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Microchemical Preparation of Tricyclopentadienyl Compounds of Berkelium, Californium, and Some Lanthanide Elements[1]

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Tricyclopentadienyl complexes of Bk, Cf, and Pm were prepared by reaction of the trichlorides of these elements with molten $Be(C_5H_5)_2$ in an apparatus developed for use with microgram quantities of radioactive substances. For comparison purposes the compounds $Sm(C_5H_5)_3$ and $Tb(C_5H_5)_3$ were prepared in the same way, and $Pr(C_5H_5)_3$, $Sm(C_5H_5)_3$, and $Gd(C_5H_5)_3$ were made in gram quantities. The identities of the compounds were established by X-ray powder diffraction methods. Unit-cell dimensions and the space-group symmetry of this isomorphous series were determined from single crystals. Visible absorption spectra were measured using microgram quantities of the radioactive specimens.

Introduction

Complexes of the actinide elements with cyclopentadienyl rings as the only ligands have been reported previously[3] for Th, Pa, U, Np, Pu, and Am. We have now succeeded in synthesizing the compounds $Bk(C_5H_5)_3$ and $Cf(C_5H_5)_3$ and have thus obtained the first organometallic compounds of these elements. Since a maximum of 10 μg of the isotopes ^{249}Bk (half-life 314 days, β emitter) and ^{249}Cf (half-life 360 years, α emitter) was available in each experiment, the syntheses had to be carried out by techniques appropriate to the microgram scale. The identification of the compounds was achieved by X-ray diffraction methods.

Experimental Section

Apparatus and Techniques.—Microgram quantities of the substances were always handled in specially purified quartz or platinum vessels. For the reactions with transuranic elements and where necessary with lanthanides, high-purity reagents were employed. Standard purification methods for experiments in the microgram region are described in the literature.[4] The $Be(C_5H_5)_2$ was subjected to multiple fractional sublimations under high vacuum prior to introduction into the reaction vessel.

The ^{249}Bk had been separated from its ^{249}Cf daughter shortly (2 days) before use, by oxidation with $NaBrO_3$ followed by extraction with 0.5 *M* hydrogen di(2-ethylhexyl)orthophosphoric acid (HDEHP) in dodecane,[5,6] followed by further purification steps as described elsewhere.[5] The ^{249}Cf was purified by chromatographically eluting from a cation-exchange column with α-hydroxyisobutyric acid, followed by lanthanide removal by an alcohol–HCl column.[4b] Finally, a micro "cleanup column"[4b] was employed to remove light-element impurities. The ^{147}Pm used was purified in the same way as ^{249}Cf in order to separate it from its daughter ^{147}Sm. A considerable amount of time passed between the removal of ^{147}Sm and the use of the ^{147}Pm, so that at the time of the synthesis, the preparation had a ^{147}Sm concentration of $\sim$8.3%. Because the work with ^{147}Pm was primarily to be used for obtaining certain spectral data and for study of radiolysis no detriment to the main results was caused by this.[7]

The inert gas (argon) used in the micro work was not only submitted to the usual laboratory gas-purification methods[8] but was purified of traces of oxygen by use of a Cr^{2+}–silica gel catalyst.[9]

The apparatus used for the microsynthesis of the trichlorides and tricyclopentadienyls is shown in Figure 1. The gas lines and high-vacuum lines, with the exception of the specially drawn quartz capillaries, shown in Figure 2, were made of Pyrex glass and copper.

Known laboratory techniques were used for the synthesis of gram quantities of the trichlorides and tricyclopentadienyls of the lanthanides, and, where necessary, the work was carried out either with Schlenk vessels[8] or in an inert-gas box. All solvents were purified by established methods.[8]

Commercial lanthanide oxides with a purity of >99.95% (99.999% for Gd_2O_3) were available. The anhydrous chlorides were obtained by conversion with NH_4Cl.[10]

X-Ray studies by the powder method were carried out with a 114.6-mm powder camera employing Ni-filtered Cu Kα radiation. Special precautions to shield the X-ray film from radioactive radiation were necessary only in this work with promethium. This was achieved by covering the capillary with a beryllium cap.[11] Films were measured on a film reader equipped with a steel scale which could be read to 0.05 mm. No correction was applied for film shrinkage. Single-crystal data for determination of unit-cell dimensions and space groups were obtained with a precession camera equipped with a Polaroid-film cassette. Intensity data from crystals of $Pr(C_5H_5)_3$, $Bk(C_5H_5)_3$, and $Cf(C_5H_5)_3$ were collected with a computer-controlled X-ray diffractometer. Details of these structural investigations will be dealt with in a future publication.[12]

As far as possible, attempts were made to obtain spectra of the

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[2] Supported by the Bundesministerium für wissenschaftliche Forschung, Bonn, Federal Republic of Germany.

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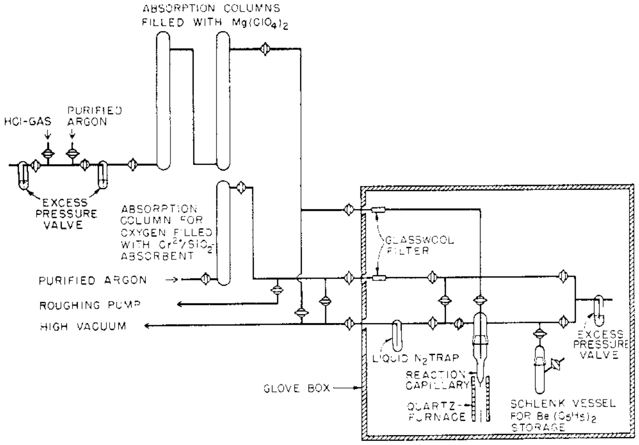

Figure 1.—Schematic drawing of the apparatus for the synthesis of the trichlorides and the tricyclopentadienyls.

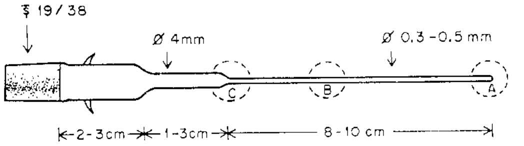

Figure 2.—Reaction capillary marked with the zones used for the different steps of the preparation.

substances in the near-infrared, the visible, and the ultraviolet regions. For this purpose we had available a specially constructed apparatus which made it possible to investigate the absorption behavior of microgram quantities of cyclopentadienyl complexes sealed in quartz capillaries. More concerning this, as well as a large part of the results obtained, will be reported separately.[13] With the technique mentioned, positions of the absorptions can be determined to an accuracy of at least ±2 nm.

Reaction Scheme.—The method of preparation of microgram quantities of tricyclopentadienyls is schematically shown by

$$\begin{array}{l} M^{3+} \text{ in } 0.05\ N\ HCl \\ \downarrow \\ M^{3+} \text{ on ion-exchange bead} \\ \downarrow \text{ oxidize in air at } 1200^\circ \\ M_2O_3 \text{ (probably}^5\ MO_2 \text{ in case of Bk)} \\ \downarrow \text{ HCl gas at } 500^\circ \\ MCl_3 \\ \downarrow \text{ } Be(C_5H_5)_2 \\ M(C_5H_5)_3 \end{array}$$

where the last reaction step corresponds to the equation

$$2MCl_3 + 3Be(C_5H_5)_2 \text{ (melt at } 70^\circ) \longrightarrow 2M(C_5H_5)_3 + 3BeCl_2$$

and M = Bk, Cf, Sm, Pm, or Tb. The pure actinide and lanthanide compounds were crystallized by fractional sublimation under high vacuum.

Syntheses on the Microgram Scale. Tricyclopentadienylberkelium.—From a supply of highly purified Dowex 50-X4 resin, seven beads (~0.33-mm diameter, each corresponding to an actual exchange capacity of about 10 μg of Bk^{3+} ions) were chosen and were loaded by a 0.5-hr treatment with 15 μl of 0.05 *N* HCl solution containing 80 μg of Bk^{3+} ions. Afterward the beads were washed twice with about 20 μl of 0.05 *N* HNO_3. The beads were then light yellow-green and transparent. A group of these beads was then transferred to a Pt boat where they hung on a Pt wire aided by a thin layer of glycerine. The Pt boat was heated carefully by means of an induction furnace over a period of several hours while the beads were observed with a microscope. At 300° the beads became completely black, at 640° light, and at 700° sand colored. After this they were heated briefly up to about 1250° and finally allowed to cool.

From the oxide beads so obtained, one with a diameter of about 0.18 mm was transferred to the quartz capillary shown in Figure 2 in such a manner that it came to rest at zone A. Then the capillary was attached to the reaction apparatus as shown in Figure 1.

The capillary, as well as the related parts of the gas-transfer system, was evacuated to a pressure of $<10^{-6}$ Torr. Then the capillary was heated to 500° by means of a quartz tube furnace, which permitted observation of the hot zone by a microscope; at this temperature HCl gas was introduced into the capillary. Within a short time, during which HCl gas was continually admitted to the reaction zone, the substance became light green. In order to ensure that the reaction in the end of the capillary went to completion, the heating was interrupted twice with the system under HCl atmosphere; the system was allowed to cool and then was evacuated at room temperature to ≤ 1 Torr; HCl was introduced again and the system was heated for 10 min at 500°. Following this, it was allowed to cool under HCl flow, evacuated at room temperature to $<10^{-6}$ Torr, and finally heated under vacuum to 430° for 2 min. To the chlorinated product so obtained, which it can be assumed without further investigation was $BkCl_3$, $Be(C_5H_5)_2$ was sublimed in under high vacuum from the attached storage Schlenk tube by cooling the capillary with liquid N_2. Next, by suitable cooling, the main quantity of $Be(C_5H_5)_2$ was transported into the part of the capillary indicated as C in Figure 2, and subsequently a portion of it sublimed into the principal reaction zone, A in Figure 2. The fraction remaining in zone C served as scavenger for possible entering traces of moisture or oxygen during the reaction.

After sufficient $Be(C_5H_5)_2$ was sublimed into the capillary, normal pressure was restored in the reaction system by introduction of Ar, and it was heated to 70° with the quartz tube furnace forming a colorless to light green, 1–2-mm high, molten zone in the capillary. The reaction was then allowed to proceed for 9 hr with continual stirring of the melt, *i.e.*, by vibration of the capillary, during which the melt became a distinct red-brown.

At the end of the reaction time almost all of the $Be(C_5H_5)_2$ was distilled off leaving behind a residue of an inhomogeneous red-orange appearance. It was allowed to cool and carefully evacuated. After reaching high vacuum and after it was established that all of the excess $Be(C_5H_5)_2$ was sublimed out of the capillary and the attached tube, the entire capillary was heated to ~100° to remove any readily volatile components. Then the end zone of the capillary was heated again with zone B held at room temperature by proper shielding. In a temperature interval of 135–165° the resulting $Bk(C_5H_5)_3$ was sublimed into zone B in the form of amber crystals.

The time between the separation of the ^{249}Bk from ^{249}Cf and isolation of the $^{249}Bk(C_5H_5)_3$ was about 4 days. From this fact there was an impurity of ^{249}Cf in the preparation due to nuclear decay calculated to be about 0.9%.

At the end of the sublimation, the sublimation zone of the capillary was sealed off under a pressure of $<10^{-6}$ Torr, and there was obtained directly a sample suitable for obtaining X-ray powder diagrams. By resublimation of the substance sealed in the capillary at temperatures up to 300° it was possible, 24 hr after isolation of the compound, to unite in a single crystal the entire $Bk(C_5H_5)_3$ preparation and to study it by X-ray diffraction.[12] By microscopic measurement of the crystal, calculation of its volume, and use of the X-ray density, a mass of 5 μg of $Bk(C_5H_5)_3$ was found to be the yield; this amounts to $\geq 36\%$ assuming a starting quantity of ≤ 10 μg of Bk ions.

Tricyclopentadienylcalifornium.—The method of preparation

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of this compound was analogous to that described for $Bk(C_5H_5)_3$. First, a light green oxide bead was obtained, of which only about one-fourth of the original quantity was successfully transferred into the capillary, so that only about 1 μg of Cf was available for the rest of the synthesis. It was allowed to react at a maximum temperature of 525° to the dark green chloride; and finally $CfCl_3$ was treated for a period of 24 hr with $Be(C_5H_5)_2$, during which the temperature was raised to 150°. The $Be(C_5H_5)_2$ melt, colorless at first, became red-brown during this time. After completion of the reaction and subliming off the excess $Be(C_5H_5)_2$, there remained behind a brown residue out of which, under high vacuum and in the temperature range 135–220°, tricyclopentadienylcalifornium could be sublimed in the form of ruby red crystals. Measurement of the product in the form of one crystal showed it to amount to 1.2 μg of $Cf(C_5H_5)_3$.

Tricyclopentadienylpromethium.—As with the method described for $Bk(C_5H_5)_3$, three oxide beads (mass in each case $\sim$10 μg) were obtained from a promethium stock solution which were then transformed in a reaction capillary to light rose-colored promethium chloride by reaction with HCl gas at a maximum temperature of 560°. The chloride was then treated with a $Be(C_5H_5)_2$ melt for 20 hr, during which a change of color of the melt from yellow to orange occurred. By the subsequent separation of the reaction mixture by sublimation a little yellow-orange product was isolated in the temperature range 145–260°.

Powder photographs as well as visible absorption spectra established the existence of the expected tricyclopentadienyl complex of Pm. A small single crystal was also grown from which X-ray photographs could be made.

Tricyclopentadienylsamarium and Tricyclopentadienylterbium.—In a manner analogous to the preparation described above, starting from a Sm^{3+} and a Tb^{3+} solution, respectively, $Sm(C_5H_5)_3$ and $Tb(C_5H_5)_3$, previously obtained by other means,[14,15] were prepared. The time for the reaction with $Be(C_5H_5)_2$ was somewhat longer than 12 hr. Orange-red $Sm(C_5H_5)_3$ and colorless $Tb(C_5H_5)_3$ could be obtained by vacuum sublimation from the reaction mixture at temperatures above 160°. Of special advantage for observation of the progress of the preparation in the case of terbium was the property of $Tb(C_5H_5)_3$ of fluorescing in ultraviolet light. Identification of the substance was achieved by Debye–Scherrer patterns and precession photographs.

Preparations on the Gram Scale. Tricyclopentadienylpraseodymium.—By a method analogous to that described in the literature[14,16] for preparation of lanthanide tricyclopentadienyls, we prepared the known $Pr(C_5H_5)_3$.[15] Accordingly $PrCl_3$ was allowed to react with KC_5H_5 in benzene, and subsequently a product was obtained by fractional sublimation of the solvent-free residue, which was then subjected to several further purifications by sublimation. *Anal.* Calcd for $Pr(C_5H_5)_3$: C, 53.49; H, 4.49. Found: C, 53.44; H, 4.53.

Cyclopentadienyl Complexes of Sm and Gd.—Trichlorides of Sm and Gd were each allowed to react in a melt of $Mg(C_5H_5)_2$ (at least a sixfold molar excess) for 2 hr at $\sim$220°. In this application of the method of Reid and Wailes[17] the reaction was not carried out in an ampoule but in an inert-gas box in a $\sim$30-cm tube (2-cm diameter) closed on one end and standing upright. By suitable heating with an aluminum block and gentle stirring of the melt with a stirring magnet, practically no loss occurred during the reaction time due to sublimation of the $Mg(C_5H_5)_2$.

From the resolidified melts, the cyclopentadienyl complexes could be isolated by fractional sublimation under high vacuum at temperatures of 170–220°. The reaction vessel itself could be employed for the first sublimation. This was followed by two further purification sublimations. The sublimate was collected on warm tube walls in order to achieve the best possible fractionation. Under these conditions it was observed, in each case, that different zones of substances separated.

The deposit from samarium gave a yellow, less volatile zone and an orange, more volatile zone. Only the X-ray diagram of the orange zone corresponded to the diffraction pattern of $Sm(C_5H_5)_3$ as was reported by Watt and Gillow[18] and as can be calculated from the data of Wong, *et al.*[19] Incomplete studies suggest that the yellow substance is the known $(C_5H_5)_2SmCl$.[20]

For our X-ray studies of the $Gd(C_5H_5)_3$ sublimate, only that fraction was taken which showed the same powder pattern as is known for $Sm(C_5H_5)_3$.

Results and Discussion

The compounds $Bk(C_5H_5)_3$ and $Cf(C_5H_5)_3$, prepared for the first time in the course of this work, and $Pm(C_5H_5)_3$, prepared for the first time in a weighable quantity,[16,21] showed essentially the expected properties of tricyclopentadienyls of actinides and lanthanides, because of which identification was made easier. The existence of these compounds was established by comparison of X-ray powder diagrams.

In Table I are presented the powder diagrams of the tricyclopentadienyls of Bk, Cf, and Pm alongside those of the tricyclopentadienyls of Pr, Sm, Gd, and Tb obtained by us. In the case of Sm, the *d* values found by Watt[18] are also given in Table I and, in another column, are the *d* values calculated from the data of Wong, *et al.*[19] Since we had available excellent elemental analyses of $Pr(C_5H_5)_3$, the comparison of X-ray data not only supported the previously known data on $Sm(C_5H_5)_3$, but the diagram obtained for $Pr(C_5H_5)_3$ could also be regarded as a standard pattern.

The choice of the lanthanide compounds $Pr(C_5H_5)_3$ and $Sm(C_5H_5)_3$, as well as $Gd(C_5H_5)_3$ and $Tb(C_5H_5)_3$, as substances for comparison was made because it was assumed that, in view of the structural similarity to be expected among these compounds, structural differences would result primarily from different radii of the central atom. These atoms, in the compounds chosen for X-ray comparison, should possess radii which encompass the possible range of radii of the metal atoms in $Bk(C_5H_5)_3$, $Cf(C_5H_5)_3$, and $Pm(C_5H_5)_3$. The lanthanide radii given by Templeton and Dauben[22] and the actinide radii by Peterson and Cunningham[23] are quoted in Table II.

From Table I it is apparent that a very good agreement exists between the powder diagrams found for the compounds of Bk, Cf, and Pm with those of $Pr(C_5H_5)_3$, $Sm(C_5H_5)_3$, and $Gd(C_5H_5)_3$, from which the existence of the compounds $Bk(C_5H_5)_3$, $Cf(C_5H_5)_3$, and $Pm(C_5H_5)_3$ was concluded.

The dimensions of the orthorhombic unit cells of these cyclopentadienyl complexes were obtained from single-crystal data and are shown in Table II. Sys-

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TABLE I

INDEXED POWDER PATTERNS

	$Sm(C_5H_5)_3$					$Pr(C_5H_5)_3$	$Pm(C_5H_5)_3$	$Gd(C_5H_5)_3$	$Tb(C_5H_5)_3$	$Bk(C_5H_5)_3$	$Cf(C_5H_5)_3$
hkl	I_{obs}[a]	d_{obs}, Å	d_{calc}, Å	d_{calc}[b], Å	d_{obs}[c], Å	d_{obs}, Å	d_{obs}, Å	d_{obs}, Å	d_{obs}, Å	d_{obs}, Å	d_{obs}, Å
120	m	7.47	7.44	7.42	7.46	7.56	7.50	7.45	7.36	7.49	7.39
200	s,br	7.04	7.06	7.11	7.02	7.11	7.04	7.04	6.98	7.07	7.00
021	vw	6.63	6.52	6.49				6.45	6.68		
121	vs	5.93	5.92	5.90	5.88	5.94	5.92	5.88	5.89	5.91	5.89
002	s	4.85	4.88	4.86	4.86	4.87	4.87	4.82	4.82	4.81	4.83
102	vw	4.65	4.61	4.60				4.63	4.64		4.63
310			4.55	4.58							
040	w	4.40	4.38	4.35				4.39	4.38	4.42	4.40
320	w	4.16	4.15	4.16		4.15		4.19	4.10	4.15	4.12
122			4.08	4.07				4.11			
202	s	3.982	4.015	4.016		4.022		3.982	3.965	3.974	3.960
041			3.994	3.971							
321	vw	3.806	3.817	3.829		3.818		3.809		3.809	3.834
222	vw	3.611	3.650	3.646		3.655		3.500			
400	w,br	3.490	3.532	3.557		3.485	3.487	3.450	3.473	3.472	3.471
241			3.477	3.468							
042	m	3.341	3.259	3.243		3.270	3.283	3.240	3.240	3.236	3.237
322	vw	3.153	3.160	3.164		3.167		3.140	3.148	3.089	
250			3.138	3.126							
123	s	2.975	2.981	2.972	2.97	3.051	2.969	2.950	2.950	2.946	2.950
242			2.959	2.951		2.981					
402	m	2.855	2.861	2.872	2.84	2.871	2.865	2.876	2.844	2.856	2.860
160			2.858	2.842				2.838			
440	vw		2.749	2.754		2.757				2.747	
161			2.743	2.728							
520	vw		2.689	2.705		2.694					
441	w	2.661	2.646	2.650		2.655	2.656	2.657	2.647	2.666	2.659
043	m	2.603	2.611	2.600		2.599	2.595	2.622	2.585	2.593	
521			2.593	2.606				2.594			
143			2.568	2.558				2.571			
530			2.543	2.555							
323	m	2.549	2.559	2.559		2.562		2.537	2.523	2.531	2.520
062	vw	2.501	2.505	2.491				2.500			
360	s,br	2.470	2.481	2.474	2.45	2.486	2.468	2.465	2.457	2.460	2.461
162			2.466	2.454		2.457					
170			2.463	2.449							
531			2.461	2.471							
243			2.449	2.442							

[a] Visually estimated intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad. [b] Based on data of C. Wong, T. Lee, and Y. Lee, Proceedings of the Tenth International Conference on Coordination Chemistry, Tokyo and Nikko, Japan, 1967, p 95. [c] G. W. Watt and E. W. Gillow, *J. Am. Chem. Soc.*, **91,** 775 (1969).

TABLE II

UNIT-CELL DIMENSIONS[a] OF TRICYCLOPENTADIENYLS

Metal, M	Radius (M^{3+}), Å	*a*, Å	*b*, Å	*c*, Å	Vol, Å^3	d_{calcd},[b] g cm^{-3}
Pr	1.103	14.20	17.62	9.79	2449	1.82
Pm	0.979	14.12	17.60	9.76	2425	1.88
Sm	0.964	14.15	17.52	9.77	2422	1.90
Bk	0.954	14.11	17.55	9.63	2385	2.47
Cf	0.944	14.10	17.50	9.69	2391	2.47
Gd	0.938	14.09	17.52	9.65	2382	1.97
Tb	0.923	14.20	17.28	9.65	2368	1.99

[a] Accurate to about 0.5%. [b] Density is calculated assuming 8 formula weights per unit cell.

tematic absences of the type 0*kl* for $k = 2n + 1$ and *h*0*l* for $l = 2n + 1$ were observed. These are characteristic for the space groups Pbcm and Pbc2$_1$; the first of these was chosen by Wong, *et al.*,[19] as the correct one.

For some of the crystals studied, a second modification was obtained in which the *b* axis given in Table II was halved (the other axes essentially unchanged), and the pattern of systematic absences was changed to indicate C-centering and no glide planes (diffraction symbol mmmC...). The appearance of the crystals of this form under the polarizing microscope, the splitting of certain diffraction spots on the photographs, and the relative lack of extinctions all suggest that these crystals are twinned specimens, but it is also possible that the second form is a single crystal obtained from the first by an order–disorder transformation. However, indexing of the powder diagrams is based on the values in Table II.

Since all the cyclopentadienyl complexes listed in Table II appear to have the same structure, with a trend in unit-cell volume following the radius of the trivalent ion, the question arises as to the limiting size which the central atom can have and the structure be maintained. In this regard we have examined a cyclopentadienyl preparation of Tm made by the same macroscopic method as for $Sm(C_5H_5)_3$. This chloride-free product gave a powder pattern distinctly different from those in Table I. However, single-crystal diffraction studies showed it to be orthorhombic with a = 19.98 Å, b = 13.82 Å, and c = 8.59 Å and systematic absences characteristic of Pnam or Pna2$_1$. These unit-cell data yield a volume close to that expected by extrapolating those in Table II, indicating that this substance is probably $Tm(C_5H_5)_3$. If this is true, we have found a change in structure type but as yet have not determined at which lanthanide element it first occurs.

The colors of freshly sublimed cyclopentadienyl complexes of Bk, Cf, and Pm appear as follows: $Bk(C_5H_5)_3$, amber (with a maximum of 1% ^{249}Cf impurity); $Cf(C_5H_5)_3$, ruby red; $Pm(C_5H_5)_3$, dark orange (with a maximum of 8.3% ^{147}Sm impurity). A reliable determination of the colors was naturally limited by the minuteness of the samples and by possible effects of radiolysis. In addition an adulteration of the colors by contamination with another actinide or lanthanide, respectively, would be conceivable, especially in the case of ^{249}Bk by ^{249}Cf and ^{147}Pm by ^{147}Sm, the daughter elements from nuclear decay.

For none of the three compounds studied could direct indication of the presence of impurities be detected by survey of the f–f spectra in the region 400–700 nm. The visible spectrum of $Cf(C_5H_5)_3$ was characterized essentially by broad absorptions, beginning at 600 nm and extending into the blue, which can be attributed to electron-transfer processes.[13]

The $Bk(C_5H_5)_3$ spectrum has comparatively better solved absorptions at 435–450 (br), 462, 477 (sh), 483, 494 (sh), 514, 540 (br), 615-640 (br), and 650–660 nm (sh) which can be tentatively attributed to f–f transitions. The complexity of the spectra taken so far has not allowed as yet a detailed analysis in the case of $Bk(C_5H_5)_3$. The spectrum is however in reasonable agreement with that expected for Bk^{3+}, such as that calculated by Fields, *et al.*,[24] and as was found experimentally by various workers[4c,25,26] in different systems. No apparent evidence for the presence of ^{249}Cf or lanthanide impurities was observable.

The spectrum obtained for $Pm(C_5H_5)_3$ was characterized by a multitude of very sharp absorptions in the regions 490–520 and 545–620 nm. In particular, absorptions were found at 497, 505, 510, 550, 552, 554, 558, 562, 564, 568, 570, 577, 579, 582, 584, 587, 590, 592, 595, 599, 601, 608, and 620 nm. Although some of the absorptions lie in the same wavelength region as some $Sm(C_5H_5)_3$ absorptions obtained under equivalent conditions (*e.g.*, at 518, 566, 570, and 580 nm), the quantity of Sm^{3+} present in this sample is not sufficient to allow the observation of Sm^{3+} f–f lines here; however, a slight hint of the much stronger $Sm(C_5H_5)_3$ electron-transfer band[13] in the region <540 nm is evident.

The cyclopentadienyl complexes of ^{249}Bk, ^{249}Cf, and ^{147}Pm proved to be comparatively stable against radiolytic decomposition. All of the compounds could still be resublimed with high yield after 8 days of storage (estimated resublimation yield of $Cf(C_5H_5)_3$ after 8 days was about 50%). Most obvious were radiolytic effects in $^{249}Cf(C_5H_5)_3$, where in 1 day the compound became noticeably darker.

The sublimation behavior of the tricyclopentadienyls of Bk, Cf, and Pm correspond to the known tricyclopentadienyls of rare earths and actinides. When resublimation attempts on the substances in sealed capillaries required gradually higher temperatures (to 350°), we attributed this to a buildup of pressure in the capillary, such as could arise from radiolysis.

Under the given conditions no melting points could be observed. It can be said, however, that the compounds, sealed under vacuum, are certainly stable up to 250°.

On the question of solubility of the compounds, the only observation available is that $Bk(C_5H_5)_3$, $Cf(C_5H_5)_3$, and $Pm(C_5H_5)_3$ are soluble in molten $Be(C_5H_5)_2$.

Summarizing, it is established that the properties of $Bk(C_5H_5)_3$, $Cf(C_5H_5)_3$, and $Pm(C_5H_5)_3$ are in close agreement with those of the known tricyclopentadienyls of the lighter rare earths and actinides. This especially applies with respect to all the structural data, so that it is justifiably assumed that also the character of the metal–ligand bonds is probably of the same nature. We hope to obtain precise information on this from a complete structure analysis.

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