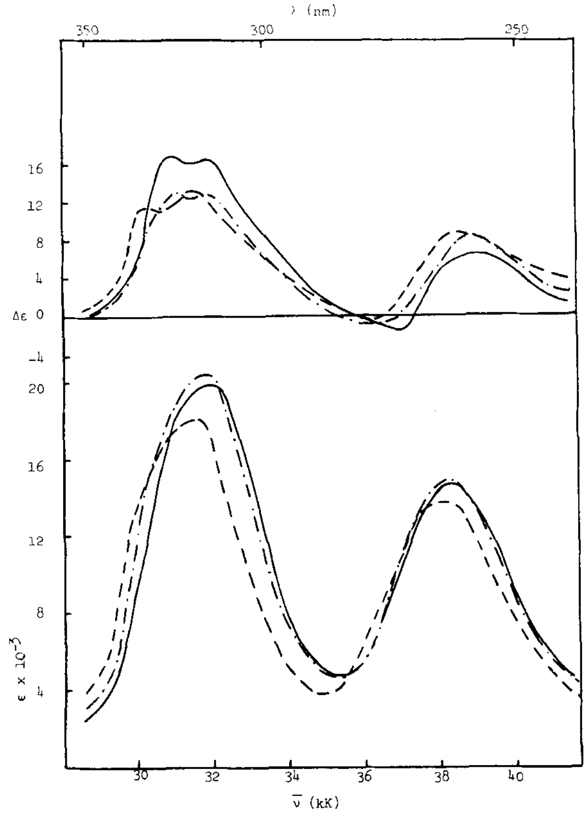

FIGURE 6 Ultraviolet absorption and circular dichroism spectra of Cu((+)-hmc)$_2$ (– – –), Cu((+)-3-ac)$_2$ (——), and Cu((+)-3-pc)$_2$ (–.–.) in cyclohexane.

in the CD into two components, a weak negative maximum followed by a relatively more intense positive band.

The low energy CD bands corresponding to *d–d* transitions are essentially alike for the three complexes of the series. The change in the R substituent on the chelate ring does not influence the *d–d* transitions to any great extent. The Δε values of the CD bands are relatively high for a vicinal effect.

TABLE IV
Transition energies and assignments for Copper(II) 1,3-diketonate complexes. Energies are given in kK.

Transition	Cu((+)-hmc)$_2$	Cu((+)-3-ac)$_2$	Cu((+)-3-pc)$_2$
$\sigma \rightarrow d_{xy}$	38.02	38.17	38.17
$\pi \rightarrow \pi^*$	31.45	31.95	31.85
	sh	sh	sh
$d \rightarrow \pi^*$	23.60(sh)	24.30(sh)	24.40(sh)
$d \rightarrow d$	15.50	15.15	14.93

REFERENCES

1. Present address: Mobil Research and Development Corporation, Paulsboro, New Jersey 08066.
2. Author to whom correspondence should be addressed.
3. A. Combes, *Compt. Rend.*, **105**, 871 (1887).
4. J. Lifschitz, *Rec. Trav. Chim.*, **41**, 627 (1922).
5. J. Lifschitz, *Z. Phys. Chem.*, **105**, 27 (1923).
6. J. H. Dunlop, R. D. Gillard and R. Ugo, *J. Chem. Soc. A*, 1540 (1966).
7. Y. T. Chen and G. W. Everett, Jr., *J. Am. Chem. Soc.*, **90**, 6660 (1968).
8. R. M. King and G. W. Everett, Jr., *Inorg. Chem.*, **10**, 1237 (1971).
9. C. S. Springer, Jr., R. E. Sievers and B. Feibush, *Inorg. Chem.*, **10**, 1242 (1971).
10. G. W. Everett, Jr. and A. Johnson, *Inorg. Chem.*, **13**, 489 (1974).
11. G. W. Everett, Jr. and R. R. Horn, *J. Am. Chem. Soc.*, **96**, 2087 (1974).
12. V. M. Potapov, N. K. Vikulova and G. V. Panova, *Zh. Obshch. Khim.*, **43**, 930 (1973).
13. V. M. Potapov, G. V. Panova and N. K. Vikulova, *Zh. Obshch. Khim.*, **43**, 939 (1973).
14. R. L. Lintvedt and A. M. Fatta, *Inorg. Chem.*, **7**, 2489 (1968).
15. J. W. Brühl, *Ber.*, **37**, 746 (1904).
16. D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).
17. D. W. Barnum, *J. Inorg. Nucl. Chem.*, **22**, 183 (1961).
18. A. I. Scott, *Ultraviolet Spectra of Natural Products*, Pergamon Press, N. Y., 1964.
19. C. K. Jørgensen, *Acta Chem. Scand.*, **16**, 2406 (1962).
20. F. A. Cotton, C. B. Harris and J. J. Wise, *Inorg. Chem.*, **6**, 909 (1967).
21. F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **6**, 917 (1967).