These values are marginally consistent with a substitution-limited rate on V^{2+} for this reaction also.[24-26]

The $Cr(N_3)_3$–Cr^{2+} reaction appears to proceed by a double-bridged activated complex, with a second-order rate constant of ca. 98 $M^{-1}\ s^{-1}$ at 0 °C. The value of the rate constant for the double-bridge pathway in the isotopic exchange reaction between *cis*-$Cr(N_3)_2^+$ and Cr^{2+} is 60 $M^{-1}\ s^{-1}$ at 0 °C.[11] Thus, the two double-bridged reactions proceed with similar rates, as do the single-bridged pathways[9] in the Cr^{2+} reactions with CrN_3^{2+} and *cis*-$Cr(N_3)_2^+$. Again, this feature can be interpreted as an indication of similar cis nonbridging ligand effects of azide and water. The same feature is illustrated in the single-bridging rates of the V^{2+} reductions of the azidochromium(III) complexes, although these systems appear to be limited by substitution on V^{2+}.

Registry No. $(H_2O)_5CrN_3^{2+}$, 18517-09-4; *cis*-$(H_2O)_4Cr(N_3)_2^+$, 53023-12-4; $(H_2O)_3Cr(N_3)_3$, 58512-47-3; $(H_2O)_5VN_3^{2+}$, 58512-48-4; Cr, 7440-47-3; V, 7440-62-2.

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Contribution from the Department of Chemistry,
Indiana University–Purdue University at Fort Wayne, Fort Wayne, Indiana 46805

Partial Photoresolution. V. Substituted β-Diketonate Complexes of Chromium(III)[1,2]

KENNETH L. STEVENSON* and RONALD L. BAKER

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The partial photoresolution at 5461 Å in chlorobenzene solution of tris-chelate complexes of chromium(III) with propanedialato, 1,3-diphenylpropanedionato, 3-chloro-2,4-pentanedionato, 3-bromo-2,4-pentanedionato, 3-iodo-2,4-pentanedionato, and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato ligands is reported. The quantum yield results are very similar to those obtained previously for tris(2,4-pentanedionato)chromium(III), except in the cases of tris(propanedialato)chromium(III), and tris(1,3-diphenylpropanedionato)chromium(III), which have quantum yields 3 times and 0.03 times that for $Cr(acac)_3$, respectively. The circular dichroism spectra for these compounds are reported. Only the hexafluoro diketonate exhibited any noticeable thermal racemization at 34 °C.

Introduction

The partial resolution of a number of the β-diketonate–chromium(III) complexes has been reported using gas chromatography[3] and liquid chromatography.[4,5] The use of circularly polarized light as a partial resolving agent has been employed for several Cr complexes in aqueous solution[2a,b,6-8] as well as for β-diketonate complexes[2c,d,9] in organic solvents. An advantage of the latter technique is that the degree of resolution at the photostationary state is the result of the dissymmetry factor, $(\epsilon_l - \epsilon_r)/\epsilon$, at the irradiating wavelength, and hence the molar circular dichroism spectra can be obtained from a partially resolved system. This is particularly useful for determining CD spectra of compounds which are not charged and are therefore difficult to resolve chemically.

In addition, if the photokinetics are studied, the quantum yields for photolytic inversion of enantiomers are obtained. The two previous papers on $Cr(acac)_3$[2c] and $Cr(tfa)_3$[2d] have established that the quantum efficiency of photolytic inversion is essentially wavelength independent and slightly temperature and solvent dependent and that the mechanisms for inversion include both twisting and bond-rupture processes.

The purpose of this report is to determine what effects substituent groups on the β-diketone ligand have on optical activity and quantum efficiency parameters. Accordingly, Table II lists those complexes which have been subjected to photoresolution attempts as reported in this paper and the two preceding articles.[2c,d]

Experimental Section

Most of the compounds were prepared according to the established procedures referred to in Table I. The percentage compositions of the purified samples are also given in this table. $Cr(hfa)_3$ was obtained from Apache Chemicals, Seward, Ill., and was purified by recrystallization from CCl_4.

Solutions of the desired concentrations were prepared in reagent grade chlorobenzene. Irradiations in circularly polarized light at 5461 Å were carried out in an optical system described previously.[2] Both

Table I

Ligand name	Ligand abbrev	% calcd			% found			Prepn ref
		C	H	Halogen	C	H	Halogen	
Propanedialato	pda	40.74	3.40		40.74	3.34		10
1,3-Diphenylpropanedionato	dbm	74.70	4.58		74.73	4.77		11
3-Chloro-2,4-pentanedionato	Cl(acac)	39.76	3.98	23.49	39.93	4.03	23.24	12
3-Bromo-2,4-pentanedionato	Br(acac)	30.71	3.07	40.95	30.85	3.06	41.00	12
3-Iodo-2,4-Pentanedionato	Iacac	24.78	2.49	52.37	25.06	2.28	52.19	12
1,1,1,5,5,5-Hexafluororo-2,4-pentanedionato	hfa	26.75	0.45	50.82	26.58	0.43	50.62	13
Dipavaloylmethanato	dpm	65.89	9.48		65.87	9.44		14

Table II. Photostationary-State Value of Complexes in Chlorobenzene Solution

Compd	$\Delta\alpha_{pss}$, deg	C, M	$\Delta\alpha/\Delta A_{5461}$, deg	$\Delta\epsilon_{5461}$, cm^{-1} M^{-1}	g_{5461}
$Cr(pda)_3$	0.189	0.0200	51.8	−4.63	−0.078
$Cr(dbm)_3$	0.0138	0.0050	33.0	−5.23	−0.042
$Cr(acac)_3$[a]	0.150	0.0200	50.0	−4.45	−0.067
cis-$Cr(tfa)_3$[b]			53.5	−4.4	−0.070
trans-$Cr(tfa)_3$[b]			55.0	−3.9	−0.060
$Cr(hfa)_3$[c]	0.0247	0.0040	51.4	−4.3	−0.080
$Cr(Cl(acac))_3$	0.192	0.0200	48.4	−5.27	−0.075
$Cr(Br(acac))_3$	0.201	0.0200	49.0	−5.50	−0.073
$Cr(Iacac)_3$	0.162	0.0150	49.6	−6.05	−0.072

[a] From ref 2c. [b] From ref 2d. [c] This system had considerable thermal racemization and therefore did not conform to the simple formula (vida infra).

1000-W mercury–xenon and 200-w mercury high-pressure lamps were employed. Light intensities were measured using the well-known potassium Reineckate actinometer.[15] During a kinetic run, the amount of induced optical activity was measured in the form of an ORD Cotton effect amplitude, $\alpha_{max} - \alpha_{min}$, using a Bendix Polarmatic spectropolarimeter. The circular dichroism spectra were obtained on either a Cary 60 or a JASCO ORD-UV-5 spectropolarimeter, and the absorption spectra were taken on a B & L Spectronic 505. The procedure used for determination of the quantum yields has been previously described.[2c]

Results and Discussion

I. Optical Activity. Table II shows the value of the ORD amplitude at the photostationary state ($\Delta\alpha_{pss}$), the concentration of the solutions, the ratio $\Delta\alpha/\Delta A_{5461}$ obtained from ORD–CD spectra, the value of $\Delta\epsilon_{5461}$ which is calculated from the formula[2]

$$\Delta\epsilon = (2\Delta A_{pss}\epsilon/cl)^{1/2}$$

and the value of g_{5461} for this series of compounds including those studied previously. The quantity g is probably the best measure of the chirality of the compound since it represents the fractional difference between the extinction coefficients in left- and right-handed circularly polarized light. Thus, all of these complexes exhibit nearly the same degree of chirality, except for the dbm complex. Obviously, the benzene rings on the ligand tend to diminish the chirality. This effect has been observed by Yoneda et al.[9] with the 1-phenyl-1,3-butanedionato complex of Cr which exhibits a dissymmetry factor at 520 nm between that of $Cr(dmb)_3$ and $Cr(acac)_3$, although it should be pointed out that their values are apparently for a mixture of the cis and trans isomers since they did not report the separation and study of the two isomeric forms.

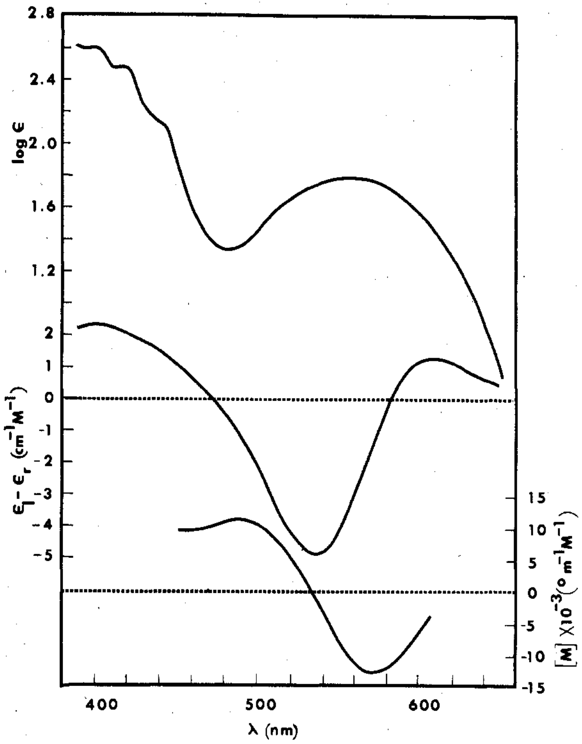

Figure 1. Visible absorption, circular dichroism, and ORD spectra of $(-)_{546}$-$Cr(pda)_3$ in chlorobenzene.

The ORD and CD spectra of these complexes are so similar that it was not deemed necessary to depict all of them. Instead, the main features of these spectra are listed in Table III, and the absorption, ORD, and CD spectra of two representative compounds, $Cr(pda)_3$ and $Cr(hfa)_3$, are shown in Figures 1 and 2, respectively.

Table III. Features of Visible CD, ORD, and Absorption Spectra[c]

Compd	Circular dichroism peaks						Abs peaks		ORD				
	λ_1	$\Delta\epsilon_1$	λ_2	$\Delta\epsilon_2$	λ_3	$\Delta\epsilon_3$	λ_{max}	ϵ	λ_{max}	[M]	λ_{min}	[M]	$[M]_{NaD}$
$Cr(pda)_3$	400	2.4	540	−4.9	605	1.3	557	61	488	11 220	571	−12 750	−10 300
$Cr(dbm)_3$			540	−5.3	636	1.9	568	139	518	8 330	571	−9 080	−7 330
$Cr(acac)_3$[a]	423	1.4	536	−4.8	606	1.4	567	68	492	11 300	575	−13 000	−10 500
cis-$Cr(tfa)_3$[b]			540	−4.4	615	1.1	566	71	500	11 300	588	−12 000	−12 000
trans-$Cr(tfa)_3$[b]			540	−4.0	615	2.2	566	71	500	10 400	580	−10 500	−9 700
$Cr(hfa)_3$			544	−6.0	618	1.9	572	63	497	10 900	583	−11 200	−10 000
$Cr(Cl(acac))_3$	450	0.9	545	−5.5	620	1.3	566	75	500	11 700	577	−13 800	−12 600
$Cr(Br(acac))_3$	456	1.01	540	−5.6	616	1.5	566	81	497	12 400	573	−14 500	−13 600
$Cr(Iacac)_3$	450	0.75	540	−6.0	620	1.5	566	89	490	14 700	576	−15 300	−14 000

[a] See ref 2c. [b] See ref 2d. [c] Units: λ, nm; ε, cm^{-1} M^{-1}; [M], deg m^{-1} M^{-1}

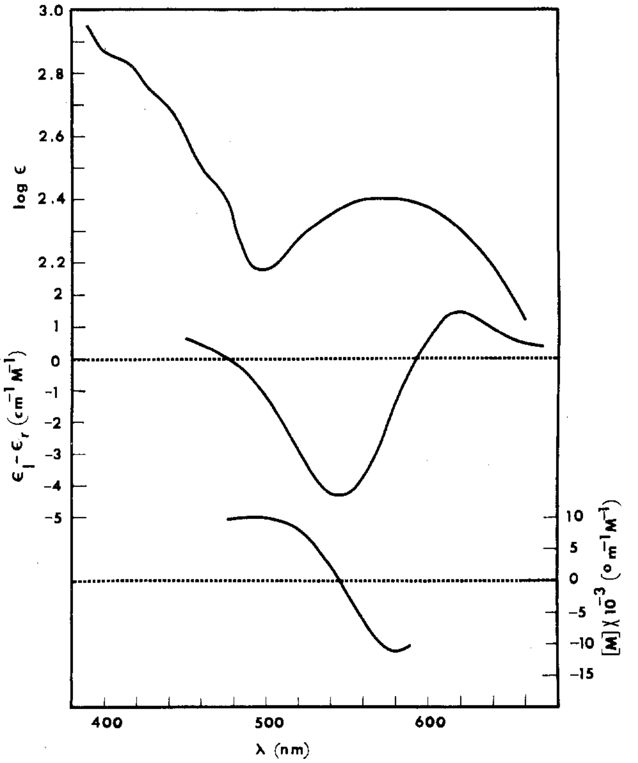

Figure 2. Visible absorption, circular dichroism, and ORD spectra of $(-)_{546}$-Cr(hfa)$_3$ in chlorobenzene.

The Cr(dpm)$_3$ compound is not listed in Tables II or III because no photoresolution was observed at 34 °C, the temperature used for most of the runs. This was interpreted as meaning that the quantum yield for photolytic inversion is vanishingly small at 5461 Å since there is no reason to suspect that the compound would have no optical activity even though its chirality might be reduced for the same reasons as for the Cr(dbm)$_3$.

II. Photokinetics. The quantum yields of photolytic inversion were determined as in the preceding studies.[2] In contrast to the other β-diketone complexes, the Cr(hfa)$_3$ system had a thermal racemization rate which was large enough so that it could not be ignored. In order to determine ϕ a sample was irradiated to a photostationary state, and then the thermal racemization rate constant was determined for that particular sample by plotting the log optical activity vs. time and taking the slope. The value of the thermal racemization constant at 34 °C was determined to be $3.9 \times 10^{-5}\ s^{-1}$.

The quantum yields for this series of compounds in chlorobenzene, including those reported in the two preceding papers, are listed in Table IV. It is of interest that the compounds appear to fall roughly into three groups with respect to quantum yield values. The high quantum yield group, of which Cr(pda)$_3$ is the only member, consists of the complex with the smallest and least massive ligand, namely, the propanedialato skeleton which has only three carbon atoms. The middle group consists of all those complexes containing the five carbon atom acetylacetone ligand. It is notable that the substitution of halogen atoms for hydrogen atoms seems to be less important than the fact that the skeletons all have the same number of carbon atoms. This would suggest that it is perhaps the number of degrees of vibrational freedom of the ligands which determines how much thermal energy can be carried away from the photoexcited state thus lowering the efficiency of the inversion reaction. The low quantum yields of the third group, consisting of complexes with the diphenylpropanedionato and dipivaloylmethanato ligands, further bear out this general observation. Although steric factors might also be important in the third group, their effect on the second group appears to be minimal as evidenced by the fact that the hexafluoro-substituted acetylacetonato complex has almost the same quantum yield as the unsubstituted one.

Table IV. Quantum Yields of Inversion at 5461 Å in Chlorobenzene Solution

Compd	$10^3\theta$	Temp, °C	Compd	$10^3\theta$	Temp, °C
Cr(pda)$_3$	17.5	33	Cr(hfa)$_3$	6.1	34
Cr(dbm)$_3$	0.17	34	Cr(Cl(acac))$_3$	4.0	34
Cr(acac)$_3$[a]	5.5	35.8	Cr(Br(acac))$_3$	3.9	34
cis- and *trans*-Cr(tfa)$_3$[b]	2.0	34	Cr(Iacac)$_3$	3.9	34
			Cr(dpm)$_3$	~0	34

[a] See ref 2c. [b] See ref 2d. The value reported here is an average of the six quantum efficiencies for the various pathways of isomerization.

The actual mechanism of photolytic inversion is probably the same as for the Cr(tfa)$_3$, reported in the preceding paper, namely, a combination of twisting and bond dissociation processes. The overall similarities of the quantum yields of these compounds to those of the Cr(tfa)$_3$ seem to bear this out.

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Registry No. Cr(pda)$_3$, 15636-02-9; Cr(dbm)$_3$, 14284-05-0; Cr(hfa)$_3$, 14592-80-4; Cr(Cl(acac))$_3$, 13963-55-8; Cr(Br(acac))$_3$, 15025-13-5; Cr(I(acac))$_3$, 15169-09-2.

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