were applied. In the final refinement all of the atoms with the exception of the carbon atoms in the dithiocarbamate ligand were assigned anisotropic thermal parameters. Hydrogen atoms were not included.

The discrepancy indices for 2175 data where $F^2 > 3\sigma$ are $R = 0.039$ and R_w[14] = 0.052. R for all 2327 data is 0.041. The error in an observation of unit weight is 1.84. In the last cycle, no parameter changed more than 0.1σ. In the final difference Fourier the largest electron density peak was ~0.5 e/Å^3 and was near the Yb atom.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

Registry No. $(Me_5C_5)_2Yb(S_2CNEt_2)$, 81276-69-9; $(Me_2C_5)_2Yb(O_2CCMe_3)$, 81276-70-2; $(Me_5C_5)_2Yb(O_2CCF_3)$, 81293-71-2; $(Me_5C_5)_2Nd(S_2CNEt_2)$, 81276-71-3; $Na(OEt_2)_2(Me_5C_5)_2YbCl_2$, 78128-21-9; $Li(OEt_2)_2(Me_5C_5)_2NdCl_2$, 78128-14-0.

Supplementary Material Available: Listings of thermal parameters and structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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(14) $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$.

Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
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Bis(pentamethylcyclopentadienyl)bis(pyridine)ytterbium(II)

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Received October 5, 1981

Crystals of $(C_5Me_5)_2Yb(C_5H_5N)_2$ crystallize in the monoclinic system, $P2_1/c$, with $a = 16.092$ (6) Å, $b = 9.883$ (4) Å, $c = 17.872$ (7) Å, and $\beta = 98.46$ (3)° at 21 °C. For $Z = 4$ the calculated density is 1.42 g cm^{-3}. Two pentamethylcyclopentadienyl rings and the nitrogen atoms of the two pyridine molecules coordinate to the Yb atom in a distorted tetrahedral arrangement with approximate C_2 symmetry. The Yb–N distances average 2.56 Å, the Yb–C distances average 2.74 Å, and the Yb–Cp(centers) average 2.46 Å. The C_5Me_5 rings are in a staggered configuration with respect to each other. The methyl groups of the C_5Me_5 rings are bent 0.13–0.31 Å out of the planes of the C_5 rings away from the Yb atom. The 3278 data with $F^2 > 3\sigma(F^2)$ refined by full-matrix least squares to an R factor of 0.031.

Introduction

Bonding of cyclopentadienyl groups and its substituted analogues to f-block metals is thought to be predominantly ionic, i.e., there is very little electron exchange between the metal atom and the organic ligand. A structural criterion has been advanced by Raymond that is remarkably accurate in predicting f-metal to carbon bond lengths, given the simplicity and therefore utility of the model.[1] The fundamental principle of the model is that metal–carbon bond lengths are a sensitive function of the oxidation state and coordination number of a given metal ion. Subtraction of the ionic radius of a metal atom, which is a function of the oxidation state and coordination number, from the observed metal–carbon bond length gives the effective ionic radius of a cyclopentadienyl group. Ligand–ligand repulsions also play a role in determining the metal–carbon bond length; however, for the f-block metals the effective ionic radius of the cyclopentadienyl ligand is observed to be fairly constant, 1.64 ± 0.04 Å. Thus, it may be said that the bonding in these organometallic molecules is largely ionic.

In the course of our investigations into the chemistry of pentamethylcyclopentadienyl derivatives of the lanthanide metals, we have prepared a number of compounds whose structures can be used to test this model. The compound whose structure is reported here, $(C_5Me_5)_2Yb(py)_2$, offers an interesting test of the ionic bonding model for divalent lanthanide complexes since its coordination number is one greater than that of the divalent $(C_5Me_5)_2Yb(THF)$, which has been structurally characterized.[2]

Results and Discussion

The compound $Yb(C_5Me_5)_2(py)_2$ is prepared by the reaction of $Yb(C_5Me_5)_2(OEt_2)$ and excess pyridine in toluene and crystallizes from toluene as dark green prisms.

Table I. Positional Parameters in $(C_5Me_5)_2Yb(C_5H_5N)_2$[a]

atom	x	y	z
Yb	0.24809 (2)	0.07142 (3)	0.29227 (2)
N(1)	0.3320 (5)	0.2724 (7)	0.3581 (4)
N(2)	0.1425 (4)	0.1403 (6)	0.3781 (3)
C(1)	0.1985 (5)	0.0471 (6)	0.1378 (4)
C(2)	0.1294 (4)	0.1069 (7)	0.1661 (4)
C(3)	0.1531 (5)	0.2384 (7)	0.1911 (4)
C(4)	0.2377 (5)	0.2589 (7)	0.1788 (4)
C(5)	0.2650 (4)	0.1408 (7)	0.1466 (4)
C(6)	0.1933 (6)	−0.0828 (8)	0.0899 (5)
C(7)	0.0408 (5)	0.0469 (8)	0.1558 (4)
C(8)	0.0941 (6)	0.3447 (8)	0.2152 (5)
C(9)	0.2841 (6)	0.3926 (8)	0.1843 (5)
C(10)	0.3495 (5)	0.1255 (9)	0.1183 (5)
C(11)	0.3247 (6)	−0.0951 (8)	0.4068 (5)
C(12)	0.3714 (5)	−0.1114 (8)	0.3470 (5)
C(13)	0.3186 (5)	−0.1785 (7)	0.2877 (5)
C(14)	0.2399 (5)	−0.1983 (7)	0.3111 (5)
C(15)	0.2436 (6)	−0.1476 (8)	0.3852 (5)
C(16)	0.3614 (8)	−0.039 (1)	0.4848 (6)
C(17)	0.4666 (6)	−0.085 (1)	0.3473 (7)
C(18)	0.3500 (6)	−0.2374 (8)	0.2180 (6)
C(19)	0.1665 (6)	−0.2773 (9)	0.2692 (6)
C(20)	0.1751 (7)	−0.165 (1)	0.4338 (6)
C(21)	0.4146 (7)	0.271 (1)	0.3705 (7)
C(22)	0.4634 (8)	0.380 (1)	0.3960 (9)
C(23)	0.4239 (9)	0.503 (1)	0.4061 (7)
C(24)	0.3394 (7)	0.5075 (9)	0.3939 (6)
C(25)	0.2963 (6)	0.3905 (9)	0.3702 (5)
C(26)	0.1686 (5)	0.1870 (9)	0.4474 (5)
C(27)	0.1152 (7)	0.215 (1)	0.4990 (5)
C(28)	0.0321 (6)	0.1929 (9)	0.4783 (5)
C(29)	0.0035 (5)	0.1436 (9)	0.4086 (5)
C(30)	0.0597 (6)	0.1194 (8)	0.3610 (5)

[a] In this and the following tables, the numbers in parentheses are the estimated standard deviations in the least significant digits.

An ORTEP view of the molecule (Figure 1) shows a distorted tetrahedral array of the ligands about ytterbium, with ap-

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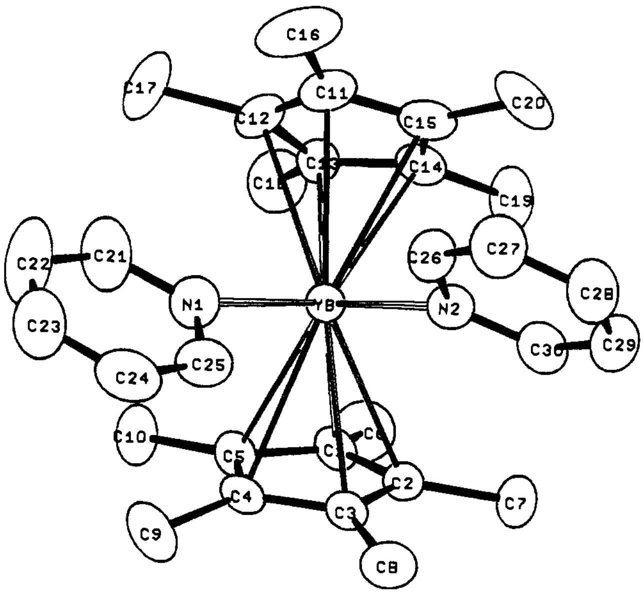

Figure 1. ORTEP drawing of $(C_5Me_5)_2Yb(C_5H_5N)_2$ as viewed down the pseudo-2-fold axis.

Table II. Selected Interatomic Distances (Å)

Yb-C(1)	2.769 (7)	Yb-C(11)	2.770 (8)
-C(2)	2.754 (7)	-C(12)	2.754 (7)
-C(3)	2.742 (7)	-C(13)	2.724 (7)
-C(4)	2.734 (6)	-C(14)	2.692 (7)
-C(5)	2.743 (7)	-C(15)	2.736 (7)
-N(1)	2.586 (7)	-N(2)	2.544 (6)

Table III. Selected Angles (Deg)

N(1)-Yb-N(2)	82.5 (2)	N(2)-Yb-Cp(1)	107.7 (3)
N(1)-Yb-Cp(1)[a]	103.6 (2)	N(2)-Yb-Cp(2)	102.0 (3)
N(1)-Yb-Cp(2)	111.5 (3)	Cp(1)-Yb-Cp(2)	136.3 (3)

[a] Cp is the centroid of a C_5Me_5 ring.

proximate C_2 symmetry. Atomic positions and selected distances and angles are given in Tables I–III. The angles about the coordination sphere range from 136.3 (3)° for the C_5Me_5(centroid)–Yb–C_5Me_5(centroid) angle to 82.5 (2)° for the N(1)–Yb–N(2) angle. The pyridine rings have normal geometry, as do the C_5Me_5 rings, which are arranged in a staggered conformation (Figure 2).

The displacements of the methyl carbon atoms from the planes of their respective C_5 rings, which range from 0.13 to 0.31 Å, are greater than the corresponding displacements in $Yb(C_5Me_5)_2(THF)$, which range from 0.03 to 0.21 Å. This is a result of more steric crowding in $Yb(C_5Me_5)_2(py)_2$, which has a higher coordination number.

The pyridine rings are directed almost linearly away from the ytterbium atom (∠Yb–N(1)–C(23) = 171.0 (4)° and ∠Yb–N(2)–C(28) = 174.6 (3)°), and the planes of the pyridine rings are canted by ca. 35° from the plane of Yb, N(1), and N(2). The Yb–N(1) and Yb–N(2) distances are 2.586 (7) and 2.544 (6) Å, respectively. If one subtracts the ionic radius of a eight-coordinate ytterbium(II) ion, 1.14 Å,[3] from the Yb–N distances, one obtains 1.45 and 1.40 Å, respectively, for the ionic radii of the pyridine nitrogen atoms. A value of 1.40 Å can be calculated from the structure of the eight-coordinate bis(pyridine)tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III).[4]

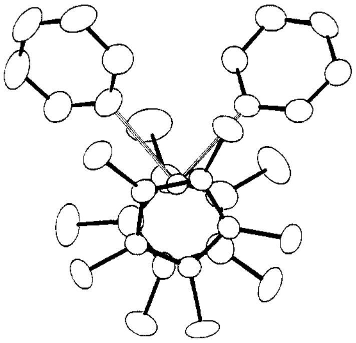

Figure 2. ORTEP drawing looking down the centers of the pentamethylcyclopentadiene rings showing the staggered configurations of the rings with respect to each other.

Table IV. Effective Ionic Radius (Å) of the Me_5C_5 Group

compd	M–C, Å	M ion radius, Å	eff $C_5Me_5^-$ radius, Å	ref
$Yb(C_5Me_5)_2(py)_2$	2.74 (4)	1.14	1.60	this work
$Yb(C_5Me_5)_2(THF)$	2.66 (2)	1.08	1.58	*a*
$Yb(C_5Me_5)_2(S_2CNEt_2)$	2.63 (3)	0.985	1.64	*b*
$Yb(C_5Me_5)_2(THF)[Co(CO)_4]$	2.596 (2)	0.985	1.61	*c*
$[Yb(C_5Me_5)_2]_2[Fe_3(CO)_{11}]$	2.57 (1)	0.985	1.59	*d*
$[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$	2.611 (4)	0.985	1.63	*e*
$Yb(C_5Me_5)_2AlCl_4$	2.584 (5)	0.985	1.60	*e*

[a] Reference 2. [b] Tilley, T. D.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.*, preceding paper in this issue. [c] Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* 1981, 985. [d] Tilley, T. D.; Andersen, R. A. *J. Am. Chem. Soc.* 1982, *104*, 1772. [e] Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* 1981, *20*, 3271.

Though the ytterbium–carbon distances in ring 1 do not show any systematic variation, those in the ring 2 range from 2.691 (8) Å for C(14) to 2.786 (9) Å for C(11), resulting in a tilt by ring 2 of ca. 2° away from the nitrogen atoms. The average ytterbium–carbon distance is 2.74 (4) Å, which is 0.08 Å greater than the corresponding average in $Yb(C_5Me_5)_2$(THF) [2.66 (2) Å]. Thus, if one counts the C_5Me_5 ligand as being three-coordinate, the ionic radius of ytterbium(II) in eight-coordination is 0.08 Å greater than that in seven-coordination. Shannon suggests a difference of 0.06 Å.

Using the ionic radii tabulated by Shannon,[3] one can estimate the effective ionic radius of the C_5Me_5 ligand in the bis(pentamethylcyclopentadienyl)ytterbium complexes that have been structurally characterized. As shown in Table IV, these radii are consistent with the value suggested by Raymond for predominantly ionic bonding, 1.64 ± 0.03 Å. On the basis of these structural data alone, the bonding in ytterbium(II) pentamethylcyclopentadienyl complexes appears to be largely ionic and in this regard does not differ greatly from the bonding observed in ytterbium(III) cyclopentadienyl complexes.

Experimental Section

Bis(pentamethylcyclopentadienyl)bis(pyridine)ytterbium(II). Pyridine (1 mL, an excess) was added to (diethyl ether)–bis(pentamethylcyclopentadienyl)ytterbium(II) (1.75 g, 3.38 mmol) dissolved in toluene (15 mL). A dark green solid precipitated. After the mixture was stirred for 1 h, the volatile material was removed under reduced pressure. The residue was washed with pentane (2 × 30 mL) and extracted into toluene by being stirred overnight (2 × 100 mL). The combined extracts were concentrated to ca. 60 mL, and cooling (−10 °C) resulted in formation of green prisms; yield 1.77 g (87%). When heated in a sealed capillary, the compound darkens above ca. 190 °C

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and melts at 208-210 °C. ^1H NMR (26 °C, benzene-d_6): δ 2.12 (s, C_5Me_5). Resonances due to coordinated pyridine were not observed. Anal. Calcd for $C_{30}H_{40}N_2Yb$: C, 59.9; H, 6.70; N, 4.66. Found: C, 60.3; H, 6.70; N, 4.47. IR (Nujol): 3092 w, 3063 w, 3037 w, 2720 w, 1594 s, 1486 w, 1213 m, 1159 m, 1107 w, 1069 m, 1033 m, 998 m, 984 w, 942 w, 886 w, 800 w, 759 s, 729 w, 702 s, 662 m, 618 m, 591 m, and 419 m cm^{-1}.

X-ray Data. Crystals of the complex were sealed in quartz capillaries under an atmosphere of argon. A crystal of dimensions 0.06 × 0.22 × 0.22 mm was examined with a Picker FACS-I automated diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda(K\alpha_1)$ = 0.709 30 Å). Least-squares refinement of the setting angles of 12 manually centered reflections (45° < 2θ < 50°) gave a = 16.092 (6) Å, b = 9.883 (4) Å, c = 17.872 (7) Å, β = 98.46 (3)°, and V = 2811.4 Å^3 at 21 (1) °C. The observed extinctions are unique to space group $P2_1/c$. For Z = 4 and a molecular weight of 601.70, the calculated density is 1.42 g cm^{-3}.

Intensity data for two forms ($\pm h,+k,\pm l$) to 50° in 2θ were collected with θ-2θ with a scan speed of 2°/min on 2θ. Three standard reflections, measured after every 150 reflections, decreased in intensity by 2% during data collection, and the measured intensities were corrected accordingly.

An analytical absorption correction was applied[5] (μ = 33.3 cm^{-1}), and the correction factors were varied from 1.27 to 2.42. Intensities of the 10 699 reflections measured were also adjusted for the Lorentz and polarization factors,[6] extinctions were removed, and equivalent reflection were averaged to obtain a set of 4985 unique reflections.

Trial coordinates for the ytterbium atom were obtained from a three-dimensional Patterson function and were refined by least squares. An electron density map then revealed all nonhydrogen atoms. In the final cycles of least-squares refinement, all nonhydrogen atoms were refined anisotropically with the pyridine hydrogen atoms included in their calculated positions (with the assumption of a C-H bond distance of 0.95 Å) with a fixed isotropic thermal parameter of 8.0 Å^2. An empirical extinction correction was applied where $F_c = (1 + (4.54 \times 10^{-8})I)F_o$, where F_c and F_o are the corrected and observed structure factors and I is the observed intensity. The refinement converged smoothly to the positions given in Table I with the changes in parameters in the last cycle all less than 0.02σ. Thermal parameters, hydrogen atoms positions, and structure factor amplitudes are included in the supplementary material.

Scattering factors for neutral atoms were those of Doyle and Turner[7] for Yb, N, and C with anomalous dispersion corrections[4] applied; hydrogen scattering factors of Stewart, Davidson, and Simpson[8] were used. Discrepancy indices for 298 parameters varied with 3278 data having $F^2 > 3\sigma(F^2)$ are

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.031$$

$$R_w = \sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.037$$

R for all 4985 data is 0.061, and the estimated standard deviation of an observation of unit weight is 1.15. A difference Fourier calculation after the final cycle of least-squares refinement had a maximum electron density of 0.88 e Å^{-3}.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. W-7405-Eng-48. B.S. was on leave from the Chemistry Department, Beloit College, Beloit, WI. We thank Dr. P. L. Watson for providing us with some of her X-ray structural results in advance of publication.

Registry No. $Yb(C_5Me_5)_2(py)_2$, 81276-72-4; $Yb(C_5Me_5)_2(OEt_2)$, 74282-47-6.

Supplementary Material Available: Listings of anisotropic thermal parameters, calculated hydrogen positions, observed and calculated structure factors, and interatomic distances and angles (23 pages). Ordering information is given on any current masthead page.

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Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
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Stereochemistry of Bis(carboxylato)dichlorobis(tertiary phosphine)dimolybdenum Complexes. Crystal and Molecular Structure of Two Isomers of $Mo_2(O_2CCMe_3)_2Cl_2(PEt_3)_2$

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Reactions of $Mo_2Cl_4(PEt_3)_4$ with Me_3CCO_2H or $Mo_2(O_2CCMe_3)_4$ with Me_3SiCl and PEt_3 give $Mo_2(O_2CCMe_3)_2Cl_2(PEt_3)_2$. The product of the former reaction yields a red isomer of C_2 symmetry whereas the latter reaction gives an orange isomer of C_{2h} symmetry. The crystal structures of both isomers have been determined by X-ray techniques. The red A isomer, space group $P2_12_12_1$, has the unit cell dimensions a = 12.542 (4) Å, b = 25.344 (8) Å, c = 10.437 (4) Å, Z = 8, and d_x = 1.40 g/cm^3. The orange B isomer, space group $P\bar{1}$, has the unit cell dimensions a = 8.989 (3) Å, b = 10.640 (4) Å, c = 8.978 (3) Å, α = 91.46 (4)°, β = 81.63 (4)°, γ = 110.10 (4)°, Z = 2, and d_x = 1.45 g/cm^3. The Mo-Mo distances are 2.113 and 2.098 Å for the A and B isomers, respectively.

Introduction

Compounds of the type $Mo_2(O_2CR)_2X_2(PR_3)_2$ provide a potentially rich area for investigating stereochemical phenomena in quadruply bonded, binuclear molecules since a variety of isomers are possible. In this paper we describe the synthesis and crystal structure of two such geometrical isomer of $Mo_2(O_2CCMe_3)_2Cl_2(PEt_3)_2$. The preparation and solution spectroscopy of the whole family of isomers of the type $Mo_2(O_2CCMe_3)_2X_2(PR_3)_2$, where X = Cl, Br, and I and PR_3 = PMe_3, PEt_3, and PMe_2Ph, will be described shortly. This is only the second example, in molecules of this general type, in which two structural isomers have been structurally characterized, the others being the two geometrical isomers of $Re_2Cl_4(O_2CMe)_2(H_2O)_2$.[3]

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