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Synthetic, Structural, and Magnetic Properties of the Pyrazine-Bridged Lanthanide Organometallic Complex μ-Pyrazine-bis[tris(cyclopentadienide)ytterbium(III)], $(C_5H_5)_3Yb(NC_4H_4N)Yb(C_5H_5)_3$

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The synthesis, characterization, and structural and magnetic properties of the title compound are reported. The reaction of $Yb(C_5H_5)_3$ with pyrazine under inert atmosphere conditions in benzene gives the dinuclear product. Slow sublimation under vacuum begins at 75 °C and gives green-brown crystals. The structure has been determined from three-dimensional x-ray diffraction data collected by counter methods. The molecular unit is located about a crystallographic inversion center. Two ytterbium atoms, each with three η^5-cyclopentadienide rings, are nearly linearly bridged by a pyrazine ring coordinated through its nitrogens. The ytterbium–nitrogen distance is 2.61 Å and the average ytterbium–carbon distance is 2.68 (1) Å. The coordination about the ytterbium is nearly C_{3v} in symmetry. The crystals conform to space group $C2/c$ with a = 14.006 (5) Å, b = 8.299 (3) Å, c = 24.637 (9) Å, β = 102.83 (1)°, Z = 4, and ρ_{calcd} = 1.94 g/cm^3. A total of 4857 reflections were collected of which 1304 independent reflections with $F^2 \geq 3\sigma(F^2)$ were used in the final refinement to give a weighted R factor of 4.5%. The magnetic susceptibility of the title compound has been measured in the range 3–100 K and shows linear Curie–Weiss behavior with C = 1.51 (4), Θ = 1.3 (6) K, and μ_{eff} = 3.48 μ_B. There is no evidence of any magnetic interaction between metal centers or reduction of magnetic moment due to f-orbital covalency. This lack of interaction and the consistency of the MCp_3 bonding parameters in both lanthanide and actinide compounds make an ionic formulation of the bonding most appropriate, in contrast to some previous suggestions for related compounds.

Introduction

The organometallic compounds of the lanthanides and actinides have a chemistry which is distinct from both the organometallic chemistry of the d-transition elements and the usual coordination chemistry of the f-block elements. We have been interested in delineating the structural and bonding characteristics of these compounds and have recently reviewed this subject.[1] The preparation of species in which two paramagnetic metal centers are isolated in a single molecule is of particular interest because the magnetic properties of such complexes can give important information about the chemical bonding. Previous studies[2-4] of such lanthanide compounds have involved $Ln(C_5H_5)_2^+$ or $Ln(C_8H_8)^+$ moieties bridged by simple anions such as Cl^-, $CH_3CO_2^-$, or CH_3^-, but only three structural studies have appeared[5-7] and there are no low-temperature magnetic data available. In the case of the actinides, the synthesis of $[(C_5H_5)_3UC_6H_4U(C_5H_5)_3]$ has been reported,[8] but no further studies or characterizations have been forthcoming.

The strong Lewis acidity of $Ln(C_5H_5)_3$ complexes,[9] the recent use of pyrazine as an effective electron-transfer agent in transition-metal chemistry,[10] and our desire for a complex with a continuous π-bridging ligand system to complement previous studies suggested to us the possibility of a pyrazine-bridged molecule. Such a complex would place the metal atoms far enough apart to eliminate through-space magnetic interactions so that any electron exchange would have to take place through the ligand π system. Furthermore, the anticipated approximate C_{3v} site symmetry at the metal center would allow structural comparison with the $(C_5H_5)_3U–X$ complexes of uranium(IV). We now report the successful synthesis and the structural and magnetic characterization of the pyrazine-bridged complex μ-pyrazine-bis[tris(cyclopentadienide)ytterbium(III)].

Experimental Section

All reactions were carried out under an inert atmosphere of high-purity nitrogen or argon on a vacuum line. Transfer and handling of the organometallic complexes were facilitated by the use of Schlenk techniques or a Vacuum Atmospheres HE 93-A inert-atmosphere glovebox having an oxygen- and moisture-free argon atmosphere. Samples for elemental ytterbium analyses were weighed on a Cahn Model 4400 electrobalance in the glovebox. The Yb analyses were performed by carefully decomposing a weighed (approximately 50 mg) sample with water, oxidizing with H_2O_2 until a clear solution was obtained, and titrating with standard ~0.01 M EDTA solution at pH 5–6 using xylenol orange as indicator. The C, H, and N analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Engelskirchen, West Germany. Infrared spectra were measured with a Perkin-Elmer Model 337 spectrophotometer; an AEI-MS12 mass spectrometer was used to record mass spectral data; a Cary 14 spectrophotometer was used to measure optical spectra. Crystalline samples for x-ray diffraction were handled in a horizontal-format glovebox equipped with a binocular microscope.

Materials. Dried and degassed solvents were used in all syntheses and characterizations. Toluene, benzene, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were dried by reflux over sodium–benzophenone ketyl, while hexane was dried by distillation from phosphorus pentoxide. All solvents were degassed under vacuum prior to use.

Sodium cyclopentadienide was prepared from sodium hydride and cyclopentadiene monomer as its DME adduct, $NaC_5H_5{\cdot}DME$, and recrystallized from DME prior to use.[11] Ytterbium trichloride (from ROC/RIC) and pyrazine (from Aldrich) were used without further purification. Ytterbium tricyclopentadienide was prepared via literature procedure[12] and purified by sublimation at 10^{-4} mmHg between 110 and 130 °C. It was characterized as the adductless product by its infrared spectrum,[13] optical spectrum,[14] and metal analysis. (Calcd for $Yb(C_5H_5)_3$: Yb, 47.0. Found: Yb, 46.6.)

$[Yb(C_5H_5)_3]_2C_4H_4N_2$. To a rapidly stirred solution of 0.38 g (1.03 mmol) of $Yb(C_5H_5)_3$ in 75 mL of benzene was added via syringe under an argon flush 0.041 g (0.51 mmol) of pyrazine in 20 mL of benzene. A dull green precipitate formed within several seconds. The reaction mixture was stirred for 12 h, filtered, washed with small portions of benzene and hexane, and dried under vacuum to yield 0.38 g of crude product. This product was transferred to a sublimation apparatus and sublimed onto a cold finger at 10^{-5} mmHg between 80 and 105 °C for 60 h to give 0.28 g of green-brown sublimate: IR (Nujol), cm^{-1} (relative intensity), 3072 (w–m), 2722 (w), 1660 (w, br), 1450 (m), 1410 (m), 1260 (w, m), 1140 (m), 1112 (m), 1065 (w, br), 1045 (m), 1015 (s), 890 (w, br), 840 (w), 795 (vs), 775 (vs), 760 (s, sh), 470 (m).

Anal. Calcd for $Yb_2C_{34}H_{34}N_2$: Yb, 42.4; C, 50.0; H, 4.2; N, 3.4. Found: Yb, 42.2; C, 48.9; H, 4.3; N, 3.2.

No parent ion was found in the mass spectrum run at 70 eV; the fragmentation pattern was very similar to that of $Yb(C_5H_5)_3$ with the addition of a large peak at m/e of 80 due to pyrazine; no peaks were observed attributable to any sort of metal–pyrazine combination. Attempts at lower ionization potentials were not tried, as the compound was by this time fully characterized by x-ray diffraction methods. The complex is slightly soluble in DME and very slightly soluble in benzene or toluene but insoluble in other hydrocarbon solvents. Strongly coordinating solvents such as THF displace the pyrazine to form adducts, as shown by the superimposability of the optical spectra of such solutions with those of solutions of the actual adduct. Although the compound is not very soluble in benzene, a near-infrared spectrum can be obtained using 10-cm cells and is nearly identical with the spectrum of adductless $Yb(C_5H_5)_3$[14] with the exception of an additional set of lines centered at 986 nm.

Magnetic Susceptibility. Magnetic susceptibility measurements were obtained with a PAR Model 155 vibrating sample magnetometer used with a homogeneous magnetic field produced by a Varian Associates 12-in. electromagnet capable of a maximum field strength of 12.5 kG. Approximately 100-mg samples were carefully weighed in the glovebox into diamagnetic, calibrated sample holders machined from Kel-F rod and lightly sealed with grease. A variable-temperature liquid-helium Dewar produced sample temperatures in the range 3–100 K which were measured by a calibrated GaAs diode placed approximately 0.5 in. above the sample. The magnetometer was calibrated with $HgCo(CNS)_4$.[15] The resulting susceptibilities were corrected for underlying diamagnetism[16] and the results appear in Figure 4.

Data Collection. Attempts to grow crystals by cooling hot saturated solutions or slowly evaporating solvent or mixtures of solvents were unsuccessful. However satisfactory, though somewhat small, single crystals suitable for x-ray diffraction were obtained by very slow hot-tube sublimation. These were mounted in silicone grease in thin-walled quartz capillaries and sealed under a nitrogen atmosphere. A series of precession photographs exhibited Laue symmetry $2/m$, but extinctions were difficult to ascertain because of the small crystal size and consequent weak scattering. Further examination on the diffractometer revealed the extinctions hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$, consistent with either of the space groups Cc (C_s^4, No. 9) or $C2/c$ (C_{2h}^6, No. 15).[17]

The greenish brown crystal chosen for data collection was mounted on a eucentric goniometer head so that the {012} axis was nearly parallel to the ϕ axis of a Picker FACS-1 automated four-circle diffractometer equipped with a graphite monochromator and molybdenum tube.[18] The lattice constants and orientation angles were determined from a least-squares refinement of the angular positions of 11 manually centered reflections whose 2θ values ranged from 15 to 23°. The crystal gave ω scan widths at half-height of about 0.10° for several low-angle reflections. The refined cell parameters and other pertinent crystal data are given in Table I.[19]

Table I. Summary of Crystal Data and Intensity Collection

Compd	$[Yb(C_5H_5)_3]_2$-$C_4H_4N_2$	Temp	23 °C
Formula wt	816.74	Radiation	Mo $K\alpha_1$ (λ 0.70930 Å), monochromated
Space group	$C2/c$ (C_{2h}^6)		
Cell parameters	$a = 14.006$ (5) Å	μ	70.26 cm^{-1}
	$b = 8.299$ (3) Å	Transmission factors	0.39–0.75
	$c = 24.637$ (9) Å		
	$\beta = 102.83$ (1)°	Data collection	θ–2θ scan (1°/min along 2θ)
	$V = 2792.1$ Å^3		
Z	4		
ρ_{calcd}	1.94 g/cm^3		$2\theta_{max} = 45°$
Crystal shape	Prism with 7 faces: 001, 00$\bar{1}$, $\bar{1}$10, 110, 1$\bar{1}$0, 0$\bar{1}$0, $\bar{1}$00; 0.10 × 0.10 × 0.04 mm		4857 total data, 1992 independent data
		Refinement	1304 data, $F_o^2 > 3\sigma(F_o^2)$ 172 variables $R_w = 0.0455$

Data reduction and processing were carried out as described elsewhere.[20] The intensities were corrected for Lorentz and polarization effects and converted to values of F^2. The factor $p = 0.04$ was used in the calculation of $\sigma(F^2)$. Absorption corrections were calculated using an analytical algorithm.[21] The morphology of the crystal was difficult to determine because grease distorted both transmitted and reflected light and measurement was hampered by the capillary, but the crystal shape was approximated by seven surface planes. Azimuthal scans of integrated intensity were performed for three strong reflections in different regions of reciprocal space and the dimensions of the crystal adjusted to give the best fit of corrected intensities to these scans. The scans showed about a 2:1 difference between maximum and minimum intensities before correction and about a 1.25:1 difference after correction, with the principal discrepancy coming over the small range of ψ corresponding to maximum absorption. Thus, although necessarily approximate, the correction appears quite good except for those few reflections oriented near the maximum of their absorption. After this correction the data were averaged to give the 1304 reflections with $F^2 > 3\sigma(F^2)$ used in the final refinements. The R factor for averaging, based on F^2, was 3.4%.

Solution and Refinement of the Structure.[22] Comparison of observed and calculated densities suggested one molecule per asymmetric unit in the noncentric space group or one-half molecule in the centric group. After some false starts in the acentric space group Cc, the structure was solved by routine heavy-atom methods in the centric space group $C2/c$.

Full-matrix least-squares refinements on F were used in which the function minimized was $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are observed and calculated structure factors and the weighting factor, w, is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for neutral Yb, N, and C were taken from the values tabulated by Cromer and Mann[23] and those for neutral hydrogen from Stewart, Davidson, and Simpson.[24] Corrections for anomalous dispersion effects of ytterbium using both $\Delta f'$ and $\Delta f''$ were included.[25]

No attempts were made to locate hydrogen atoms. In the final refinements all nonhydrogen atoms were treated anisotropically and hydrogen atoms were fixed in calculated positions with a C–H distance of 0.95 Å and an isotropic temperature factor of 6.0 Å^2. The model converged to give weighted and unweighted R factors of 4.55 and 3.91%, respectively.[26] On the final cycle no parameter shifted more than its standard deviation. The final error in an observation of unit weight was 1.49 and did not vary systematically with either $(\sin\theta)/\lambda$ or $|F_o|$. Examination of the final difference Fourier showed no peak greater than 1.5 e/Å^3 (approximately 30% of a carbon atom), and several of the highest peaks were located near the ytterbium atom. Table II gives the positional and thermal parameters for the nonhydrogen atoms. Additional material is also available.[27]

Description of the Structure

The crystal structure consists of discrete dinuclear units which are located about inversion centers. There are four molecules per unit cell and their centers occupy the symmetry-related positions $^1/_4$, $^1/_4$, 0; $^3/_4$, $^3/_4$, 0; $^3/_4$, $^1/_4$, $^1/_2$; and $^1/_4$, $^3/_4$, $^1/_2$.

Table II. Positional and Thermal Parameters for the Atoms of $[Yb(C_5H_5)_3]_2C_4H_4N_2$

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Yb	0.24634 (4)	−0.05467 (8)	0.12655 (3)	2.16 (4)	7.77 (12)	0.88 (1)	−0.63 (8)	0.29 (2)	0.21 (5)
N	0.2490 (8)	0.1369 (15)	0.0427 (5)	2.7 (7)	7.0 (21)	2.1 (3)	−0.3 (11)	1.8 (7)	1.8 (7)
$C_{B_1}{}^c$	0.1687 (10)	0.1816 (19)	0.0063 (6)	3.1 (10)	11 (3)	1.2 (4)	−2.4 (13)	0.5 (5)	0.8 (9)
$C_{B_2}{}^c$	0.3293 (10)	0.2122 (19)	0.0359 (7)	2.6 (9)	11 (3)	1.8 (4)	−1.2 (13)	0.0 (5)	1.6 (9)
C_{11}	0.1165 (10)	−0.2950 (18)	0.0777 (8)	3.4 (9)	3.6 (29)	2.8 (5)	−1.1 (13)	0.2 (5)	0.2 (9)
C_{12}	0.0842 (9)	−0.1496 (20)	0.0525 (6)	2.8 (9)	14 (3)	0.7 (3)	0.4 (14)	−0.4 (4)	0.2 (9)
C_{13}	0.0522 (11)	−0.0489 (23)	0.0907 (9)	3.6 (10)	9 (3)	2.8 (5)	−0.7 (17)	−0.2 (6)	−1.4 (13)
C_{14}	0.0669 (10)	−0.1372 (28)	0.1385 (7)	1.6 (8)	29 (5)	1.8 (5)	−3.9 (17)	1.6 (5)	−1.2 (13)
C_{15}	0.1146 (12)	−0.2859 (21)	0.1332 (7)	5.7 (11)	15 (4)	1.3 (4)	−3.1 (16)	−0.6 (5)	2.2 (9)
C_{21}	0.2310 (15)	0.2497 (21)	0.1589 (8)	9.0 (16)	9 (3)	1.6 (4)	−0.7 (18)	1.0 (7)	−0.9 (9)
C_{22}	0.1802 (12)	0.1639 (24)	0.1890 (8)	6.5 (13)	16 (4)	2.0 (5)	−2.1 (19)	1.8 (7)	−3.2 (11)
C_{23}	0.2448 (14)	0.0615 (26)	0.2262 (7)	7.5 (14)	21 (4)	1.0 (4)	−1.6 (23)	0.5 (6)	−3.2 (12)
C_{24}	0.3375 (12)	0.0982 (27)	0.2170 (9)	3.6 (11)	26 (5)	2.4 (5)	0.6 (18)	−0.4 (6)	−3.8 (13)
C_{25}	0.3298 (18)	0.2115 (25)	0.1762 (9)	11.6 (20)	14 (4)	1.9 (5)	−7.4 (23)	1.9 (8)	−3.1 (12)
C_{31}	0.4022 (12)	−0.2255 (23)	0.1689 (8)	4.6 (11)	12 (4)	2.3 (5)	3.5 (16)	0.6 (6)	2.9 (12)
C_{32}	0.4393 (13)	−0.1119 (23)	0.1379 (10)	5.9 (12)	11 (4)	3.2 (6)	2.7 (16)	0.2 (7)	−2.9 (12)
C_{33}	0.4001 (12)	−0.1491 (22)	0.0821 (8)	5.7 (12)	10 (3)	2.3 (5)	2.3 (17)	1.6 (6)	1.8 (11)
C_{34}	0.3396 (11)	−0.2835 (22)	0.0796 (8)	4.6 (11)	15 (4)	2.5 (5)	3.9 (16)	1.1 (6)	−1.5 (11)
C_{35}	0.3455 (13)	−0.3347 (20)	0.1334 (10)	6.7 (14)	4 (3)	3.8 (7)	1.1 (16)	1.8 (8)	2.4 (12)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^3$. [c] Carbon of pyrazine ring.

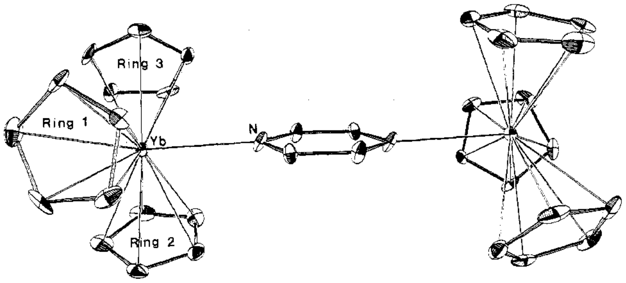

Figure 1. A perspective view of the complex $(C_5H_5)_3Yb(NC_4H_4N)Yb(C_5H_5)_3$. The thermal ellipsoids are drawn at the 50% probability level.

A perspective drawing of the complex is shown in Figure 1. The molecular structure consists of two ytterbium atoms, each with three η^5-bound cyclopentadienyl rings, which are nearly linearly bridged by a pyrazine ring coordinated through its nitrogens. The ytterbium–nitrogen distance is 2.61 (1) Å and the Yb–N–N′ angle is 176°.

The coordination about the ytterbium atom is nearly C_{3v} in symmetry, with the centers of the cyclopentadienyl rings forming the base and the pyrazine nitrogen the apex of a flattened tetrahedron. The cyclopentadienyl moieties, due to their size and occupation of multiple coordination sites, are at an angle somewhat greater than the tetrahedral but maintain an approximately trigonal distribution, the vectors from the center of the ring to the metal forming angles of 115.6, 118.1, and 119.9°. The pyrazine nitrogen is a single atom occupying a single coordination site and the nitrogen–metal–ring angles are accordingly reduced and average 98.5°. These and other important bond distances and angles are listed in Table III.[28]

The pyrazine ring has an average N–C distance of 1.328 (12) Å and a C–C distance of 1.367 (20) Å, consistent with previous structural studies of pyrazine-containing compounds.[29] The three independent atoms of the ring define a plane, but the inversion center is 0.04 Å out of this plane, so that the entire ring is not strictly planar. Nevertheless the average deviation from a least-squares plane through all six atoms is only 0.013 Å. The ytterbium atom is only 0.16 Å out of this plane so that the entire bridge is nearly planar.

Table III. Bond Distances and Angles in $[Yb(C_5H_5)_3]_2C_4H_4N_2$

	Bond Distances, A		
Yb-Yb (nonbonded, intramolecular)	8.047 (2)	Yb-C_{15}	2.69 (1)
		Yb-C_{21}	2.67 (2)
Yb-Yb (nonbonded, intermolecular)	7.049 (2)	Yb-C_{22}	2.67 (2)
	7.345 (2)	Yb-C_{23}	2.64 (2)
	8.140 (2)	Yb-C_{24}	2.63 (2)
Yb-N	2.61 (1)	Yb-C_{25}	2.67 (2)
N-C_{B_1}	1.33 (2)	Yb-C_{31}	2.62 (1)
N-C_{B_2}	1.33 (2)	Yb-C_{32}	2.70 (2)
C_{B_1}-$C_{B_2}{}'^a$	1.37 (2)	Yb-C_{33}	2.74 (1)
Yb-C_{11}	2.79 (1)	Yb-C_{34}	2.71 (1)
Yb-C_{12}	2.70 (1)	Yb-C_{35}	2.69 (2)
Yb-C_{13}	2.67 (1)	Yb-C (av)^b	2.684 (11)
Yb-C_{14}	2.68 (1)	C_i-C_{i+1} (av)^c	1.387 (5)
	Bond Angles, Deg		
Cp_1-Yb-$Cp_2{}^d$	118.1	Cp_3-Yb-N	98.3
Cp_2-Yb-Cp_3	120.0	C_{B_1}-N-C_{B_2}	113 (1)
Cp_3-Yb-Cp_1	115.6	$C_{B_2}{}'$-C_{B_1}-N	122 (1)
Cp_1-Yb-N	102.5	$C_{B_1}{}'$-C_{B_2}-N	124 (1)
Cp_2-Yb-N	94.6	C_i-C_{i+1}-C_{i+2} (av)	107.9 (6)

[a] The primed atoms are related to the unprimed by inversion through ($^1/_4$, $^1/_4$, 0). [b] The average in this and other quantities reported is calculated as $\bar{x} = (\Sigma x_i)/n$ and the standard deviation of the average as $\sigma(\bar{x}) = [\Sigma(x_i - \bar{x})^2/n(n-1)]^{1/2}$. [c] C_i-C_{i+1} refers to adjacent carbons on cyclopentadienyl rings. [d] Cp represents the centroid of the cyclopentadienyl ring.

The five carbon atoms of each cyclopentadienyl ring also conform to good planes, although there is substantial thermal motion in the plane of the ring. The maximum deviation from the weighted least-squares plane is 0.05 Å. The carbon–carbon distances for adjacent carbons average 1.387 (5) Å and C–C–C angles average 107.9 (6)°. The rings are symmetrically bound to the ytterbium with an average Yb–C distance of 2.684 (11) Å. The closest carbon–carbon nonbonded contact is 3.07 Å, an intramolecular contact between rings 1 and 2. No intermolecular carbon–carbon contacts are less than 3.5 Å.

While there are no unusually short intermolecular contacts in the structure, several of the intermolecular metal–metal distances are actually shorter than the intramolecular metal–metal distance. In fact if the metal atoms are considered alone, they produce an approximately hexagonal array.

Alternatively, the ytterbium ion can be considered the center of a somewhat distorted sphere embracing the cyclopentadienyl carbon atoms and half of the bridging pyrazine ring. The crystal structure is then approximately hexagonal close packed with the 12 "nearest neighbor" metal–metal distances ranging from 7.05 to 8.30 Å. The metal atoms of different molecules can approach this closely without significant carbon–carbon interaction, despite the presence of bulky cyclopentadienyl groups, because the metal–metal vector lies approximately

Table IV. Summary of Molecular Parameters for MCp_3-X Compounds

	$[YbCp_3]_2$-pyz	Nd(Me-Cp)$_3$	$PrCp_3 \cdot CNC_6H_{11}$	UCp_3-(2-methallyl)	UCp_3-(*n*-Bu)	UCp_3F	U(Bz-Cp)$_3$Cl
Av Cp-M-Cp angle, deg[a]	117.9	117.4	118.9	117.3	116.7	117.2	117.0
Av Cp-M-X angle, deg	98.5	99.4	96.2	99.7	100.6	99.7	100.0
M-X bond, Å	2.61	2.98	2.65	2.48	2.48	2.11	2.63
Av M-C dist, Å (π-cyclopentadienyl)	2.68	2.79	2.78	2.74	2.72	2.74	2.73
Formal coordination no.[b]	10	10	10	10	10	10	10
Metal ionic radius[c]	1.08	1.19	1.22	1.09	1.09	1.09	1.09
Ref	This work	31	32	34	35	36	37

[a] Cp denotes center of cyclopentadienyl ring. [b] The coordination number assumes the cyclopentadienide anion, with six electrons, occupies three coordination sites. [c] Interpolated from radius vs. CN data from ref 33.

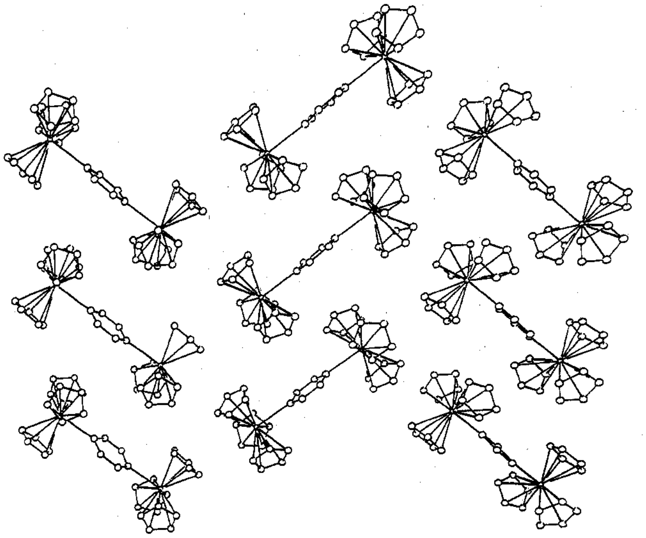

Figure 2. Crystal packing of a layer at $x = {}^1/_4$. The *b* axis is nearly vertical and the *c* axis is horizontal. A similar layer at $x = {}^3/_4$ completes the unit cell.

along the pseudo-threefold axis of one molecule and roughly perpendicular to the intervening cyclopentadienyl group of the other molecule. This is illustrated for one layer of metal atoms in Figure 2.

Discussion

Structural Properties. Pyrazine-bridged complexes of d-transition elements have been known for some time, but the compound reported here represents the first such complex of an f-transition element. An example of the strong desire of the lanthanides to saturate their coordination sphere, the complex forms very rapidly from adductless $Yb(C_5H_5)_3$ and pyrazine. The metal–nitrogen bond, however, appears to be rather weak. It is readily displaced by solvents known to form adducts with $Yb(C_5H_5)_3$, such as THF, although not by DME, which is a less polar ligand. The Yb–N bond must be broken readily in a mass spectrometer with a 70-eV ionization potential, since no evidence of a metal–pyrazine linkage was discernible in the spectrum. The pyrazine electronic transitions observable in the near-UV are unshifted in the complex relative to free pyrazine in the same solvent. Nevertheless, the complex is remarkably thermally stable. It begins to sublime at a surprisingly low 75 °C under high vacuum and can be sublimed over and over again with only slight decomposition. This sublimation temperature is considerably lower than any other organometallic lanthanide compound and places the complex among the more volatile of all lanthanide compounds (for example, the fluorinated β-diketonates[30]).

Structurally the compound strongly resembles the U-$(C_5H_5)_3$–X complexes of the actinide series. These latter compounds show a remarkable consistency in their metal–cyclopentadienyl bonding.[1] All are ten-coordinate species with ring–metal–ring angles close to 117°, X–metal–ring angles close to 100°, and carbon–carbon nonbonded contacts close to 3.10 Å. In the lanthanide series both our dinuclear complex, the tetrameric $Nd(C_5H_4CH_3)_3$,[31] and the cyclohexyl isocyanide adduct of $Pr(C_5H_5)_3$[32] can be formulated as $LnCp_3$–X complexes with the pyrazine nitrogen, an η^1-cyclopentadiene ring, and the isocyanide group in the X position, respectively. The parameters of these complexes and several representative actinide compounds are tabulated in Table IV, and the other actinide complexes fit the same pattern.[1] Clearly the $LnCp_3$ unit has essentially the same geometry as the UCp_3 moiety. Furthermore, the difference in average metal–carbon distance between the ytterbium and neodymium compounds is the same as the difference in ionic radii.[33] This 2.68-Å bond length in our diytterbium complex (ionic radius 1.08 Å) is also consistent with the 2.58 Å distance in the eight-coordinate chloride-bridged ytterbium dimer[5] (ionic radius 0.98 Å). The praseodymium compound appears to have a shorter metal–carbon bond length than would be expected from its ionic radius, but the rather high thermal motion of the structure will tend to shorten bond lengths, thus precluding a detailed comparison. The bond length–ionic radius comparison between Ln^{3+} complexes and U^{4+} complexes is also quite good, despite differences in charge, and, along with the constant nature of the MCp_3 unit, is indicative of predominantly ionic bonding in both the lanthanide and actinide members of this series.

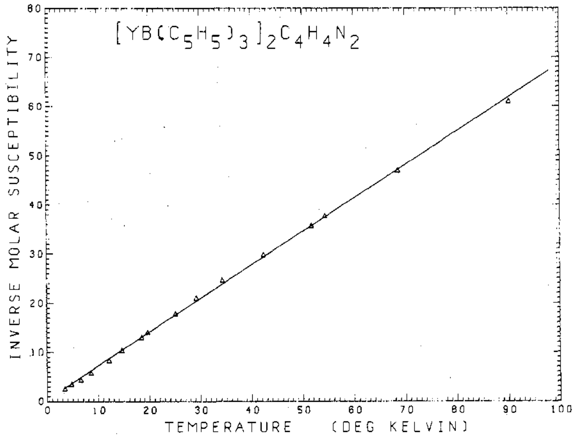

Figure 3. Inverse molar susceptibility vs. temperature for $[Yb(C_5H_5)_3]_2C_4H_4N_2$ in the range 0–100 K. The straight line is a least-squares fit to the data.

Magnetic Properties. The magnetic susceptibility of our dinuclear complex as a function of temperature is shown in Figure 3. It exhibits simple Curie–Weiss behavior, with $\chi = C/T + \Theta$. The straight line is a least-squares fit to the data and the derived parameters are $C = 1.51\ (4)$ and $\Theta = 1.3\ (6)$ K. The corresponding value of μ_{eff}, calculated from the slope, is 3.48 μ_B. No other cyclopentadienyl lanthanide complex has had its moment measured below 77 K nor has the temperature dependence of the susceptibility been closely examined before, but reports of the effective moment at two or three temperatures have appeared. The $LnCp_2Cl$[2] and $LnCpCl_2$[38] compounds appear to follow the Curie–Weiss law down to 200 K, with $\mu_{eff} = 4.81$ and $4.33\ \mu_B$ and $\Theta = 108$ and 8 K, respectively, for the ytterbium members of the series. A moment of 4.00 μ_B with $\Theta = 21$ K has been reported for $YbCp_3$ down to 77 K.[39] Recently the moments of several dicyclopentadienide lanthanide alkyls have been measured by Tsutsui[40] to 77 K and their temperature dependence attributed to a covalent interaction involving the σ-bonded alkyl group. However, these moments appear to have been calculated from the Curie law (as $\mu = 2.83(\chi T)^{1/2}$), not from the slope, or Curie–Weiss law (as $\mu = 2.83[\chi(T + \Theta)]^{1/2}$), like all the others.[41] Recalculation of the susceptibility from the reported moment using the Curie law shows that $1/\chi$ is approximately linear with temperature. The moments recalculated from the slopes are then between 4 and 4.5 μ_B for the ytterbium complexes of Tsutsui, in agreement with the other high-temperature values.

It appears to us that there is no evidence of any magnetic coupling between metal centers in known organometallic lanthanide complexes[42] nor any suggestion of reduction of magnetic moment due to f-orbital covalency. The room-temperature moments of these complexes are usually close to the free ion values. The exact moment depends on the relative populations and splittings of the crystal field states. As this population alters with temperature, so will the moment until, at a sufficiently low temperature, only a single crystal field state will be occupied. This has been demonstrated by the agreement of crystal field calculations and experimental susceptibilities for octahedral lanthanide compounds of the form $Cs_2NaLnCl_6$.[43] Our pyrazine-bridged complex nearly obeys the Curie law below 100 K, suggesting occupation of a single-crystal field state at that temperature. Preliminary results[44] have also been obtained for $ErCp_2Cl$ and $YbCp_2$(benzoate), also dimeric complexes. They exhibit linear Curie–Weiss behavior above 20 K with a Weiss constant close to those previously observed, but a slow change in slope around 15 K to approximate Curie behavior, with a correspondingly lower moment. This is consistent with the occupation of multiple crystal field states to a lower temperature than for the pyrazine-bridged compound.

In summary, we have synthesized a novel pyrazine-bridged diytterbium complex which is remarkably volatile and whose structural properties are quite similar to the MCp_3X compounds of the actinides. A comparison of molecular parameters and an analysis of the magnetic susceptibility as a function of temperature suggest a largely ionic formulation of the bonding is most appropriate.

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Registry No. $[Yb(C_5H_5)_3]_2C_4H_4N_2$, 63950-86-7; $Yb(C_5H_5)_3$, 1295-20-1.

Supplementary Material Available: A listing of structure factor amplitudes, a table of calculated hydrogen atom positions, a table of carbon–carbon bond lengths and angles, the root-mean-square amplitudes of vibration of nonhydrogen atoms, and the parameters of the least-squares planes (14 pages). Ordering information is given on any current masthead page.

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(17) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1965, pp 89 and 101.
(18) The programs used by the PDP8/E computer were those written by Busing and Levy as modified by the Picker Corp. and further modified locally.
(19) Intensity data were collected in the θ–2θ scan mode using monochromatic Mo Kα radiation and a scintillation counter. The Bragg angle for the highly oriented graphite monochromator was 12.02° and the x-ray tube takeoff angle was 3°. The pulse height analyzer was set to admit 90% of the maximum intensity at full window width. The detector was located 33 cm from the source with a 7 × 7 mm receiving aperature. The 2θ scans were from 0.5° below the Kα_1 peak to 0.5° above the Kα_2 with a scan rate of 1.0°/min. Copper foil attenuators were automatically inserted in the path of the diffracted beam to keep the count rate for a given reflection below 10^4 counts/s. Stationary 20-s background counts were taken at the start and finish of each scan. Throughout the data collection the intensities of three standard reflections (200, 004, and $\bar{1}12$) were measured every 47 reflections as a check on crystal stability. A linear isotropic reduction in intensity amounting to about 9% by the end of data collection was noted, and the data were corrected accordingly. A total of 4857 reflections were collected, including one unique form ($\pm h$, $+k$, $+l$) to $2\theta = 45°$ and all remaining forms to $2\theta = 30°$.
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