Inorg. Chem. 1982, 21, 2644–2647

Concluding Remarks

From the results presented in this paper it is concluded that both Cu^{I} and Cu^{II} coordination compounds of the ligand BBDHp (Figure 1, $n = 3$) exist. Cu^{II}(BBDHp) compounds, however, are not stable and were not obtained in the solid state. The design of the BBDHp ligand implies that not all four potentially coordinating atoms may bind to one copper ion at the same time. This causes in solution a rapid interconversion of various coordination geometries in which only two or three ligand atoms are involved. Linear coordination by the imidazole nitrogen atoms stabilizes Cu^{I}. Crystals of Cu^{I}(BBDHp) with large counterions, which provide the possibility of hydrogen bridge formation (PF_6^-, BF_4^-), are easily obtained.

Comparison of Cu^{I} and Cu^{II} chelates of the closely related ligand BBDH (Figure 1, $n = 2$) reveals that stabilization of a particular oxidation state of copper is strongly influenced by ligand constraints. Although the distance between the copper ion and the "soft" (Cu^{I} stabilizing) thioether sulfur atoms in $[Cu^{II}(BBDH)Cl]Cl{\cdot}2C_2H_5OH$ is shorter than in $[Cu^{I}(BBDHp)](PF_6)_{0.66}(BF_4)_{0.34}$ nevertheless in the former the Cu^{II}, in the latter the Cu^{I} oxidation state is preferred. This is due to the fact that in the solid Cu^{II}(BBDH) compound the coordinating thioether sulfur atoms and a chloride ion complete trigonal-bipyramidal stereochemistry, whereas in the solid Cu^{I}(BBDHp) compound linear coordination by two imidazole nitrogen atoms occurs and coordination of the thioether sulfur atoms is prevented. In copper-containing electron-transporting enzymes a small change in the coordination geometry of the copper ion, brought about by changes in the tertiary structure of the protein, may cause destabilization of a particular oxidation state. The low molecular weight ligands BBDH and BBDHp resemble this property of biological macromolecules.

Studies on related systems are under investigation.

Acknowledgment. Experimental assistance with the measurements of ESR spectra and magnetic susceptibility by F. B. Hulsbergen and B. J. M. van der Griendt is gratefully acknowledged.

Registry No. BBDHp, 57698-68-7; $[Cu^{I}(BBDHp)](PF_6)_{0.66}(BF_4)_{0.34}$, 81372-13-6; $[Cu^{I}(BBDHp)](BF_4)$, 81372-14-7; $[Cu^{I}(BBDHp)](PF_6)$, 81372-15-8; 3,7-dithianonanedioic acid, 5065-18-9; 1,2-diaminobenzene, 95-54-5; Cu, 7440-50-8.

Supplementary Material Available: Listing of observed and calculated structure factors and a table with additional interbond angles for the PF_6^- anion (7 pages). Ordering information is given on any current masthead page.

Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
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Bis(pentamethylcyclopentadienyl)carboxylato and -dithiocarbamato Derivatives of Neodymium(III) and Ytterbium(III). Crystal Structure of Bis(pentamethylcyclopentadienyl)(diethyldithiocarbamato)ytterbium(III)

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The pentamethylcyclopentadienyl derivatives $(Me_5C_5)_2Yb(O_2CR)$, where R is Me_3C or CF_3, $(Me_5C_5)_2Yb(S_2CNEt_2)$, and $(Me_5C_5)_2Nd(S_2CNEt_2)$ have been prepared by metathetical exchange reactions on the anionic species, $[(Me_5C_5)_2MCl_2]^-$. The crystal structure of $(Me_5C_5)_2Yb(S_2CNEt_2)$ has been determined by single-crystal X-ray diffraction methods. The crystals are monoclinic, $C2/c$, with cell dimensions $a = 12.268$ (4) Å, $b = 15.536$ (6) Å, $c = 14.269$ (5) Å, $\beta = 105.23$ (3)°, and $V = 2624$ Å^3. For $Z = 4$ the calculated density is 1.50 g/cm^3. The structure was refined to a conventional R factor of 0.039 with 2179 data where $F^2 > 3\sigma(F^2)$. The Yb(III) atom is bonded to two sulfur atoms and to two pentamethylcyclopentadienyl groups. The Yb atom lies on a crystallographic twofold axis. The dithiocarbamato ligand is disordered in the structure. The Yb–S distance is 2.70 (1) Å, and the average of five Yb–C distances is 2.63 (3) Å.

Introduction

In attempting to develop the chemistry of reactive organometallic lanthanide systems, we have had an interest in preparing neutral, base-free pentamethylcyclopentadienyl derivatives of the di- and trivalent metals. The strong Lewis acid nature of these metals has led to isolation of trivalent species such as $(C_5Me_5)_2YbCl_2Na(OEt_2)_2$ and $(C_5Me_5)_2YbCl(THF)$,[1,2] as well as the divalent species $Yb(C_5Me_5)_2(THF)$ and $Eu(C_5Me_5)_2(THF)$.[3] The neutral base-free systems are of interest since these coordinatively unsaturated species are expected to exhibit a rich chemistry and, perhaps, to lead to compounds of unusual structural types.

Isolation of $(C_5Me_5)_2YbCl_2Na(OEt_2)_2$ and $(C_5Me_5)_2YbCl(THF)$ suggests that a chelating ligand that can donate four electrons to the metal could yield neutral, base-free trivalent compounds. Such compounds might then be useful for preparation of the base-free ytterbium(II) metallocenes if reduction in a noncoordinating solvent can be effected. Since carboxylate (RCO_2^-) ligands have been effectively utilized as leaving groups in transition-metal chemistry, they seemed to be ideally suited for this task. Another chelating ligand, diethyldithiocarbamate ($Et_2NCS_2^-$), is electronically similar but contains the softer sulfur atoms as donors. Because little is known about the properties of sulfur-based ligands in molecular lanthanide systems, we have conducted a low-temperature magnetic susceptibility study as well as an X-ray crystal structure determination of $(C_5Me_5)_2Yb(S_2CNEt_2)$.

Results and Discussion

Preparation of the carboxylate and dithiocarbamate derivatives of ytterbium is straightforward. The analogous neo-

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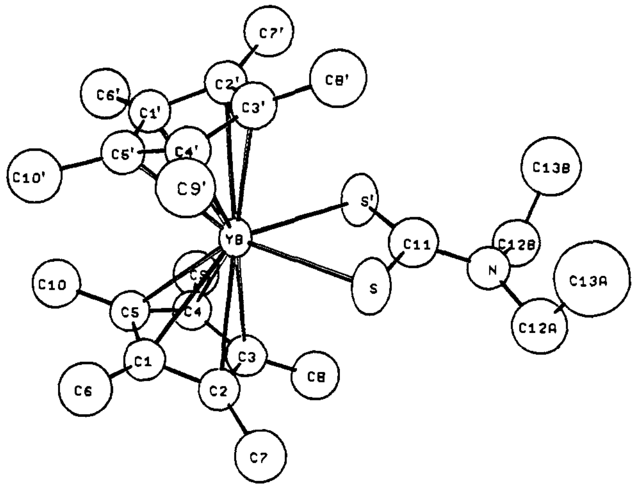


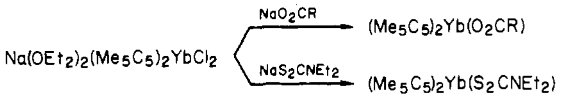
Figure 1. ORTEP drawing of the molecule.

Table I. Positional Parameters[a]

atom	*x*	*y*	*z*
Yb	0	0.20917 (2)	0.250
S	0.0541 (2)	0.3539 (1)	0.3565 (1)
N	0.0376 (8)	0.4957 (6)	0.2433 (9)
C(1)	0.1806 (5)	0.1109 (4)	0.3012 (4)
C(2)	0.2238 (5)	0.1953 (4)	0.2979 (5)
C(3)	0.1918 (6)	0.2255 (4)	0.2007 (5)
C(4)	0.1295 (5)	0.1593 (4)	0.1426 (4)
C(5)	0.1228 (5)	0.0883 (4)	0.2039 (4)
C(6)	0.2073 (6)	0.0528 (6)	0.3897 (6)
C(7)	0.3044 (7)	0.2424 (7)	0.3808 (6)
C(8)	0.2298 (8)	0.3101 (6)	0.1665 (8)
C(9)	0.0840 (8)	0.1608 (6)	0.0334 (5)
C(10)	0.0880 (7)	-0.0017 (5)	0.1665 (7)
C(11)	0	0.4078 (8)	0.250
C(12A)	0.108 (2)	0.544 (1)	0.330 (2)
C(13A)	0.031 (3)	0.580 (2)	0.384 (3)
C(12B)	0.005 (1)	0.541 (1)	0.151 (1)
C(13B)	-0.116 (2)	0.577 (2)	0.125 (2)

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

dymium dithiocarbamate, $(Me_5C_5)_2Nd(S_2CNEt_2)$, was prepared similarly.



The physical properties are described in the Experimental Section. Because two donor atoms are present, $R_2CO_2^-$ and the softer $Et_2NCS_2^-$ allow isolation of ether-free complexes. Unfortunately the ytterbium(III) species could not be reduced with sodium amalgam in refluxing toluene. Further, $(Me_5C_5)_2YbN(SiMe_3)_2$[1] could not be reduced under similar conditions.

The similarity in the magnetic behavior of $(C_5Me_5)_2Yb(O_2CCMe_3)$ and $(C_5Me_5)_2Yb(S_2CNEt_2)$ at low temperature (see Experimental Section) suggests that the magnetic properties of the ytterbium ions in these complexes are not effected by the change from carboxylate to dithiocarbamate ligand. The magnetic moments (5–45 K) 3.29 and 3.39 μ_B respectively are close in value to those observed for other ytterbium(III) complexes over this temperature range.[1,4,5]

Table II. Interatomic Distances (Å)

Yb–2 C(1)	2.63 (1)	C(1)–C(2)	1.42 (1)
Yb–2 C(2)	2.66 (1)	C(2)–C(3)	1.42 (1)
Yb–2 C(3)	2.64 (1)	C(3)–C(4)	1.41 (1)
Yb–2 C(4)	2.60 (1)	C(4)–C(5)	1.42 (1)
Yb–2 C(5)	2.60 (1)	C(5)–C(1)	1.43 (1)
Yb–2 S	2.70 (1)	C(1)–C(6)	1.52 (1)
S–C(11)	1.71 (1)	C(2)–C(7)	1.52 (1)
C(11)–N	1.45 (2)	C(3)–C(8)	1.52 (1)
N–C(12A)	1.50 (2)	C(4)–C(9)	1.51 (1)
N–C(12B)	1.46 (2)	C(5)–C(10)	1.52 (1)
C(12A)–C(13A)	1.49 (4)		
C(12B)–C(13B)	1.53 (3)		

Table III. Selected Angles (Deg)[a]

S–Yb–S'	67.1 (3)	C(5)–C(1)–C(2)	107 (1)
C(1)–Yb–S	105.2 (3)	C(1)–C(2)–C(3)	109 (1)
C(2)–Yb–S	80.7 (2)	C(2)–C(3)–C(4)	108 (1)
C(3)–Yb–S	88.0 (2)	C(3)–C(4)–C(5)	108 (1)
C(4)–Yb–S	118.9 (2)	C(4)–C(5)–C(1)	108 (6)
C(5)–Yb–S	132.2 (2)	C(6)–C(1)–C(2)	125 (1)
C(1)–Yb–S'	134.8 (2)	C(6)–C(1)–C(5)	127 (1)
C(2)–Yb–S'	107.3 (2)	C(7)–C(2)–C(1)	126 (1)
C(3)–Yb–S'	82.8 (2)	C(7)–C(2)–C(3)	124 (1)
C(4)–Yb–S'	90.8 (3)	C(8)–C(3)–C(2)	125 (1)
C(5)–Yb–S'	122.2 (3)	C(8)–C(3)–C(4)	127 (1)
S–C(11)–S'	121.4 (8)	C(9)–C(4)–C(3)	126 (1)
S–C(11)–N	117.6 (6)	C(9)–C(4)–C(5)	125 (1)
S'–C(11)–N	117.2 (6)	C(10)–C(5)–C(1)	126 (1)
C(11)–N–C(12A)	122 (1)	C(10)–C(5)–C(4)	124 (1)
C(11)–N–C(12B)	120 (1)		
N–C(12A)–C(13A)	108 (2)		
N–C(12B)–C(13B)	114 (2)		

[a] Primed atoms are at positions $-x$, y, $^1/_2 - z$.

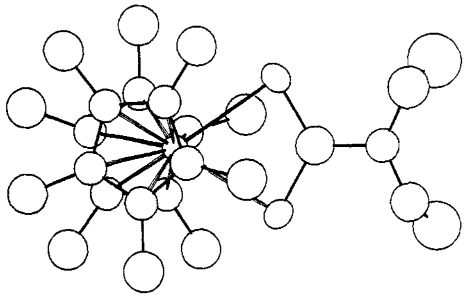


Figure 2. ORTEP view of the molecule parallel to a line through the ring centers.

The ytterbium dithiocarbamate complex crystallizes as well-formed, purple prisms that are monoclinic, space group *C*2/*c*, with cell dimensions $a = 12.268$ (4) Å, $b = 15.536$ (6) Å, $c = 14.269$ (5) Å, and $\beta = 105.23$ (3)°. For $Z = 4$ and a molecular weight of 591.84, the calculated density is 1.50 g/cm^3. A few structures containing lanthanide to sulfur bonds have been determined,[6-8] but the present structure is the first example of an Yb–S bond.

Positional parameters, with labeling as shown in Figure 1, are given in Table I. A list of selected distances and angles are given in Tables II and III.

The molecule consists of the Yb atom bonded to two pentamethylcyclopentadienyl rings and to two sulfur atoms of the diethyldithiocarbamate ligand (Figure 1). The average of five Yb–C distances is 2.63 ± 0.03 Å, and the Yb–S distance is 2.70 Å. The pentamethylcyclopentadienyl rings are in a staggered configuration with respect to each other (see Figure 2). The diethyldithiocarbamate ligand is disordered; atoms N, C(12A), C(13A), C(12B), and C(13B) are in general

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positions with half of the molecules in the given conformation (Figure 1) and half in the conformation that would result from a 180° rotation about the twofold axis. The sulfur atoms are most probably disordered as well, as seen by their elliptical shape in Figure 1, but the separation of the two positions was too small to be treated in the least squares as separate half-atoms and instead was refined as a large thermally anisotropic atom. The molecule as a whole has C_1 symmetry; however, the $(Me_5C_5)_2Yb$ portion of the molecule has perfect C_2 symmetry. Attempts to refine the structure in a lower symmetry space group were unsuccessful.

The Yb-C distances (to the C_5 ring) average 2.63 ± 0.03 Å. The Yb atom is 2.33 Å from the mean plane of atoms C(1)-C(5). These ring atoms are all within 0.006 Å of this plane. The five methyl carbon atoms of the pentamethylcyclopentadienyl group are all bent out of the mean plane away from the Yb atom; the distances from the plane are 0.18, 0.19, 0.12, 0.07, and 0.34 Å for atoms C(6)-C(10), respectively.

The ytterbium-carbon bond length of 2.63 ± 0.03 Å in the trivalent, dithiocarbamate complex is equal within experimental error to that found for this bond length (2.66 ± 0.01 Å) in the divalent species, $(Me_5C_5)_2Yb(THF)$.[3] The change of oxidation number from 3 to 2 tends to increase the distance, while reduction of coordination number from 8 to 7 tends to decrease it. In these two molecules the trends cancel and the bond lengths are equal.[9]

Experimental Section

All operations were carried out under nitrogen. Microanalyses were performed by the microanalytical laboratory of this department. Infrared spectra were recorded on a Perkin-Elmer instrument as Nujol mulls between cesium iodide windows. The ^1H NMR spectra were recorded on a JEOL FX90Q instrument on toluene-d_8 solutions and are reported in δ units (positive values to high field of Me_4Si). Solid-state magnetic susceptibilities were obtained as previously described.[10]

Bis(pentamethylcyclopentadienyl)(2,2-dimethylpropionato)ytterbium(III). Sodium bis(pentamethylcyclopentadienyl)dichloroytterbate-bis(diethyl ether)[5] (1.7 g, 0.0025 mol) in diethyl ether (30 mL) was added to a suspension of sodium 2,2-dimethylpropionate (prepared by stirring sodium hydride with pivalic acid in diethyl ether for 12 h) (0.31 g, 0.0025 mol) in diethyl ether (20 mL). After 6 h of stirring, the red solution was evaporated to dryness and the residue was extracted with pentane (35 mL). The extract was filtered and cooled (−70 °C). The red prisms (0.65 g, 48%) were collected and dried under reduced pressure; mp 154–155 °C. Anal. Calcd for $C_{25}H_{39}O_2Yb$: C, 55.1; H, 7.22. Found: C, 55.2; H, 7.19. The mass spectrum gave a monomeric molecular ion (545) as well as peaks due to higher oligomers at 924, 889, 820, 802, 749, 612, and 571. ^1H NMR (+35 °C): δ 10.95 ($\nu_{1/2}$ = 107 Hz, 30 H), −26.45 ($\nu_{1/2}$ = 21 Hz, 9 H). IR: 2713 w, 1503 m, 1489 m, 1430 m, 1225 s, 1169 w, 1064 w, 1026 m, 940 w, 896 s, 810 m, 793 m, 617 m, 474 w, 408 m, 388 m, 319 s cm^{-1}. The magnetic susceptibility followed Curie behavior from 5 to 35 K, with μ_{eff} = 3.29 μ_B.

Bis(pentamethylcyclopentadienyl)(trifluoroacetato)ytterbium(III). The salt $Na(OEt_2)_2(Me_5C_5)_2YbCl_2$ (1.1 g, 0.0016 mol) in tetrahydrofuran (30 mL) was added to NaO_2CCF_3 (0.22 g, 0.0016 mol) in tetrahydrofuran (10 mL), and the red solution was stirred for 12 h. The tetrahydrofuran was removed under reduced pressure, and the residue was extracted with diethyl ether (2 × 40 mL). The extract was filtered, and cooling (−10 °C) yielded violet prisms in 57% (0.50 g) yield; mp 262–263 °C. Anal. Calcd for $C_{22}H_{30}F_3O_2Yb$: C, 47.5; H, 5.43. Found: C, 47.7; H, 5.49. The mass spectrum afforded a monomeric molecular ion at 557. IR: 3140 w, 3092 w, 2726 w, 1680 s, 1204 s, 1158 s, 1023 w, 847 m, 785 m, 718 m, 614 w, 592 w, 523 w, 468 w, 385 m, 312 s cm^{-1}.

Bis(pentamethylcyclopentadienyl)(diethyldithiocarbamato)ytterbium(III). The anionic complex $Na(OEt_2)_2(Me_5C_5)_2YbCl_2$ (1.4 g, 0.0020 mol) in diethyl ether (40 mL) was added to sodium diethyldithiocarbamate (0.35 g, 0.0020 mol) in diethyl ether (20 mL). After 8 h of stirring, the diethyl ether was removed under reduced pressure. The residue was extracted with pentane (40 mL) and filtered. Concentration of the filtrate to ca. 10 mL and cooling (−10 °C) yielded purple prisms in 81% (0.97 g) yield; mp 226–227 °C. Anal. Calcd for $C_{25}H_{40}NS_2YB$: C, 50.7; H, 6.81; N, 2.37; S, 10.8. Found: C, 50.7; H, 6.76; N, 2.29; S, 10.7. The mass spectrum gave a monomeric molecular ion at 592. ^1H NMR (+35 °C): δ 7.45 ($\nu_{1/2}$ = 61 Hz, 30 H), −5.76 ($\nu_{1/2}$ = 18 Hz, 4 H), −9.00 ($\nu_{1/2}$ = 13 Hz, 6 H). All of the resonances were singlets. IR: 2723 w, 1487 s, 1424 s, 1360 m, 1306 w, 1277 s, 1209 m, 1241 m, 1089 m, 1023 w, 987 m, 911 m, 841 m, 800 w, 779 w, 608 w, 593 w, 564 m, 473 w, 392 m, 360 m, 311 s cm^{-1}. The magnetic susceptibility followed Curie behavior (5–55 K), giving μ_{eff} = 3.39 μ_B.

Bis(pentamethylcyclopentadienyl)(diethyldithiocarbamato)neodymium(III). The anionic complex $Li(OEt_2)_2(Me_5C_5)_2NdCl_2$ (2.2 g, 0.034 mol) in diethyl ether (40 mL) was added to NaS_2CNEt_2 (0.58 g, 0.0034 mol) in diethyl ether (20 mL). After 8 h of stirring, the green solution was filtered and the filtrate was concentrated to ca. 30 mL. Cooling (−10 °C) yielded green prisms in 72% (1.4 g) yield; mp 229–231 °C. Anal. Calcd for $C_{25}H_{40}NNdS_2$: C, 53.3; H, 7.16; N, 2.49. Found: C, 53.5; H, 7.03; N, 2.47. The mass spectrum gave a monomeric molecular ion at 562. ^1H NMR (+70 °C): δ 7.00 ($\nu_{1/2}$ = 23 Hz, 30 H), −0.10 ($\nu_{1/2}$ = 17 Hz, 4 H), −0.94 ($\nu_{1/2}$ = 16 Hz, 6 H). The resonances were singlets. IR: 2722 w, 1482 s, 1420 s, 1357 m, 1402 w, 1273 s, 1203 s, 1138 m, 1087 m, 1063 w, 1021 w, 979 m, 905 m, 836 m, 798 w, 773 w, 607 w, 560 m, 470 w, 430 w, 382 m, 348 m, 310 s cm^{-1}. The magnetic susceptibility followed Curie behavior (5–50 K), giving μ_{eff} = 2.75 μ_B.

Some of the air-sensitive purple crystals were inserted into thin-walled quartz capillaries in an argon-filled drybox. A crystal 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). ω scans of several low-angle reflections showed peaks with half-widths of 0.13–0.20°. The space group is $C2/c$. The setting angles of 12 manually centered reflections ($4 < 2\theta < 49°$) were used to determine cell parameters by least squares.

Intensity data were collected with a θ–2θ scan technique with a scan speed of 2°/min on 2θ. Each peak was scanned 0.9° before the $K\alpha_1$ peak to 0.9° after the $K\alpha_2$ peak, and backgrounds were counted for 10 s at each end of the scan range. The temperature during the data collection was 24 ± 1 °C. Three standard reflections were measured every 250th scan. A total of 4748 scans ($4° < 2\theta < 45°$) yielded 2327 unique data of which 2175 had $F^2 > 3\sigma$. Absorption correction (μ = 37.0 cm^{-1}) was applied[11] which ranged from 1.53 to 1.98. The intensities of the three standard reflections decayed about 4% during the data collection period, and the data were corrected for this effect.

A three-dimensional Patterson calculation showed the Yb and S atom positions, and a subsequent least-squares refinement and Fourier calculation revealed all the nonhydrogen atoms in the structure. After a few cycles of least-squares refinements of the structure in which only the Yb and S atoms were assigned anisotropic thermal parameters, the R factor, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, was 0.055.

The ethyl carbon atoms of the diethyldithiocarbamate ligand were ill-behaved in the refinements as indicated by large thermal parameters and chemically unsatisfactory bond distances to adjacent atoms. A difference Fourier map showed additional electron density in the region of the ethyl carbon atoms as well as the nitrogen atom, indicating disorder. The two ethyl carbon atoms were subsequently described as four half-atoms, and the nitrogen atom was allowed to wander from the special position on the twofold axis. With further refinements the structural parameters converged to their final and satisfactory results. Several attempts were made to refine the structure in the noncentric space group Cc, but the resulting structure would not converge to a reasonable chemical model, and the resulting R factors, despite the increased number of parameters, were not significantly different from the centric refinements. The least-squares function used minimizes the function $\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$. The expressions used in processing the data and estimating weights are given in the supplementary material; the "ignorance factor" was set to 0.05. Scattering factors from ref 12 and anomalous dispersion corrections[13]

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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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Bis(pentamethylcyclopentadienyl)bis(pyridine)ytterbium(II)

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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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