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SPECTROSCOPY AND PHOTOCHEMISTRY OF TETRANEOPENTYLCHROMIUM(IV)

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Summary

Tetraneopentylchromium(IV) displays ultraviolet absorptions attributable to ligand-to-metal (LMCT) charge transfer transitions, and visible absorptions assignable to ligand field (LF) transitions. The observed photochemistry is consistent with metal-neopentyl homolytic cleavage arising from an LMCT excited state. Lower values for quantum yields in the visible region imply that the LF excited states are substantially inactive.

Introduction

Alkylmetal complexes have been reported to be useful as catalysts for photoinduced polymerization of alkenes [1–3]. Hence, the understanding of the primary photoprocess(es) of alkylmetal complexes is of great interest. In our previous studies of the spectroscopy and photochemistry of tetraalkyl transition metal complexes [4–6], we have concentrated on systems containing norbornyl ligands, primarily because of their excellent stability [7,8]. Complexes of other elimination-stabilized alkyls [9] such as neopentyl, although thermally stable, are more air-sensitive than their norbornyl counterparts, and hence more difficult to handle, but are of interest to us because of their reported use in photoassisted polymerizations [1].

As a consequence of the photochemical reactivity of the tetraalkylchromium complexes, the electronic structures have been of interest [4,6,10–12]. Given the similar nature of the norbornyl and neopentyl ligands, the electronic structures of their isomorphous complexes, and hence the corresponding absorption spectra, should be very similar. The literature contains conflicting reports of the electronic spectrum for tetraneopentylchromium with differences of up to 11 nm for some band maxima [10,12]. Consequently, a study of the spectroscopy and photochemistry of this compound was undertaken.

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Results and discussion

Tetraneopentylchromium, Cr(np)$_4$ [13], is an air-sensitive deep purple solid, very soluble in nonpolar solvents. Its physical characteristics are essentially as reported in the literature [10,12]. For samples that are rigorously purified by sublimation, the melting point (114.5–115°C) is higher than previously reported (lit. 110°C [10]).

Spectroscopy. Two major band systems are present in the electronic spectrum of the title complex, see Fig. 1. In hexane solutions of the sublimed complex at room temperature, the maximum of the ultraviolet band is at 262 nm with shoulders at 300 and 325 nm, and the visible band system has a maximum at 490 nm with shoulders at 545 and 650 nm, see Table 1. The positions of these features are not markedly affected by the nature of the solvent, with the ultraviolet band being slightly red-shifted in ethanol (+1.5 nm) and the visible band blue-shifted in carbon tetrachloride (−4 nm). Cooling to liquid nitrogen temperature does not result in any substantial shifts of the major bands, but sharpens the shoulders on the visible band, as well as making apparent another shoulder at 525 nm. Samples that have been purified only by column chromatography are the same in physical appearance as those purified by sublimation, but have the visible absorption maximum shifted to as low as 475 nm.

Solvent and temperature-induced shifts allow the assignment of the ultraviolet absorptions as ligand-to-metal charge transfer (LMCT) transitions. The close correspondence of the band positions in the CrL$_4$ complexes (L = norbornyl, neopentyl; see Table 1) leads to analogous assignments of the transitions. In this way, the most intense band (262 nm) can be assigned to ${}^3A_2(a_1^2t_2^6e^2) \rightarrow {}^3T_1(a_1^2t_2^5e^3)$ under strict tetrahedral symmetry. This transition is split into two components (${}^3B_1 \rightarrow {}^3E$,

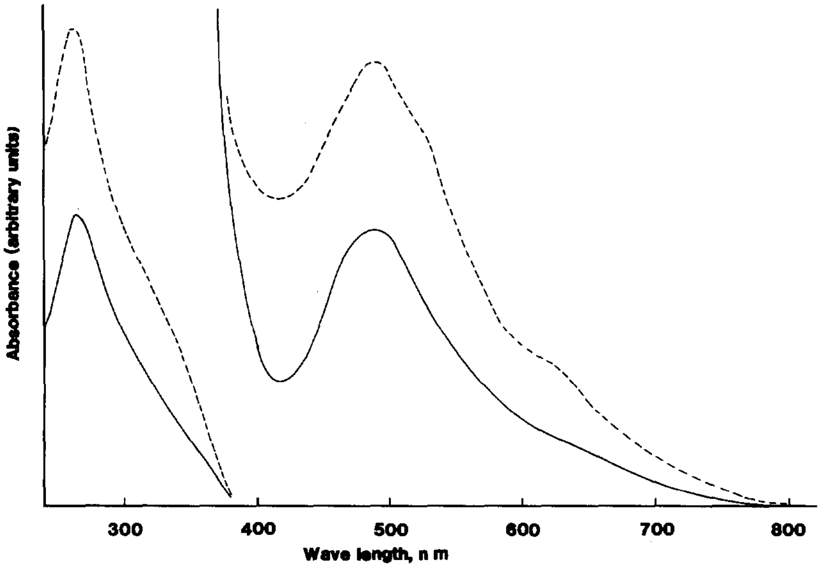

Fig. 1. Electronic absorption spectra of Cr(np)$_4$, in 1/1 isopentane/methylcyclohexane solvent. Solid line is the room temperature spectrum, and the dashed line is the spectrum at 77 K. The low temperature spectrum has been corrected for solvent contraction.

TABLE 1

ELECTRONIC SPECTRAL FEATURES OF $Cr(NOR)_4$ AND $Cr(np)_4$ [a]

Complex	Band max (nm) (ϵ, M^{-1} cm^{-1})	Complex	Band max (nm) (ϵ, M^{-1} cm^{-1})
$Cr(np)_4$	262 (21000)	$Cr(NOR)_4$ [b]	265 (29700)
	300 (sh)		294 (sh)
	325 (sh)		335 (sh)
	490 (1080)		486 (1340)
	525 (sh) [c]		534 (sh)
	545 (sh)		553 (sh)
	650 (sh)		620 (sh, 270)

[a] In Hexane solution at 25°C. [b] Ref. 6. [c] Observable only at low temperature.

$^3B_1 \rightarrow {}^3A_2$) under the D_{2d} symmetry inferred from previous ESR measurements [10]. A possible assignment for one of the shoulders on the ultraviolet band is $^3A_2 \rightarrow {}^3T_2(a_1^2t_2^5e^3)$ which is orbitally forbidden under T_d symmetry, but has an allowed component ($^3B_1 \rightarrow {}^3E$) under D_{2d}. Another possible assignment is the spin-forbidden, but orbitally allowed $^3A_2 \rightarrow {}^1T_1$.

In the visible region of the spectrum, there is a remarkable correspondence between the electronic spectra of the title complex and its norbornyl analog. Although the neopentyl complex has a simpler spectrum at room temperature, spectra at liquid nitrogen temperature both show the same weak features between 500 and 600 nm. (Compare Fig. 1 to Fig. 1b in ref. 6.) A previous report [10] of the visible absorptions of $Cr(np)_4$ lists the visible band maximum as occurring at 21100 cm^{-1} (474 nm, ϵ 1090 M^{-1} cm^{-1}), instead of at the lower energy 490 nm (20400 cm^{-1}, ϵ 1080 M^{-1} cm^{-1}) found here for rigorously purified samples (another report [12] gives 485 nm, ϵ 850 M^{-1} cm^{-1}). In our hands, only unsublimed samples give absorptions skewed to higher energy, indicating that thermally unstable or less volatile contaminants in unsublimed material are responsible for the observed blue shifts.

As a consequence of the presence of severely overlapping bands in the lower energy maximum, the use of ligand field theory [14] to fit the excited states and thus to obtain their assignments [10], is more difficult. Reasonable fits are obtained only if the most intense band (490 nm) is assigned to $^3B_1 \rightarrow {}^3E$ and $^3B_1 \rightarrow {}^3A_2$ under D_{2d} (derived from $^3A_2(a_1^2t_2^6e^2) \rightarrow {}^3T_1(a_1^2t_2^6e^1t_2^1)$ under strict T_d symmetry), and the lowest energy shoulder is assigned to $^3B_1 \rightarrow {}^3E$ under D_{2d} (the allowed component of $^3A_2 \rightarrow {}^3T_2(a_1^2t_2^6e^1t_2^1)$ which is orbitally forbidden under T_d symmetry). This leaves the spin-pairing transitions $^3B_1 \rightarrow {}^1A_1$ and $^3B_1 \rightarrow {}^1B_1$ (derived from $^3A_2 \rightarrow {}^1E$ in T_d) as the explanation for the weak shoulders between 500 and 600 nm.

Attempts to fit room temperature spectra to a sum of Gaussians [15] require at least four bands, with a fifth becoming apparent in low temperature spectra, in accord with the above assignments. Unfortunately, the severe overlap of the broad components does not allow selection of a unique set of components; rather a number of solutions are possible, with positions varying by as much as 5 nm, see Table 2. Consequently, accurate fits of the resolved components to transitions assigned under low symmetry cannot be performed.

Photochemistry. Irradiations of degassed hexane solutions of $Cr(np)_4$ result in

TABLE 2

COMPONENT GAUSSIANS FIT TO Cr(R)$_4$ [a]

R [b]	Fit No.	Position (nm)	Height (Abs.)	Width (nm)
np	1	456	0.329	53
		493	0.642	64
		517	0.023	51
		542	0.309	70
		608	0.213	161
np	2	458	0.388	56
		494	0.558	61
		537	0.381	77
		616	0.205	149
NOR	1	467	0.668	63
		494	0.214	31
		519	0.175	41
		542	0.261	62
		620	0.151	119
NOR	2	456	0.520	50
		494	0.596	47
		529	0.127	32
		547	0.229	54
		618	0.153	122

[a] Fits performed using deconvolution program [15]. Differences in fits result from different initial peak choice, and different order of fitting components. All final fits had rms deviations less than 0.0015 for 120 points over a 240 nm range (440–679 nm for np, 450–689 nm for NOR). [b] np = neopentyl, NOR = norbornyl.

clean spectral changes in the visible region, with a decline in the 490 nm peak, an increase in the trough around 420 nm, and isosbestic points at 460 and 380 nm. This produces a change in color of the solution from purple to orange. Similar changes are seen in degassed CCl_4 solutions, except that the isosbestic points are shifted to longer wavelengths by about 10 nm.

Quantum yields for disappearance of Cr(np)$_4$ under various conditions are listed in Table 3. The disappearance of the complex can be monitored by following the

TABLE 3

QUANTUM YIELDS FOR DISAPPEARANCE OF Cr(np)$_4$ [a]

Wavelength (nm)	[M(NOR)$_4$] [b] (mM)	Quantum yield [c]
254	2.7	0.038(4)
313	1.0	0.099(6)
	1.9	0.115(9)
366	1.8	0.074(5)
	1.9	0.075(15) [d]
436	4.8	0.0071(7)

[a] In hexane solution, except as noted. Quantum yields calculated as described in the Experimental and are corrected for incomplete absorption. [b] Determined by absorption measurements on unirradiated solution. [c] Standard deviation of last digit in parentheses. [d] In neat CCl_4.

decline of the shoulder at 660 nm, as this region is free of photoproduct absorption. The quantum yields in both hexane and carbon tetrachloride are identical.

Reasonable quantum yields for the disappearance of $Cr(np)_4$ are associated with ultraviolet irradiation. The quantum yields are not constant over the ultraviolet region, but peak at 313 nm, and are smaller at both higher and lower energies. This variation indicates that there is a delicate interplay between photochemical decomposition routes and non-radiative decay in the upper excited states. Visible irradiation leads to a substantial drop in the efficiency of photodecomposition, implying that the ligand field excited states in $Cr(np)_4$ do not participate measurably in the photochemistry.

Volatile organic photoproducts are separated from photolyzed solutions by trap-to-trap distillations on a high vacuum line in order to avoid the formation of organic compounds by thermal decomposition of metal-containing products in the injection port of the gas chromatograph. Gas chromatography and GC/MS techniques are used to identify the compounds so separated. Only neopentane and 2,2,5,5-tetramethylhexane are produced by the photolysis of $Cr(np)_4$ in hexane solution. Photolyses in carbon tetrachloride produce neopentane and neopentyl chloride in a ratio of 1/10, respectively, along with hexachloroethane and trace amounts of 2,2,5,5-tetramethylhexane. After all volatiles are removed from photolyzed CCl_4 solutions of $Cr(np)_4$, the remaining orange metal-containing residue displays a positive test for chloride, suggesting the existence of a chromium–chlorine bond.

The observed organic compounds resulting from all of these photolyses are typical radical coupling and abstraction products. This accords well with previous observations of photoinduced catalysis [1] of olefin polymerization using $Cr(np)_4$. The radical products imply that homolytic cleavage of the metal–alkyl bond is the primary photoprocess, the expected result of an LMCT transition:

$$Cr(np)_4 \rightarrow \text{“}Cr(np)_3\text{”} + np^{\bullet}$$

The primary photoprocess is consistent with the characterization of the LMCT process as a formal reduction of the metal and formal oxidation of the two-electron-donor neopentyl anion to a neopentyl radical. The initial orange photoproducts are inconsistent with a simple $Cr(np)_3$ formulation [9], and are likely to be chromium(IV) products formed by further reaction of the primary photoproduct. Long-term photolyses [1] in hydrocarbon solvents yield chromium(0) products (Cr mirror or $Cr(CO)_6$) in addition to neopentane and tetramethylhexane, consistent with LMCT processes.

The quantum yields arising from either ultraviolet or visible irradiation are two to three times larger for the disappearance of $Cr(np)_4$ than for its norbornyl analog [6]. The more efficient decomposition may be due to the presence of α and γ hydrogen atoms on the neopentyl ligand. This would allow for additional decomposition via hydrogen abstraction [8,16,17], a route that is not available to the norbornyl group because of steric hindrance. Additional evidence for postulating hydrogen abstraction is the observation of neopentane as an organic product in neat carbon tetrachloride, where the only available source of hydrogen for abstraction by neopentyl radicals are the neopentyl groups still bound to the chromium. This more efficient decomposition would also be observed if the diffusion of neopentyl radicals out of the solvent cage is more facile than for norbornyl radicals.

Experimental

Materials. Neopentyl chloride, lithium wire (Alfa) and magnesium turnings (Baker) were used as received, while $CrCl_3(THF)_3$ [18] was available from previous studies in this laboratory [4,6]. Diethyl ether and isopentane were reagent grade and used as received, but hexane and methylcyclohexane were purified by following a reported procedure [19]. Solvents for spectral studies were deoxygenated by purging with dry nitrogen gas.

Synthesis. Using standard Schlenk techniques, tetraneopentylchromium(IV) was prepared under dry nitrogen from $CrCl_3(THF)_3$ and neopentyl magnesium chloride by a literature method [10], and was additionally purified by sublimation (10^{-4} torr, 45°C). The following alternative synthesis with neopentyllithium [20] was also used: in an inert atmosphere box, $CrCl_3(THF)_3$ (0.8 g, 3.5 mmol) was added all at once to a hexane solution of neopentyllithium (0.8 g, 10 mmol) and was stirred continuously for 12 h in the dark. The solution was gravity filtered onto a grade I neutral alumina column, and the column eluted with hexane. The solvent was removed from the purple eluant under vacuum, and the resulting solid sublimed at 10^{-4} torr and 45°C to produce a 40% yield of pure $Cr(np)_4$. The melting point for a sublimed sample was 114.5–115°C under nitrogen (lit. 110°C [10]).

Spectroscopic procedures. All manipulations involving the $Cr(np)_4$ complex were performed in a nitrogen-filled VAC inert atmosphere box. Spectra were recorded on Hitachi 100-80 and Cary 118 UV-vis spectrophotometers. Liquid nitrogen spectra were obtained with the Cary 118 using a locally constructed all-quartz dewar flask with optical flats for windows. Solutions of the complex were prepared in the drybox and loaded into 13 mm OD cylindrical quartz cells and tightly capped with polyethylene-covered corks. After a room temperature spectrum was recorded in the optical dewar, the sample was cooled by adding liquid nitrogen to the dewar, doing so slowly to avoid formation of bubbles or severe dimpling of the sample solution. After boil-off slowed and the liquid nitrogen level had dropped below the windows, the spectrum was again recorded. The metal sample holder projects below the level of the windows enough so that it remains in contact with the liquid nitrogen throughout the acquisition of the low temperature spectrum.

Photochemical procedures. The solutions used for quantum yield determinations were prepared in a VAC dry box in a nitrogen atmosphere, loaded into a cell with a degassing sidearm [21], removed from the box, and degassed by at least three freeze-pump-thaw cycles on a high vacuum line. After transfer of the solution to the cell side, and sealing it with a teflon valve (Kontes), the sample was irradiated at 25°C. The progress of the reaction was followed by absorbance measurements at 660 nm, and concentrations calculated from the absorbances using ϵ_{660} 195 M^{-1} cm^{-1}. Corrections for incomplete absorption were made using absorbances measured at the irradiating wavelength. Lamp intensities were determined with ferrioxalate actinometry [22]. Quantum yields were calculated from plots of concentration versus time, with total conversions of less than 15%. Corrections for inner filter effects of products were not done, but are expected to affect the quantum yields less than 5%, based on previous experience with similar systems [6].

Photoproduct characterization. All of the volatile organic compounds were removed from a photolyzed solution of $Cr(np)_4$ in carbon tetrachloride by a trap-to-trap distillation. The remaining solid was mixed with concentrated aqueous

KOH and neutralized with nitric acid. Silver nitrate was added and a characteristic AgCl precipitate formed. A parallel test on a blank sample gave no precipitate. The volatile products were identified by GC and GC/MS using Varian 1400 and Hewlett-Packard 5985B instruments.

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