Inorg. Chem. **1988**, *27*, 1393–1400 **1393**

the two N–N distances being significantly different: 2.95 (2) Å and 2.89 (2) Å. The SbF_6^- anion has only a C_3 symmetry and hence two independent F atoms: Sb–F(1) = 1.80 (1) Å; Sb–F(2) = 1.83 (1) Å. The F–F distances are equal: F(1)–F(1) = 2.55 (2) Å; F(2)–F(2) = 2.56 (2) Å; F(1)–F(2) = 2.57 (2) Å. Thus, in spite of the two nonequivalent F atoms, Sb lies in a nearly regular octahedron.

Conclusion. The results of this study show that the corrosion products formed in high-temperature fluorination reactions involving BiF_5 in nickel or Monel reactors are analogous to those[2] found for SbF_5. In the formed $Ni(MF_6)_2$ products the MF_6^- anions are strongly distorted by the strong polarizing effect of the small, doubly charged Ni^{2+} cations and the resulting strong fluorine bridging. Basic ligands with good donor properties, such as CH_3CN, can add to the Ni^{2+} cations and form ternary adducts of the composition $[Ni(CH_3CN)_6](MF_6)_2$. The increased size and softness of the new cations diminishes the strong polarizing effect of the Ni^{2+} cations on the MF_6^- anions in the $Ni(MF_6)_2$ type compounds.

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Note Added in Proof. After submission of this paper, the results of an independent crystal structure determination of $[Ni(CH_3CN)_6](SbF_6)_2$ have been published by: Leban, Gantar, Frlec, Russell, and Holloway, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *43*, 1888.

Registry No. $Ni(BiF_6)_2$, 112817-17-1; NiF_2, 10028-18-9; BiF_5, 7787-62-4; $[Ni(CH_3CN)_6]^{2+}(SbF_6^-)_2$, 69102-75-6; $[Ni(CH_3CN)_6]^{2+}(BiF_6^-)_2$, 112817-18-2; $[Ni(CD_3CN)_6](SbF_6)_2$, 112839-66-4.

Supplementary Material Available: Tables of bond distances, bond angles, atomic positional parameters, anisotropic thermal parameters, and lattice constants and space group (7 pages); a table of calculated and observed structure factors (2 pages). Ordering information is given on any current masthead page.

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Luminescence Spectra and Lifetimes of Cerium(III) Compounds as Indicators of Solution Behavior and Radiative Efficiency

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The luminescence spectra and radiative lifetimes of a number of cerium(III) organometallics and halide compounds have been obtained by using a picosecond laser single-photon-counting system. These spectra, which can be determined for solids or solutions, are very useful for determining the exact nature of organocerium species in solution. Herein we report the solution behavior of some bis(pentamethylcyclopentadienyl)cerium compounds, including the tendency of $[K(THF)_2][(C_5Me_5)_2CeI_2]$ (**1**) to adopt a $(C_5Me_5)_2CeIL_n$ solution structure in either THF (n = 1) or CH_3CN (n = 2). While crystallization from THF regenerates the salt adduct **1**, the salt-free material $(C_5Me_5)_2Ce(I)(NCCH_3)_2$ (**3**) crystallizes from CH_3CN in high yield. A crystallographic study of **3** shows that the compound adopts a highly distorted trigonal bipyramidal solid-state geometry with axial nitrile ligands; the steric bulk of the C_5Me_5 rings causes the nitriles to bend toward the iodide. Crystal data: space group *Pnab*, a = 13.952 (3) Å, b = 14.768 (3) Å, c = 12.831 (3) Å, V = 2643.59 Å^3, Z = 4 (−150 °C). Lastly, the study of lifetimes has revealed a correlation between luminescence energy and lifetime, in accord with theoretical predictions. This correlation holds for a wide range of compounds, indicating that most of them have a high radiative efficiency (ca. 1); a noteworthy exception is **3**, which has a radiative efficiency of ca. 0.02. The presence of nonradiative decay channels resulting from the structural characteristics of **3** is considered.

Introduction

Recently we reported the luminescence spectra of a series of cerium(III) organometallic and halide compounds.[1] All of the cerium(III) compounds we have studied to date exhibit such emissions, and we noted a strong dependence of luminescent wavelength on the nature of the ligand sphere. As such, halide complexes such as $CeX_3(THF)_x$ (X = Cl, I; x = 3, 4) emit at higher energies (ca. 350 nm) while bis(pentamethylcyclopentadienyl)cerium(III) species (e.g. $[Li(Et_2O)_2][(C_5Me_5)_2CeX_2]$) were found to emit at lower energies (ca. 550–600 nm). The compounds typically show two broad bands in their emission spectra, which are assigned to emission from the lowest ^2D excited-state component to the two spin–orbit components of the ground state, $^2F_{5/2}$ and $^2F_{7/2}$.[2] The energetic separation of these emission bands (ca. 2000 cm^{-1}) reflects the magnitude of the ground-state splitting; the relative constancy from one compound to another indicates that the f orbitals are largely unaffected by the nature of the ligand sphere. However, the wide range of emission energies exhibited across the series of compounds (ca. 350–600 nm) illustrates that the energies of the excited ^2D states vary considerably as a function of ligand sphere. In this regard cerium(III) is very different from other trivalent lanthanides that are known to luminesce as a result of f–f transitions;[3] the latter are considerably less sensitive to the nature of the ligand sphere.

The cerium(III) emissions can also be used empirically to gather information regarding the nature of the medium in which the compound is located. This can be highly useful since most of the trivalent lanthanides are paramagnetic,[4] and thus NMR studies are of limited utility. Moreover, the luminescence method operates in a time regime which is considerably shorter than that of the NMR experiment. As such, we presented data in our previous paper[1] regarding the spectra of compounds such as $[Li][(C_5Me_5)_2CeCl_2]$ and $(C_5Me_5)CeI_2(THF)_3$ in various solvents as well as the solid state; substantial differences were noted as a

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function of medium. This is an important aspect of the chemistry of organolanthanide(III) compounds, which can adopt any of a number of possible ion-paired or oligomeric structures in solution.[5] In this contribution we have extended our studies of medium effects to other compounds of general formula $(C_5Me_5)_2CeX_n$ (X = halide, THF, CH_3CN), and we will present evidence regarding their solution structures. We have also obtained luminescent lifetimes for a wide range of cerium(III) compounds; these are relatively short, as expected for the fully allowed d–f luminescent transition. In addition to providing another means of characterizing the compounds, the comparison of lifetimes within the series uncovers some interesting behavioral trends. Lastly, we also report the facile high-yield synthesis of the neutral, monomeric cerium(III) complex $(C_5Me_5)_2Ce(I)(NCMe)_2$.

Experimental Section

General Methods. Proton NMR spectra were obtained on a Varian XL-400 FT-NMR instrument. Solution infrared spectra were determined in 0.05 mm path length liquid cells on a Perkin-Elmer M1500 FT-IR spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

All manipulations were carried out under an atmosphere of either nitrogen or argon. Both gases were dried and deoxygenated by passage through columns of Linde 4A molecular sieves and activated BTS catalyst. Solutions were handled by using standard Schlenk methods in glassware equipped with Solv-seal joints; solids were transferred in a Vacuum Atmospheres Corp. glovebox. Toluene, tetrahydrofuran, ether, and hexanes were purchased from J. T. Baker and distilled from sodium benzophenone ketyl under nitrogen. Acetonitrile (Aldrich Gold Label) was distilled from calcium hydride under nitrogen. Anhydrous cerium(III) chloride was obtained from Aldrich and used as received. Pentamethylcyclopentadiene (Aldrich) was metalated in THF with either *n*-butyllithium or potassium hydride. The compounds $CeI_3(THF)_x$ (x = 3, 4),[6] $[Li(Et_2O)_2][(C_5Me_5)_2CeCl_2]$,[6,7] $\{[K(THF)][(C_5Me_5)_2CeCl_2]\}_x$,[8] $(C_5Me_5)_2CeCl(THF)$,[8] and $[K][(C_5H_5)W(CO)_3]$[9] were prepared via the literature methods.

$[K(THF)_2][(C_5Me_5)_2CeI_2]$. Crystalline $CeI_3(THF)_x$ (5.7 g, 10.9 mmol) was suspended in 50 mL of THF. To this was added 3.8 g (22 mmol) of $K(C_5Me_5)$. The resulting suspension was stirred for 12 h and then evacuated just to the dryness point; prolonged evacuation is to be avoided, since it can cause loss of a THF ligand and make workup difficult.[8] The residue was extracted with toluene, which was then removed in vacuo to leave an orange solid. This was dissolved in 5:1 THF/ether and cooled to produce orange cubic crystals (4.6 g, 50%). Anal. Calcd for $C_{28}H_{46}CeI_2KO_2$: C, 39.48; H, 5.41. Found: C, 39.58; H, 5.54. ^1H NMR (THF-d_8, ppm): 3.8 (br s, C_5Me_5), 1.8 (THF). The analogous lanthanum compound can be prepared similarly and crystallized as colorless cubes. ^1H NMR (C_6D_6, ppm): 3.56 (THF), 2.09 (C_5Me_5), 1.32 (THF).

$[K(THF)_2][(C_5Me_5)_2(I)Ce(\mu\text{-}\Sigma\text{-}OC)W(CO)_2(C_5H_5)]$. A 0.75-g (0.88-mmol) amount of $[K(THF)_2][(C_5Me_5)_2CeI_2]$ was dissolved in ca. 20 mL of THF. To this solution was added 0.33 g (0.88 mmol) of $[K][(C_5H_5)W(CO)_3]$, and the resulting solution was stirred for ca. 30 min. After filtration through Celite, the solvent was removed in vacuo and the residue extracted with a mixture of 5 mL of THF and 15 mL of toluene. Cooling this solution caused the precipitation of yellow crystals (0.49 g, 52%). Anal. Calcd for $C_{36}H_{51}CeKIO_5W$: C, 41.06; H, 4.84. Found: C, 41.76; H, 4.70. IR (THF solution, cm^{-1}): 1911 (s), 1819 (s), 1663 (s). IR (CH_3CN solution, cm^{-1}): 1892 (s), 1773 (s). ^1H NMR (THF-d_8, ppm): 4.74 (v br, full width at half-maximum 240 Hz, C_5Me_5), 4.31 (C_5H_5), 3.56 (THF) 1.78 (THF).

$(C_5Me_5)_2Ce(I)(NCCH_3)_2$. This compound is obtained in nearly quantitative yield via slow crystallization of $[K(THF)_2][(C_5Me_5)_2CeI_2]$ from warm (70 °C) CH_3CN, from which it forms large yellow cubes. IR (Nujol, cm^{-1}): 2299 (m), 2267 (s), 1026 (m), 933 (w). ^1H NMR (CD_3CN, ppm): 4.95 (C_5Me_5), ca. 1.95 (CH_3CN and residual CD_2HCN). Analyses are consistently low in carbon and hydrogen, presumably due to loss of the labile nitrile ligands. The analogous lanthanum compound can be prepared similarly and crystallized as colorless cubes. ^1H NMR (CD_2Cl, ppm): 2.25 (CH_3CN, 6 H), 2.01 (C_5Me_5, 30 H).

Luminescence Spectra. Samples for solution luminescence spectroscopy were prepared volumetrically in the glovebox by using the appropriate solvent. The resulting solution was transferred to a 1 cm square quartz luminescence cell on which a Kontes valve had been attached with use of a graded seal. For solid-state spectra the appropriate crystalline compound was added to a 5-mm NMR tube that was closed under nitrogen in the glovebox. Spectra and lifetimes were obtained with a picosecond laser single-photon-counting system. The laser system consists of a frequency-doubled CW mode-locked Nd:YAG laser (Spectra-Physics 3000) synchronously pumping a cavity-dumped dye laser. The dye laser, operating with rhodamine 6G, produced ca. 10-ps pulses at 40 nJ/pulse. The visible pulses were frequency-doubled and used to excite the samples. The excitation wavelength, over the range investigated, was found to have no influence on the emission spectra or lifetimes and so was set in all cases at ca. 304 nm. At this wavelength the Pyrex NMR tubes used with solid samples absorbed some fraction of the laser and emitted light, but this was compensated for. The sample luminescence was focused into a 0.3-m McPherson monochromator and detected by a Hamamatsu R955 photomultiplier wired for fast single-photon response. The output of the PMT was discriminated (Tennelec 454) and input to the stop channel of a time-to-amplitude converter (TAC, EG & G 457). To record a spectrum, the number of PMT pulses versus monochromator wavelength was recorded by a multichannel analyzer (MCA, Ortex Norland 5500) in the multichannel scaling mode. The bandwidth of the monochromator was never a factor in the resolution since the inhomogeneous emission line widths are so great (ca. 1000–1200 cm^{-1}). To measure lifetimes, the start pulse for the TAC was obtained by a fast photodiode triggered by the visible laser pulses. The pulse height distribution from the TAC was recorded by the multichannel analyzer in the pulse height analysis mode. The system response function fwhm is ca. 500 ps. Data from the MCA were transferred via a personal computer to a DEC Microvax computer for data plotting and analysis. The transient luminescence decays were fit to an exponential form by using a nonlinear least-squares routine based on a Marquardt algorithm. Deconvolution of the system response function is incorporated routinely but is only necessary for the fastest decays observed (<1 ns). It was generally found that luminescence from the solids gave more nearly pure exponential decay (χ^2 near 1), whereas the solution data often exhibited $\chi^2 \geq 2$. This must be ascribed to some inherent nonexponential component of the dynamics or a combination of several contributing emission rate constants. Biexponential decay was observed in a number of cases and fit accordingly.

X-ray Crystallography. An irregularly shaped yellow crystal of suitable dimensions was obtained by cleaving a larger crystal in a nitrogen glovebag. This crystal was affixed to the goniometer head by using standard inert-atmosphere handling techniques and cooled to −150 °C. The compound is thermochromic and changed from bright yellow to pale green on cooling. Space group *Pnab* was assigned on the basis of Laue symmetry and systematic absences in the intensities found in a search of a limited hemisphere of reciprocal space. Subsequent solution and refinement confirmed this choice. Data were collected by using a continuous θ–2θ scan technique and reduced in the usual manner.[10] Data processing gave a residual of 0.063 for the averaging of 1636 redundant data. The data contained a large number of weak intensities, with only 760 of the 1728 unique data having $I \geq 2.33\ \sigma(I)$. The structure was solved by determining the Ce and I positions from a Patterson map and the remainder of the structure from difference Fourier maps. Many hydrogen positions became apparent in latter difference maps, thus giving probable orientations for the methyl groups.

Attempts to correct for absorption and to refine all non-hydrogen atoms anisotropically were unsuccessful, probably due to the irregular crystal shape and the large number of weak data. Least-squares refinement was carried out by using the uncorrected data, anisotropic thermal parameters on Ce and I, and isotropic parameters on all other non-hydrogen atoms. Hydrogens were placed in calculated positions prior to the final cycles of refinement, which gave $R(F)$ = 0.042. A final difference map was reasonably clean. There were a number of peaks with intensities less than 1 e/Å^3, the largest of which were near the methyl groups; there is presumably some degree of disorder in the methyl group

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Table I. Crystal Data for **3**

empirical formula	$CeC_{24}H_{36}IN_2$
color of cryst	green
cryst dimens, mm	–1,1,1, d = 0.0700; 1,–1,–1, d = 0.0700; 1,–1,0, d = 0.0600; –1,1,0, d = 0.0600; 1,1,1, d = 0.1100; –1,–1,–1, d = 0.1100
space group	*Pnab*
cell dimens (–150 °C; 35 rflns)	
a, Å	13.952 (3)
b, Å	14.768 (3)
c, Å	12.831 (3)
Z (molecules/cell)	4
vol, Å^3	2643.59
calcd density, g/cm^3	1.557
wavelength, Å	0.71069
mol wt	619.59
linear abs coeff, cm^{-1}	29.157
max abs	0.6270
min abs	0.7770

Table II. Selected Bond Lengths and Angles for **3**[a,b]

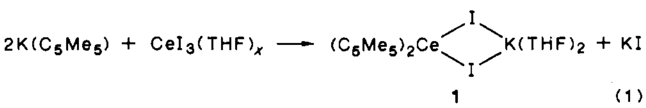
Bond Lengths (Å)			
Ce–I	3.231 (2)	Ce–C(7)	2.79 (1)
Ce–N	2.63 (1)	Ce–C(8)	2.83 (1)
N–C(4)	1.14 (1)	Ce–C(9)	2.81 (1)
Ce–Cp	2.527	Ce–C(10)	2.77 (1)
Ce–C(6)	2.78 (1)		
Bond Angles (deg)			
I–Ce–N	75.0 (3)	Cp–Ce–Cp	135
N–Ce–N	150.1 (5)	Cp–Ce–N	94
Ce–N–C	151 (1)	Cp–Ce–N′	97
N–C–C	178.0 (1)	Cp–Ce–I	112

[a] Cp refers to the C_5Me_5 centroid. [b] C(4) is the acetonitrile central carbon, and C(6)–C(10) are C_5Me_5 ring carbons.

H positions. Crystal data are collected in Table I.

Results and Discussion

Synthetic Studies. Our initial attempts to prepare the compound $[K(THF)_2][(C_5Me_5)_2CeI_2]$ were motivated by questions regarding the steric situation in such a compound. In our synthesis of (pentamethylcyclopentadienyl)cerium(III) halide complexes, we noted that $(C_5Me_5)CeCl_2(THF)_x$ was particularly difficult to prepare and isolate in crystalline form.[6] Although molecular weight studies indicated it to be monomeric in THF solution, the compound appeared to lose THF and oligomerize upon attempted isolation. In contrast, the iodide analogue is quite stable and can be isolated in good yield as the *trans,mer*-$(C_5Me_5)CeI_2(THF)_3$ isomer.[6] This indicates the importance of the difference in the steric requirements of the iodides relative to those of the chlorides in the two compounds. Further, the solid-state structure of $[Li(Et_2O)_2][(C_5Me_5)_2CeCl_2]$ has been determined by X-ray diffraction[7] and shown to exhibit some anomalously long bond lengths. Although relatively few (C_5Me_5)–Ce compounds have been studied crystallographically, the available data for cerium (as well as for other lanthanide metals) indicate that the aforementioned compound exhibits unusually large C_5Me_5(centroid)–Ce and Ce–Cl bond lengths.[8] Moreover, the two C_5Me_5 rings are eclipsed in this compound; relatively few other lanthanides exhibit such eclipsing interactions between C_5Me_5 groups.[11] Indeed, however, the synthesis of the desired cerium compound **1** (isolated as large orange cubes) proceeds readily from the known $CeI_3(THF)_x$ as indicated in eq 1; the lanthanum analogue is similarly prepared from $LaI_3(THF)_x$. The potassium counterion is presumably associated with the iodides in the solid state, as is the rule with lanthanide compounds of this general type. However, relative to the case for the chloride analogue of this same compound,[8] the potassium ion in **1** shows a reduced tendency to lose a THF ligand and cause polymerization (see Experimental Section for workup details). This is verified by elemental analysis, spectral data, and the reasonable solubility of the compound in aromatic hydrocarbons.



$$2K(C_5Me_5) + CeI_3(THF)_x \longrightarrow (C_5Me_5)_2Ce(\mu\text{-}I)_2K(THF)_2 + KI \quad (1)$$

1 (1)

The spectroscopic studies to be described herein were begun as a result of attempts to prepare heterobimetallic compounds containing cerium and tungsten. For example, the reaction of **1** and the known $[K][(C_5H_5)W(CO)_3]$[9] was carried out as in eq 2. Although this tungsten-containing anion has been used to

$$\mathbf{1} + [K][(C_5H_5)W(CO)_3] \rightarrow \underset{\mathbf{2}}{[K(THF)_2][(C_5Me_5)_2(I)Ce{-}O{=}C{-}W(CO)_2(C_5H_5)]} \quad (2)$$

prepare other heterobimetallic species exhibiting metal–tungsten bonds,[12] we anticipated that the oxophilic cerium(III) nucleus would prefer to bind at the carbonyl oxygen. This binding preference has been observed for other combinations of carbonylmetalates and lanthanide compounds.[13] Indeed, the resulting compound **2** (eq 2) exhibited infrared bands in either THF solution or the solid state that were indicative of a Ce—O═C—W linkage. The occurrence of three bands (1911, 1819, and 1663 cm^{-1}) is evidence for local C_s symmetry at tungsten, consistent with the presence of the cerium moiety on one of the carbonyls. As such, the bridging carbonyl gives rise to a localized A′ mode that is shifted to low frequency. As a result of the flow of electron density through the bridging carbonyl to cerium(III), the two terminal carbonyls on tungsten experience a decrease in back-bonding and the remaining A′ and A″ modes shift toward higher frequency.[14] Indeed, a comparison of **2** with the potassium salt from which it is prepared (bands at 1893, 1796, and 1748 cm^{-1}) confirms the greater strength of the cerium (vs. potassium) interaction with the carbonyl. The way in which the potassium counterion interacts with the heterobimetallic anion is currently not known.

Compound **2** was dissolved in a number of common solvents in an attempt to obtain crystals. In view of the reasonably strong interaction described above, we were mildly surprised to isolate large yellow cubes (**3**) from acetonitrile that exhibited no carbonyl IR bands. Subsequent infrared studies of compound **2** dissolved in acetonitrile showed very little evidence of this heterobimetallic salt, with the solution exhibiting intense bands at 1892 and 1773 cm^{-1}. The presence of only two bands is indicative of local C_{3v} symmetry in the free $(C_5H_5)W(CO)_3^-$ anion; similar behavior has been observed for the sodium salt of this anion in HMPA/THF solvent mixtures.[14] From the spectra we can infer the existence of the equilibrium shown in eq 3 and estimate an equilibrium

$$[(C_5Me_5)_2(I)Ce{-}O{=}C{-}W(CO)_2(C_5H_5)]^- \underset{MeCN}{\rightleftharpoons} \underset{\mathbf{3}}{(C_5Me_5)_2Ce(I)(NCMe)_2} + [(C_5H_5)W(CO)_3]^- \quad (3)$$

constant for dissociation of the heterobimetallic anion in acetonitrile ($K_{eq} \geq 8$ M, ca. 90–95% dissociation). Again, in THF solution the analogous equilibrium lies entirely on the left as judged by IR spectra. Also indicated in eq 3 is the presence of two nitrile ligands on cerium in **3** (vide infra). This suggestion is consistent with the infrared spectrum of the isolated yellow crystals, which

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contains absorptions at 2299 and 2267 cm^{-1}. If, instead of crystallization, the acetonitrile solvent is removed in vacuo and the residue dissolved in THF, the result is complete regeneration of the associated material **2**; this indicates that the equilibrium in eq 3 is indeed reversible and that the acetonitrile ligands in **3** are not particularly tightly bound. These ligands in **3** are not removed by evacuation, however, but are rather displaced by tungsten in THF solution. The behavior exhibited by the heterobimetallic compound **2** indicates that the tungsten anion is readily displaced by acetonitrile but not THF ligands; again, this is similar to the behavior exhibited by many alkali-metal salts of this same anion.[14]

The infrared spectrum of **3** indicated the presence of two nitrile ligands, consistent with either of two formulations: $(C_5Me_5)_2Ce(I)(NCMe)_2$ or $[K(NCMe)_2][(C_5Me_5)_2CeI_2]$. Elemental analyses gave C and H contents that were closer to the values predicted for the former, although the match between experimental and calculated values was poor (see Experimental Section). Further, its isolation from solutions of **2** was also indicative of the salt-free formulation. Assuming that this formulation is correct, the chemistry described above suggested that the large size of the iodides might also be exploited in a facile preparation of compound **3**. Indeed, simple dissolution of **1** in acetonitrile resulted in an immediate color change from the orange of **1** to the bright yellow of **3**; when the solution of **1** stood, the large cubic crystals of **3** were deposited readily. In CD_3CN compound **3** exhibits a routine NMR spectrum with a broad absorption for the C_5Me_5 groups (4.95 ppm) and a nitrile absorption superimposed on the pseudoquintet due to the residual proton in CHD_2CN. In THF-d_8 the spectrum is much more complicated and shows a clear concentration dependence. With higher concentration of cerium species (added in the form of **3**), the C_5Me_5, CH_3CN, and THF (OCH_2) signals move downfield relative to the other THF signal (due to OCH_2CH_2). This is indicative of a facile THF–CH_3CN ligand-exchange process (eq 4), analogous to the exchange of free and coordinated THF in

$$(C_5Me_5)_2Ce(I)(NCMe)_2 + THF \rightleftharpoons (C_5Me_5)_2Ce(I)(THF) + 2MeCN \qquad (4)$$

diamagnetic $(C_5Me_5)_2Lu(Cl)(THF)$.[15] This latter process exhibited a $\Delta G^{\ddagger}$ value of ca. 13 kcal/mol. Analogous NMR exchange studies on our cerium(III) system were rendered difficult by the inherent broadness of the spectral lines; hence, other spectroscopic studies were undertaken. These studies indicated that **3** exhibited some anomalous luminescence behavior in both solution and the solid state (vide infra), so a crystallographic study was carried out to verify its solid-state structure.

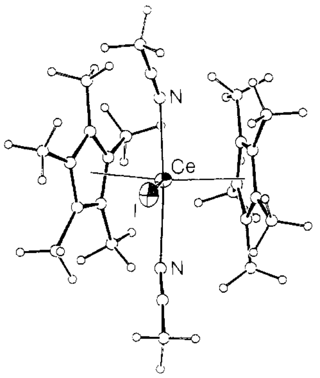

Figure 1. ORTEP drawing of $(C_5Me_5)_2Ce(I)(NCCH_3)_2$ (**3**) with a view that is approximately along the I–Ce bond.

The X-ray study indicated that the molecule is in fact the salt-free $(C_5Me_5)_2Ce(I)(NCMe)_2$ and that it adopts the structure shown in Figure 1. This structure can be described as either a bent metallocene with three equatorial ligands[16] or as a highly distorted trigonal bipyramid, but neither description is entirely accurate. The former seems particularly inadequate since even large ligands normally lead to angles between the outer two equatorial ligands of ca. 110–120°;[17] in **3** the N–Ce–N angle is 150.1 (5)°. The alternative description of **3** as a highly distorted trigonal bipyramid would lead to the assignment of an equatorial plane containing the two C_5Me_5 centroids and the iodide, while the nitriles would be in the axial positions. In this regard, it is interesting to compare **3** to $Cp_3Ce(NCMe)_2$, a more regular trigonal bipyramid with axial nitriles.[18] In the latter, the N–Ce–N angle is 178.3 (1)°, close to the perfect 180°. However, in this compound the three equatorial ligands are all C_5H_5 groups; the centroid–Ce–centroid angles are very close (120–122°) to the 120° angle expected for a regular trigonal bipyramid. For **3** the bulkier C_5Me_5 groups are forced to adopt a centroid–Ce–centroid angle of 135°. Further, the axial nitriles bend away from these groups and toward the iodide ligand, leading to a relatively acute N–Ce–N angle (150.1 (5)°). Another interesting aspect of the nitrile coordination in **3** is the angled approach of the nitrile nitrogen to cerium; this is evident from the Ce–N–C angle of 151 (1)°. In $Cp_3Ce(NCMe)_2$ one observes an angle more closely approaching linearity, namely 169.5 (4)°; the bending is ascribed in part to weak asymmetric intramolecular contacts between the nitriles and Cp rings.[18] It is tempting to equate the nonlinearity with a weakened Ce–nitrile bond in **3**, but caution must be exercised since the Ce–N bond lengths are shorter in **3** (2.62 (1) Å) than in $Cp_3Ce(NCMe)_2$ (2.749 (6) Å).[18] In spite of the large distortions noted above, it appears that the geometry of **3** can be described as being derived from a trigonal bipyramid.

The eclipsed C_5Me_5 rings are positioned so as to lead to Ce–C distances that average 2.79 Å, a value that agrees well with the averages for *trans,mer*-$(C_5Me_5)CeI_2(THF)_3$ (2.78 Å),[6] $[Li(OEt_2)_2][(C_5Me_5)_2CeCl_2]$ (2.77 Å),[7] and $[(C_5Me_5)_2CeCl_2K(THF)]_n$ (2.79 Å).[8] The Ce–I distance of 3.231 (2) Å compares reasonably well with the previously observed values of 3.227 (1) and 3.173 (1) Å for $(C_5Me_5)CeI_2(THF)_3$.[6] This distance can be compared to other Ln–I bonds in the following series: $[SmI_2(THF)_5][Co(CO)_4]$ (3.030 (2) and 3.009 (2) Å,[19] $(C_5Me_5)_2SmI(THF)$ (3.043 (2) and 3.053 (2) Å for two independent molecules),[20] and $[Li(OEt_2)_2][(C_5Me_5)_2YbI_2]$ (3.027 (1) Å).[11b] The Ce–I bonds are longer than these others by an amount greater than the differences in Ce(III) vs Ln(III) ionic radii;[21] whether this indicates a relatively weak Ce–I bond is not clear. The shortest interligand contacts in **3** (3.60 Å) are between I and N, but this distance is greater than the sum of the van der Waals radii (3.50 Å).

To our knowledge **3** is the first monomeric $(C_5R_5)_2LnL_3$ compound, a situation that is no doubt facilitated by the linearity of the nitrile ligands.[22] Further, we note that the preparation of

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Table III. Luminescent Wavelengths and Lifetimes

entry no.	compd	solvent (concn)[a]	emission bands, nm		τ, ns
1	$[Cp^*{}_2CeI]_x$	solid	579	626	95
2	$[K(THF)_2][Cp^*{}_2CeI_2]$ (**1**)	solid	566	620	143
		THF (1.0)	560	628	175
3	$Cp^*{}_2CeI(THF)$	solid	560	635	103
		THF (1.0)	560	628	181
4	$Cp^*{}_2CeCl(THF)$	THF (1.0)	550	*b*	136
5	$Cp^*{}_2Ce(I)(NCMe)_2$ (**3**)	solid	535	598	6
		THF (1.0)	560	628	175
		MeCN (1.0)	542	577	*c*
			629	662	4
6	$\{Li(OEt_2)_2\}\{[C_5H_3(SiMe_3)_2]_2CeCl_2\}$	solid	547		130
7	$[Li(OEt_2)_2][Cp^*{}_2CeCl_2]$	solid	548	591	157
		THF (1.0)	538		174
		MeCN (1.0)	510		151
8	$Cp^*CeI_2(NCMe)_x$	solid	527		60
9	$[K][(COT)_2Ce]$	solid	502	550	150, 73[d]
10	$Cp^*CeCl_2(THF)_x$	THF (1.0)	490		120
11	$Cp^*CeI_2(THF)_3$	solid	475	511	76
		THF (1.0)	465	512	116
12	$[K][Cp^*{}_2(I)Ce(OCW(CO)_2Cp]$ (**2**)	THF (0.25)	460	544	*c*
13	$CeI_3(NCMe)_x$	solid	413	455	34
14	$CeI_3(THF)_x$	solid	374	420	33
		THF (0.1)	378	411	36
15	$Ce(OSO_2CF_3)_3$	THF (1.0)	330	360	25

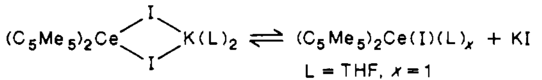
[a] Concentrations in mM. [b] Low-energy band not resolved. [c] Lifetime measurements complicated. [d] Biexponential decay curve.

monomeric, neutral lanthanide(III) compounds can be a difficult endeavor for all but the smallest lanthanides.[23] Special oxidative routes exist for lanthanides such as samarium, which can form stable divalent $(C_5Me_5)_2Ln(THF)_2$,[20] but the standard reaction of MX_3 and $M'(C_5Me_5)$ normally results in the alkali-metal halide adduct as the major product. Subsequent sublimation of these adducts usually yields $[(C_5Me_5)_2LnX]_x$ compounds of varying structure and degree of oligomerization, but these sublimations always require high temperature and very low pressure and are usually quite inefficient. In contrast, the synthesis of **3** (with its sterically demanding iodide ligand) represents a particularly convenient preparation of a salt-free $(C_5Me_5)_2Ln$ analogue.

Luminescence Studies. In our previous work[1] we noted that luminescence wavelengths can be used as an analytical tool in the identification of various cerium(III) compounds. This is particularly true when the object is to distinguish between compounds with vastly different ligand spheres. However, in the series of $(C_5Me_5)_2Ce$ analogues discussed here, the relative similarity in the ligand sets causes the emissions to appear in the fairly narrow range of ca. 530–580 nm (foı the bluer of the two emission bands). When the relative broadness of the lines is taken into account, this can lead to substantial emission spectral overlap for different compounds. As such, we have also pursued the study of lifetimes and find these to be an additional characterization tool. We will first discuss the utility of these data in identifying the nature of some of the $(C_5Me_5)_2Ce$ compounds in solution; subsequent discussion will focus on the wider series of lifetime values and their interpretation. Spectra have been obtained in both solution and the solid state for many of the compounds, as indicated in Table III.

The behavior of the heterobimetallic cerium–tungsten compound **2** prompted much of this work. In this particular compound the tungsten moiety can be considered as one of the ligands on cerium; the presence of carbonyls on this ligand allow for IR characterization of its ligating tendencies. As such, luminescence spectroscopy is not critical in this case but provides corroborating data regarding the solution behavior of the compound. For other more typical ligands no such convenient IR handle is readily available. As noted above, the IR evidence for the heterobimetallic anion **2** indicated that the dissociative equilibrium (eq 3) is pushed completely to the left (fully associated) in THF solution (local C_s symmetry at W). The pertinent luminescence spectra are described in Table III, entries 3 ($(C_5Me_5)_2CeI(THF)$) and 12 (**2**). The former is the product expected if **2** were to dissociate in THF solution, and it exhibits emission bands at 560 and 628 nm. The salt **2**, however, exhibits bands at 460 and 544 nm in THF solution, with no evidence of the bands noted above.

From the synthetic results compound **1** appeared to lose KI in CH_3CN solution but not in THF solution. As such, we were interested in studying the luminescent behavior of this compound. In the solid state **1** exhibits emission bands centered at 566 and 620 nm, with an emission lifetime of 143 ns (Table III, entry 2). This value is apparently wavelength-independent and remains constant across the width of the spectral band. Dissolution of **1** in THF leads to similar emission energies (560 and 628 nm) but an increased lifetime of 175 ns. When it is taken alone, this observation is not surprising since a number of the compounds show differing lifetimes in the solid and the solution phase. However, dissolution of compound **3** in THF (Table III, entry 5) resulted in an emission spectrum identical with that of **1** in THF; the lifetimes were also in exact agreement. Since **3** was formulated as having no associated KI, this suggests that **1** has relinquished KI in 1 mM THF solution. As a further verification of this, compound **1** was subjected to sublimation. This resulted in a pink solid of empirical formula $[(C_5Me_5)_2CeI]_x$ in low yield. Dissolution of this pink solid in THF resulted in a yellow solution with a spectrum identical with that of **1** in THF solution; the observed lifetime (181 ns) is within experimental uncertainty of the 175-ns lifetime observed for **1**. These observations indicate that the equilibrium represented in eq 5 operates in *both* THF



$$(C_5Me_5)_2Ce(\mu\text{-}I)_2K(L)_2 \rightleftharpoons (C_5Me_5)_2Ce(I)(L)_x + KI \qquad (5)$$

$$L = THF,\ x = 1 \qquad L = CH_3CN,\ x = 2$$

and CH_3CN and in fact lies almost completely to the right in both. Thus, the isolations of metal halide adduct **1** from THF and the salt-free **3** from CH_3CN are determined *exclusively* by the solubilities of the two equilibrium partners in these solvents. As such, these spectral studies reaffirm the inherent dangers of inferring the nature of lanthanide organometallics in solution from solid-state diffraction data. The results also indicate that the steric requirements of the iodide ligand is such that a second one is readily displaced by less bulky ligands. Further, the lability of all of these ligands (I, MeCN, and THF) should allow for the preparation of a number of cerium complexes of other ligands.

In view of the proposed steric importance of the iodide ligands in compound **1**, we deemed it important to see if the chloride analogue behaved similarly. As such, we sought to compare the emission spectrum and lifetime of the known $[Li(OEt_2)_2][(C_5Me_5)_2CeCl_2]$[1,7] (**4**) to those of $(C_5Me_5)_2Ce(Cl)(THF)$.[8] The latter is available from THF dissolution of $[(C_5Me_5)_2CeCl]_x$, which can in turn be prepared via vacuum sublimation of polymeric $\{[K(THF)][(C_5Me_5)_2CeCl_2]\}_x$.[8] The emission spectrum of **4** in 1.0 mM THF solution was previously reported to consist of a band

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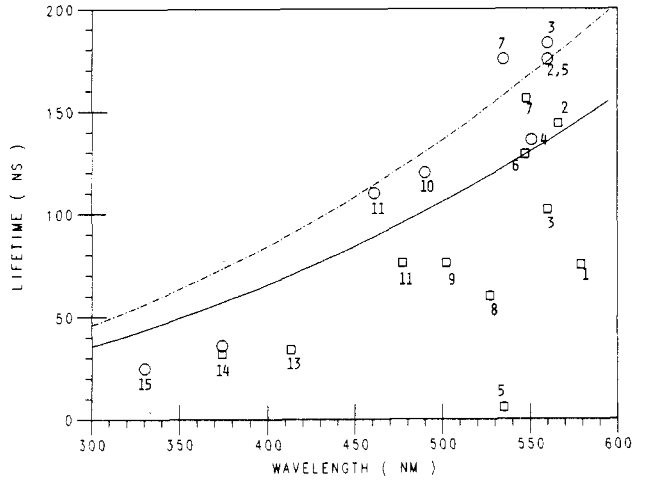

Figure 2. Plot of lifetimes (ns) as a function of emission wavelength (nm). Points are numbered to correspond to the entry numbers in Table III. Circles are solution data; squares are solid-state data. The lines represent behavior predicted by theory (using eq 6; see text).

at 538 nm with an indistinguishable shoulder on the red edge.[1] In this work we have determined the emission lifetime to be 175 ns (Table III, entry 7). The salt-free THF adduct shows an emission band at 550 nm with a shoulder on the red edge and a lifetime of 136 ns (entry 4). Thus, the lifetimes and emission wavelengths are clearly different; when they are taken together, these results indicate that an equilibrium loss of LiCl is not a dominant feature for THF solutions of **4**. Thus, the loss of alkali-metal salt in THF solution by the diiodide **1** is not a general phenomenon; the absence of such a process for the dichloride **4** leads to the conclusion that the extra steric constraints introduced by the iodides of **1** are likely the cause.

Emission Lifetimes. The measurement of luminescence lifetimes of the cerium(III) compounds was undertaken for two reasons. First, as discussed above, the lifetimes help to identify the species present in solution. Second, such measurements can be used to probe excited-state dynamic processes such as solvent quenching, coordination sphere rearrangements, and ligand dissociation. This last point is exemplified by studies of the nonaaquo complex $[Ce(H_2O)_9]^{3+}$.[24] Upon excitation ($^2D \leftarrow {}^2F$) this complex dissociates one water ligand and exhibits emission from the excited state of the octaaquocerium(III) ion. This process will be used as a reference point for the present study because the emission lifetime (45 ns) and quantum yield (ca. 1) have been measured.

The cerium(III) lifetimes in Table III fall within the range 25–195 ns; this can be compared to the lifetimes for some terbium(III) compounds with similar ligand spheres. The latter exhibit lifetimes of ca. 200 μs,[2] roughly 3 orders of magnitude longer than for the cerium compounds. This derives from the fact that the terbium f–f transitions are forbidden by the Laporte selection rule ($\Delta l = \pm 1$) while the cerium f–d transitions are fully allowed. Furthermore, the series of lifetimes in Table III exhibit another obvious trend; compounds with longer wavelength emissions typically exhibit longer lifetimes. This is shown more dramatically in Figure 2, which contains a plot of lifetime versus emission wavelength. In general the compounds exhibit solid-state lifetimes that are shorter than the solution values, so we will consider these data sets separately. Moreover, there are certain compounds (notably $(C_5Me_5)_2CeI(NCMe)_2$, vide infra) that exhibit large deviations from any trend.

To interpret these lifetime data, it is important to identify the radiative and nonradiative contributions to the emission lifetimes. The trend toward decreased lifetime at higher emission energy could conceivably be attributed to the availability of a quenching mechanism at high energy derived from the presence of intramolecular charge-transfer states. However, this is apparently obviated by the fact that the aquo complex exhibits an emission wavelength of 330 nm (blue component of the doublet), a lifetime of 45 ns, and an emission quantum yield of ca. 1 (i.e., no nonradiative pathway operative);[24a] this complex has no observable charge-transfer states in the region of interest. In fact, we find that all the compounds which emit in this region (Table III) exhibit lifetimes which are similar to that of the aquo complex; thus, a nonradiative quenching process is not required (or necessarily available) to account for the shorter lifetimes. To pursue this point further, one can calculate a purely radiative lifetime and compare this number to the actual lifetime so as to estimate the relative importance of radiative and nonradiative effects. This is made possible by the atomic nature of the transitions, the similarity of the emission bands for various compounds, and the availability of clean absorption spectra for at least some of the compounds (clean in the sense that the lowest energy f–d band is not obscured by ligand-centered or charge-transfer bands). Since the details of the spectroscopy have a bearing on this calculation, the approach will be reviewed briefly.

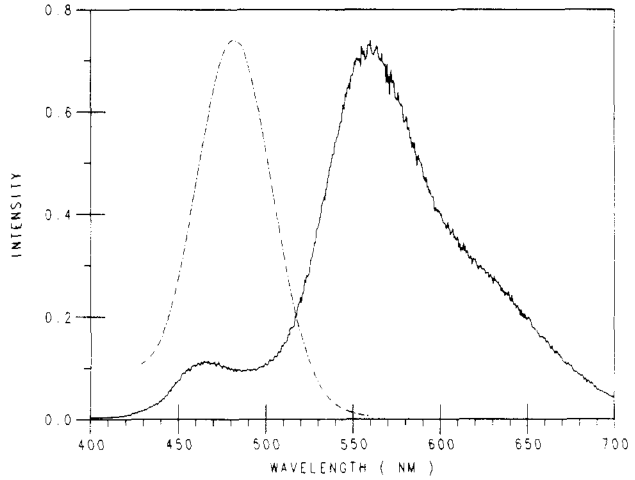

Figure 3. Absorption (–·–) and emission (—, excitation at 304 nm) spectra for $[K(THF)_2][(C_5Me_5)_2CeI_2]$ (**1**). Relative intensities are arbitrarily scaled.

We noted in the Introduction that the spectral transitions of interest are between the ground state ^2F ($4f^15d^0$) and the first excited state, ^2D ($4f^05d^1$). The ground state exhibits little evidence of ligand field effects, but there is a rather large (ca. 2000 cm^{-1}) spin–orbit splitting between the lower $^2F_{5/2}$ and the upper $^2F_{7/2}$ components. The $^2F_{5/2}$ state consists of three nearly degenerate Kramers doublets for a total degeneracy of 6, while the $^2F_{7/2}$ component has four Kramers doublets for a total degeneracy of 8.[24b,c] It is expected that the Boltzmann population of the $^2F_{7/2}$ state is very small at room temperature. The excited state, being of d origin, shows a combination of ligand field splitting and spin–orbit coupling such that there are five possible Kramers doublets in the absorption spectrum. These five components have been observed[25] in the aquo complex $[Ce(H_2O)_9]^{3+}$ but are masked in most of the compounds discussed here by strong charge-transfer bands. However, for compound **1** this absorption from the $^2F_{5/2}$ ground state to the lowest ^2D state was clearly visible (Figure 3). Okada et al. have done extensive theoretical and experimental work aimed at determining the precise ordering and energies of the ^2D sublevels for the ion $[Ce(H_2O)_9]^{3+}$.[24] They nominally assign the lower two ^2D components as $^2D_{3/2}$ and the upper three as $^2D_{5/2}$, with each component giving rise to a Kramers doublet. In the emissive transition only the lowest ^2D components are important because the others undergo rapid relaxation to these prior to emission.

With the foregoing in mind, the emission spectra can be interpreted. In all cases the two bands correspond to transitions

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from the lowest excited state (nominally $^2D_{3/2}$) to the ground state $^2F_{5/2}$ and $^2F_{7/2}$ with an intensity ratio for $^2F_{5/2}$:$^2F_{7/2}$ of ca. 4:3. The lifetime is invariant across the profile of both emission components, proving that they arise from a common upper state. We can apply the relation between absorption strength and the expected radiative lifetimes:[26]

$$1/\tau_0 = (2.88 \times 10^{-9}) n^2 \nu_f^3 g_l/g_u \int \epsilon \, d \ln \nu \tag{6}$$

This expression is derived from the Einstein A coefficient[27] ($A = 1/\tau_0$) for atomic emission rates and has been modified for molecules by incorporating a vibrational band envelope and a Stokes shift of the emission. The other terms are n, the refractive index of the solvent, g_l and g_u, the degeneracies of the lower and upper states, and ϵ, the frequency-dependent molar extinction coefficient. All the necessary data are derived from the absorption and emission spectra. The equation would apply directly for the case of one excited state decaying to one ground state, but in the cerium(III) case with two emissive transitions the overall lifetime τ_T and decay rate $k_T = 1/\tau_T$ are

$$1/\tau_T = 1/\tau_{5/2} + 1/\tau_{7/2} \tag{7}$$

$$k_T = k_{5/2} + k_{7/2} \tag{8}$$

With the application of eq 6 above to the blue emission component of a given compound, the value of $k_{5/2}$ can be obtained readily. To determine the value of $k_{7/2}$, we can use the relative intensities of the two emission bands as an approximation of the ratio $k_{5/2}$ to $k_{7/2}$. Thus, the two radiative rate constants can be summed to result in k_T, the predicted radiative decay rate constant.

The absorption spectrum of compound **1** consists of a broad f–d absorption band (Figure 3) with a peak extinction coefficient of 370 L/(mol cm). When the values $g_u = 2$ and $g_l = 6$ are used and emission to the $^2F_{7/2}$ level is accounted for as described, the application of eq 6 leads to a calculated lifetime of 135 ns. Although the agreement with the experimental value (175 ns) is not exact, we were encouraged by the fact that it was obtained without the use of any adjustable parameters. This calculation was extended across the range of cerium(III) compounds by using the appropriate values for emission and absorption wavelengths but fixing the other parameters to the values obtained for **1**. The point of this is to show the effect of the steep wavelength dependence manifested by eq 6. We believe these approximations are acceptable for two reasons: (1) the shapes of the emission bands are similar for all compounds and (2) the ϵ values for $[Ce(H_2O)_9]^{3+}$ and **1** (two very different compounds that emit near the extremes of the range covered here) are quite similar (400 vs 370 L/(mol cm)). The result of this calculation is plotted in Figure 2 (solid line), along with experimental values for the blue emission component of each compound. Also plotted in Figure 2 (dashed line) is a curve derived by fixing the leading constants (in eq 6) for the point at 560 nm (compound **1**). It is clear that both calculated lines show the trend exhibited by the experimental data, namely an intrinsic tendency toward longer lifetimes at longer emission wavelengths. The fit to the known data for $[Ce(H_2O)_9]^{3+}$ (45 ns, emission quantum yield 1)[24] is also quite good; the two calculational methods predict values of 44 and 56 ns, respectively.

The degree to which the experimental lifetimes fit the calculated line should be determined by the quantum yield for emission (Q). In the absence of any other quenching mechanisms ($Q = 1$), the observed lifetime should match the calculated value exactly; this relation can be expressed as in eq 9 (k_r and k_{nr} refer to rate

$$Q = k_r/(k_r + k_{nr}) = \tau_{obsd}/\tau_{calcd} \tag{9}$$

constants for radiative and nonradiative processes). The solution lifetimes (circles in Figure 2) are seen to fit rather well, while the solids show greater deviations. The form of the solids makes it impossible to measure molar extinction constants, so it is not clear whether the decreased lifetimes arise from increased transition oscillator strength or from the operation of other decay channels. The former seems unlikely, whereas one might expect rapid resonant energy transfer in the solid lattice to give rise to luminescence quenching by trap sites. Whichever is the case, the effect is fairly constant across the series since the lifetimes show the same trend versus wavelength as do the solutions.

The one glaring exception to the trend noted above is compound **3**, whose solid-state structure was described earlier. This species exhibits solid-state and solution lifetimes of 6 and 4 ns, respectively, whereas the calculated value falls between 160 and 190 ns. From eq 9 we can approximate the emission quantum yield $Q = 0.02$. To see if the relationship described above is a reliable predictor of luminescent quantum yields, we sought to measure the quantum yields of **1** (predicted to have a high emission quantum yield; see Figure 2) and **3**. This was done by comparison with fluorescein, which is known to have an emission quantum yield of 0.9 in 0.1 N aqueous NaOH.[28] With this method, we obtain emission quantum yields of 0.7 ± 0.1 for **1** and ≤0.01 for **3**. Since the fluorescein emission band does not match perfectly with the emission profiles of **1** and **3**, the absolute numbers are liable to be somewhat inaccurate. However, the relative comparison between **1** and **3** should be acceptable, and it serves to verify that the former is a highly efficient emitter while the latter is very inefficient. This same conclusion can be drawn from Figure 2.

The short lifetime of **3** cannot be due to direct energy transfer from the cerium(III) center to a nonemitting acetonitrile excited state, since acetonitrile has no known states with excitation energies in the requisite area of the visible spectrum. As a further check of this assertion, we prepared other nitrile complexes by dissolving the known cerium–THF complexes $(C_5Me_5)CeI_2(THF)_3$ and $CeI_3(THF)_x$ in acetonitrile and then isolating the resulting solids. Although we have not characterized the resulting products fully, the presence of acetonitrile ligands was confirmed by solid-state IR and we tentatively suggest the formulations $(C_5Me_5)CeI_2(NCMe)_z$ and $CeI_3(NCMe)_z$ where the exact number of nitrile ligands is as yet undetermined. Neither of these compounds exhibited anomalously short solid-state lifetimes, with the measured values being 60 and 34 ns, respectively. Our current explanation, then, for the short emission lifetime of **3** is based on its unusually crowded coordination sphere. The excited state of this molecule may readily deactivate via a vibrational relaxation mechanism. Note that this is to be distinguished from a full dissociation of the nitrile ligand, which seems unlikely in the solid state; we have seen no evidence for a photoinduced bleaching of the solid-state material. However, in solution such a process may well occur; the emission spectrum of **3** in acetonitrile is complicated, with at least four discernible bands; these could be the result of emission from **3** *and* some successor species derived from photoinduced ligand dissociation; a likely candidate would be $(C_5Me_5)_2Ce(I)(NCMe)$, but we have no other evidence for this formulation. More work will be required to characterize the solution quenching process(es) available for **3**.

Summary. The study of lifetimes of the cerium(III) compounds reveals that they are all rather short, as predicted for the Laporte-allowed d–f transitions. The lifetime data are useful from two standpoints. First, they allow for the distinction between two compounds whose emission bands overlap. This can be very useful since the cerium(III) emission bands are always inherently broad, and compounds with similar ligand spheres (and hence similar excited-state splittings) are bound to exhibit some overlap. As such, these studies have proven useful in revealing the nature of $[K(THF)_2][(C_5Me_5)_2CeI_2]$ in solution; this is contrary to what would have been predicted on the basis of solid-state data. Another use of the lifetime data is as an indirect indication of the luminescence efficiency of a given cerium(III) compound. The degree to which most of the experimental lifetimes conform to

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the predicted lifetimes serves to validate this treatment and points to the presence of competing nonradiative channels in the few compounds that exhibit anomalously short lifetimes.

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Registry No. 1, 113132-50-6; 2, 113159-94-7; 3, 113132-52-8; $Cp^*_2CeI(THF)$, 113132-51-7; $\{Li(OEt_2)_2\}\{[C_5H_3(SiMe_3)_2]_2CeCl_2\}$, 113132-53-9; Cp^*_2CeI, 106333-17-9; $Cp^*_2CeCl(THF)$, 111559-69-4; $[Li(OEt_2)_2][Cp^*_2CeCl_2]$, 102307-94-8; $K[(COT)_2Ce]$, 51187-43-0; $Cp^*CeI_2(THF)_3$, 105472-89-7; $Ce(OSO_2CF_3)_3$, 76089-77-5.

Supplementary Material Available: Tables of crystal and diffractometer data, positional and thermal parameters, and bond distances and angles, a listing of the standard data tape, and various diagrams detailing the structure of **3** (12 pages); a listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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Specular Reflectance Spectra of Mixed-Metal Tetracyanide Salts: Nature of In-Plane Transitions in $Ni(CN)_4^{2-}$

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The polarized single-crystal specular reflectance spectra of a series of barium salts of $Ni(CN)_4^{2-}$, $Pt(CN)_4^{2-}$, and mixtures of the two complex anions show that the in-plane spectra behave differently for transitions originating on the two complexes. The interpretation is that the lowest energy Ni and Pt complex transitions polarized in-plane are not orbitally identical and that a new assignment of $b_{2g}(xy) \rightarrow e_u(\pi^*)$ for the low-energy $^1E_u \leftarrow {}^1A_{1g}$ transition in $Ni(CN)_4^{2-}$ is required.

Introduction

Solid-state tetracyano complexes of nickel(II), palladium(II), and platinum(II) have been of considerable interest because of the one-dimensional nature of the major electronic effects,[2] the potential superconductivity among one-dimensional conductors,[3] and the inherent interest due to the dramatic spectral changes upon crystallization from solution (the "solid-state effect").[4-8] Numerous electronic spectral studies have assigned observed absorptions to a variety of transitions with some general agreement in the $Ni(CN)_4^{2-}$ system[9-12] and less in the $Pd(CN)_4^{2-}$[11,13,14] and $Pt(CN)_4^{2-}$[9,11-19] systems. Both linear and circular polarization studies have determined the excited-state symmetries in many cases, but there is still ambiguity regarding actual orbital transitions. Our approach has been to add new dimensions to the available evidence by comparing single effects across several salts of a single metal complex as in (1) a series of $Pd(CN)_4^{2-}$ compounds in which a single-molecule origin of the prominent out-of-plane solid-state peak is identified,[14] (2) a single salt of three metallocyanides as with $BaNi(CN)_4$, $BaPd(CN)_4$, and $BaPt(CN)_4$, in which the similarity of the out of plane solid-state peak is demonstrated across the series,[20] and (3) mixed-metal complexes as with $[BaNi_xPt_{1-x}(CN)_4]\cdot 4H_2O$, in which a delocalization over at least 20 centers was demonstrated for the prominent out-of-plane solid-state band.[7] In this work, we examine a more subtle aspect of these complexes, the lowest-energy in-plane bands in the barium salts of mixed $Ni(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$, which possess a significant amount of solid-state perturbation but do not lead to changes in color nor to one-dimensional conductivity. This has led to the need for a reevaluation of assignments for the lowest energy E_u transition in $Ni(CN)_4^{2-}$.

Experimental Section

We have studied the in-plane polarized visible and ultraviolet reflection spectra of crystals prepared from a range of mixed aqueous solutions of barium tetracyanonickelate(II) and barium tetracyanoplatinate(II). The parent crystals are isomorphous, with space group $C2/c$, stacking perpendicular to the square planes and a M-M distance in the range of 3.32-3.36 Å.[21,22] We have assumed that the mixed crystals have similar structures; our polarized spectra have confirmed that the planar orientations are the same for both pure and mixed-metal crystals.

Single crystals of $Ba[Ni_xPt_{1-x}(CN)_4]\cdot 4H_2O$ were grown from aqueous solutions ranging from 1:4 to 4:1 molar concentration of the pure $Ba[M(CN)_4]\cdot 4H_2O$ salts. $BaPt(CN)_4\cdot 4H_2O$ was obtained by recrystallization from aqueous solution of the material from Ventron Chemicals. $Ba[Ni(CN)_4]\cdot 4H_2O$ was obtained by the combination of an excess of barium acetate with $K_2Ni(CN)_4$. The latter had been obtained by recrystallization from material from Research Inorganic/Organic Chemical Corp. Depending upon the concentration, the long well-formed needles resembled the green body color with blue-white reflectivity of $Ba[Pt(CN)_4]\cdot 4H_2O$, the orange body with white reflectivity of $Ba[Ni(CN)_4]\cdot 4H_2O$, or an intermediate appearance. The surface quality was preserved

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