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Mononuclear η^8-cyclooctatetraenyl(thiolato)samarium(III) complexes (η^8-C_8H_8)Sm(SR)(hmpa)$_2$ (R = 2,4,6-triisopropylphenyl and 2-pyridyl; HMPA = hexamethylphosphoric triamide) derived from metallic samarium, diaryl disulfide, and 1,3,5,7-cyclooctatetraene in the presence of HMPA

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Abstract

Treatment of metallic samarium with cyclooctatetracne in the presence of an equimolar amount of diaryl disulfide afforded mononuclear cyclooctatetraenyl(thiolato)samarium(III) complexes of the formula (η^8-C_8H_8)Sm(SR)L_x (**3a**: R = 2-pyridyl, L = THF, $x = 0.5$; **3b**: R = 2-pyridyl, L = HMPA, $x = 2$; **3c**: R = 2,4,6-triisopropylphenyl, L = HMPA, $x = 2$; HMPA = hexamethylphosphoric triamide) in modest yields. These complexes have been characterized by ^{1}H-NMR spectroscopy and elemental analysis together with X-ray analysis for **3b** and **3c**. The complex **3b** has a pseudo square pyramidal and four-legged piano-stool geometry coordinated by a planar η^8-C_8H_8 ring, a chelating pyridine-2-thiolato ligand, and two HMPA ligands, while the complex **3c** has three-legged piano-stool geometry comprised of a planar η^8-C_8H_8 ring, a thiolato ligand, and two HMPA ligands. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cydooctatetraene; Samarium; Disulfide; Arene thiolato; Pyridine-2-thiolato

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1. Introduction

In view of future importance of organolanthanoid complexes, more convenient synthetic methods should be exploited because the most known methods based on the metathesis of halide ligands with alkyl or aryl anions give by-products such as metal salts which strongly interact with lanthanoid cations to disturb the isolation and purification of the organometallic product [1]. Several rational approaches to avoid this difficulty have already been reported; (1) oxidation reactions of low valent organolanthanoid complexes of samarium, europium, and ytterbium to give Ln(III) complexes [2–7], (2) the reaction of alkyl or amido lanthanoid complexes with protic organic molecules [8–11] and (3) metal vapor synthesis [12]. Some chalcogenolate complexes have been reported to be derived from amalgam of lanthanoids and diaryl disulfide [13–19]. We have been concerned with the synthesis of lanthanoid compounds direct from metallic lanthanoids with some relevant oxidants as an ideal method and already demonstrated this method to be providing various new lanthanoid complexes [20–26]; reaction of metallic lanthanoid with 1,3,5,7-cyclooctatetraene and diaryl disulfide in THF is described to give dinuclear chalcogenolate-bridged complexes such as [(η^8-C_8H_8)Sm(μ-SePh)(thf)$_2$]$_2$ (**1a**), [(η^8-C_8H_8)Sm(μ-$SC_6H_2Me_3$-2,4,6)(thf)$_2$]$_2$ (**1b**), [(η^8-C_8H_8)Sm

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(μ-SC$_6$H$^i_2$Pr$_3$-2,4,6)(thf)]$_2$ (**1c**), and [(η_8-C$_8$H$_8$)Sm(μ-SePh)(thf)$_2$]$_2$ (**2**) [22]. Whereas, by using a donating HMPA as an auxiliary ligand, mononuclear monocyclooctatetraenyl(arylthiolato)samarium(III) complexes were prepared by reaction of samarium metal, diaryl disulfide, and 1,3,5,7-cyclooctatetracne. Herein details of this convenient one-pot synthesis are the subject of this report.

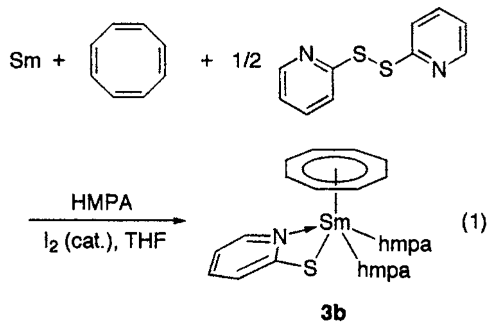
2. Results and discussion

2.1. Synthesis of mono-η^8-cyclooctatetraenyl(thiolato) complexes of samarium(III)

In the following reactions, organic disulfides and 1,3,5,7-cyclooctatetracne act as oxidizing reagents of metallic samarium to form thiolate and the dianion of 10-π annulene. A catalytic amount of iodine was used for activation of the surface of samarium metal. Thus, the one-pot reaction of metallic samarium, 1,3,5,7-cyclooctatetraene, and the disulfide afforded monocyclooctatetraenyl(thiolato) complexes of samarium(III) of the formula (η^8-C$_8$H$_8$)Sm(SR)L$_x$ (**3a**: R = 2-pyridyl, L = THF, $x = 0.5$; **3b**: R = 2-pyridyl, L = HMPA, $x = 2$; **3c**: R = 2,4,6-triisopropylphenyl, L = HMPA, $x = 2$; HMPA = hexamethylphosphoric triamide).

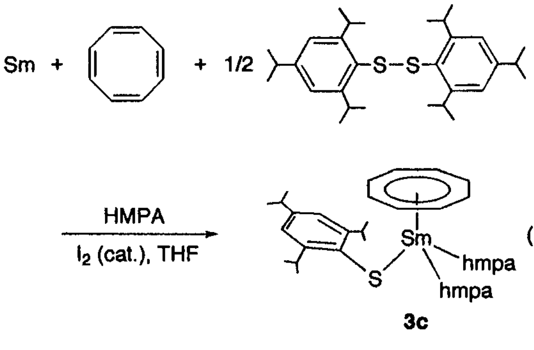
Treatment of finely divided samarium metals with an equimolar amount of 1,3,5,7-cyclooctatetraene and a half mole of 2,2′-dipyridyl disulfide in the presence of a catalytic amount of iodine in THF resulted in the gradual consumption of the metals and led to the formation of complex **3a**, which was highly air- and moisture-sensitive. The ^{1}H-NMR spectrum of **3a** in THF-d$_8$ displayed a singlet at δ 12.00 due to η^8-C$_8$H$_8$ ligand and one set of broad signals at δ 14.94, 7.82, 7.42, and 5.32 assignable to the SPy moiety, the amount of THF coordinated to the samarium center and its nuclearity could not determined on the basis of elemental analysis. The instability of **3a** toward moisture and oxygen accordingly hampered the further characterization of the structure of **3a**. We have already reported that a THF molecule bound to samarium(III) ion was labile and easily released during the isolation, and thereby the number of the coordinated THF molecules in a monocyclooctatetraenyl–iodosamarium complex such as (η^8-C$_8$H$_8$)SmI(thf) was found to be less than the corresponding lanthanum and cerium complexes such as (η^8-C$_8$H$_8$)CeI(thf)$_3$ [20,22].

When the same reaction was performed in the presence of HMPA, we can obtain in 33% yield a HMPA-adduct (η^8-C$_8$H$_8$)sm(SC$_5$H$_4$N)(hmpa)$_2$ (**3b**) (Eq. (1)). The ^{1}H-NMR spectrum of **3b** in THF-d$_8$ exhibited signals due to a fragment of (η^8-C$_8$H$_8$)Sm(SC$_5$H$_4$N) at almost the same chemical shifts and some additional signals at δ 2.76 due to two HMPA ligands. Well known stability in coordination of HMPA to lanthanoid cation [27,28] leads to X-ray quality single crystals and the structure of **3b** was determined by X-ray analysis (vice infra).



(1)

We have already reported the synthesis and crystal structure of dinuclear chalcogenolatebridged complexes such as **1a**–**c** and **2** [21,22]. The THF ligand can readily be replaced by HMPA ligand, and thus treatment of samarium metal, 1,3,5,7-cyclooctatetraene, HMPA and bis(2,4,6-triisopropylphenyl) disulfide in THF (20 ml) at 50°C for 24 h gave rise to a dark red solution, from which we obtained (η^8-C$_8$H$_8$)Sm(SC$_6$H$^i_2$Pr$_3$-2,4,6)(hmpa)$_2$ (**3c**) as dark red crystals in 68% yield (Eq. (2)). The structure of **3c** was determined by NMR spectroscopy and X-ray analysis. The ^{1}H-NMR spectrum in THF-d$_8$ at 30°C showed a singlet at δ 10.3 due to η^8-C$_8$H$_8$ together with a set of one 2,4,6-triisopropylphenylthiolato ligand and two HMPA ligands.



(2)

2.2. Crystal structures of 3b and 3c

X-ray quality crystals of **3b** and **3c** were obtained from the THF solution and utilized for structure analysis. ORTEP drawings of **3b** and **3c** are shown in Figs. 1 and 2, respectively. Selected bond distances and angles of these two complexes are given in Table 1; the somewhat high (7.3%) value for *R* of **3b** is a result of the poor quality of the crystal of **3b**, and thus the larger standard deviations for **3b** prevented the precise discussion about bond lengths and angles within a molecule of **3b**. In both of the two complexes, the η^8-C$_8$H$_8$ ligand is planar, suggesting that this has an aromaticity of a 10-π annulene system. Noteworthy is that these two

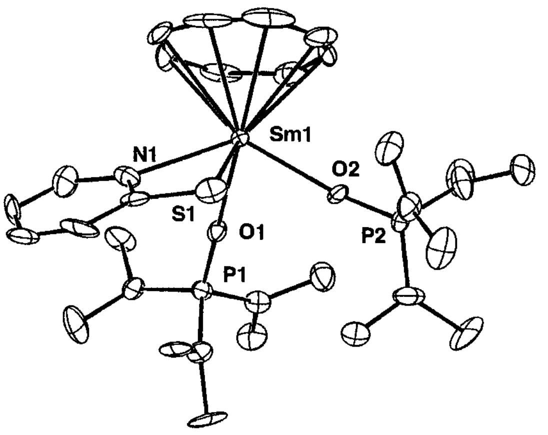


Fig. 1. ORTEP drawing of **3b** with the numbering scheme. Hydrogen atoms are omitted for clarity.

complexes are mononuclear in sharp contrast to the dinuclear structure of **1** and **2** where the chalcogenolate ligands bridge two samarium(III) ions. HMPA is a strong donating ligand for lanthanoid metals and thus mononuclear complexes formed predominantly. As a typical example, addition of HMPA to polymeric insoluble [Sm(SPh)$_3$(THF)$_x$]$_n$ led to the formation of a mononuclear complex Sm(SPh)$_3$(hmpa)$_3$ [24]. Complexes **3b** and **3c** have piano-stool geometry capped by one planar η^8-C$_8$H$_8$ ring; **3b** has four-legs of a N–S chelation of the pyridine-2-thiolato ligand, and two HMPA ligands, while **3c** has three-legs comprised of a thiolato ligand and two HMPA ligands.

The Sm–S bond distance (2.817(3) Å) of **3c** is comparable to that found for mononuclear thiolato complexes of samarium(III), Sm(SC$_6$H$_2^i$Pr$_3$-2,4,6)$_3$(py)$_2$(thf) [av. 2.740(3) Å] [23,24], [Li(tmeda)]$_3$[Sm(SBu^t)$_6$] [av. 2.827(3) Å] [29], Sm(SC$_6$H$_2$Bu$_3^t$-2,4,6)$_3$ [av. 2.644(8) Å] [8], and Sm(SPh)$_3$(hmpa)$_3$ [2.811(2)–2.837(2) Å, av. 2.821(2) Å] [24], but is shorter than those [2.894(2) and 2.846(3) Å, av. 2.870(3) Å] found for [Sm(SPy)$_2$(hmpa)$_3$]I [26]. The bond angle Sm–S–C of **3c** was 104.0(4)°, a value which is also comparable with that found for mononuclear thiolato complexes of samarium(III) [8,23,24,29]. On the other hand, the complex **3b** has a pyridine-2-thiolato ligand acting as a four-membered chelating auxiliary; the Sm–S bond distance of 2.932(7) Å in **3b** is longer than that of **3c** and the bond angle Sm–S–C of **3b** is acute [83.1(9)°]. The Sm–N bond distance [2.57(2) Å] is comparable to those found for Sm(SC$_6$H$_2^i$Pr$_3$-2,4,6)$_3$(py)$_2$(thf) [2.533(7) and 2.543(9) Å] [23] and [Sm(SPy)$_2$(hmpa)$_3$]I [2.542(7) and 2.566(7) Å] [26]. The four membered S–N chelation to lanthanoid metals has already been observed for [Ln(SPy)$_2$(hmpa)$_3$]I [26] and [PEt$_4$][Eu(SPy)$_4$] [17].

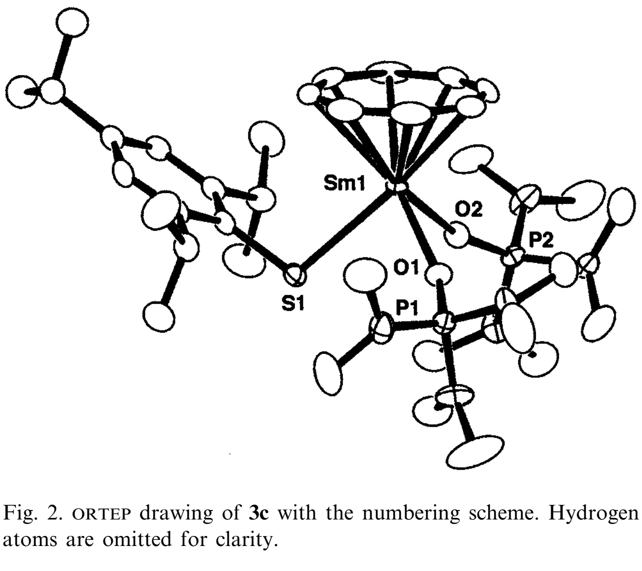


Fig. 2. ORTEP drawing of **3c** with the numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) of **3b** and **3c**

Complex	**3b**	**3c**
Bond distances (Å)		
Sm(1)–S(1)	2.932(7)	2.817(3)
Sm(1)–N(1)	2.58(2)	—
Sm(1)–O(1)	2.34(1)	2.327(8)
Sm(1)–O(2)	2.36(1)	2.355(8)
P(1)–O(1)	1.49(1)	1.505(9)
P(2)–O(2)	1.48(1)	1.487(8)
Bond angles (°)		
S(1)–Sm(1)–O(1)	97.2(4)	84.4(2)
S(1)–Sm(1)–O(2)	81.2(4)	86.2(2)
S(1)–Sm(1)–N(1)	54.5(5)	—
O(1)–Sm(1)–O(2)	80.8(5)	84.5(3)
O(1)–Sm(1)–N(1)	73.9(6)	—
Sm(1)–S(1)–C(1)	83.1(9)	104.0(4)
Sm(1)–O(1)–P(1)	179.6(9)	157.5(5)
Sm(1)–O(2)–P(2)	167.7(10)	162.2(5)

Both of the complexes **3b** and **3c** have HMPA ligands coordinated to the samarium metal in *cis*-fashion, thus bond angles O–Sm–O being 80.8(5)° for **3b** and 84.5(3)° for **3c**. The Sm–O distances [2.34(1) and 2.36(1) Å] in **3b** and [2.327(8) and 2.355(8) Å] in **3c** are comparable to those of Sm(SPh)$_3$(hmpa)$_3$ [av. 2.299(4) Å] [24] and [Sm(SPy)$_2$(hmpa)$_3$]I [av. 2.305(5) Å] [26]. These distances are much shorter than those of other O-donor ligands such as THF. Such short Sm–O distances along with larger Sm–O–P angles [179.6(9) and 167.7(10)° for **3b** and 157.5(5) and 162.2(5)° for **3c**] indicate the strong dπ–pπ interaction between the samarium atom and the oxygen atoms of HMPA. Thus, the pπ-donation from the oxygen atom of HMPA compensates the electron-deficiency of the samarium(III) center.

3. Conclusion

We have herein demonstrated that the direct reaction of metallic samarium with neutral 1,3,5,7-cyclooctatetraene and diaryl disulfide such as 2,2′-dipyridyl disulfide and bis(2,4,6-triisopropylphenyl) disulfide in the presence of HMPA affords monocyclooctatetraenyl(thiolato)samarium(III) complexes, (η^8-C_8H_8)Sm(SC_5H_4N)(hmpa)$_2$ (**3b**) and (η^8-C_8H_8)Sm ($SC_6H_2^iPr_3$-2,4,6)(hmpa)$_2$ (**3c**), both of which are characterized crystallographically. Thus, the addition of HMPA can control the nuclearity of the resulting complex, leading to the mononuclear complexes.

4. Experimental section

4.1. General

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the use of the standard Schlenk technique under argon atmosphere. Hexane and ether were dried over sodium benzophenone ketyl and then distilled before use. THF was dried over Na/K alloy and distilled before use. Samarium metal was purchased from Aldrich. 2,2′-dipyridyl disulfide was purchased from Tokyo Kasei and used as received. Bis(2,4,6-triisopropylphenyl) disulfide was obtained from oxidation of 2,4,6-triisopropylbenzenethiol by iodine. 1,3,5,7-cyclooctatetraene (Strem) was used as received. HMPA (Nacalai Tesque) was distilled from CaH_2 under argon atmosphere and dried over molecular sieves.

^{1}H-NMR spectra were measured on a JEOL EX-270 or a JEOL GSX-400 spectrometer. Elemental analyses were performed at the Elemental Analysis Center of Osaka University. All melting points were measured in sealed tubes and were not corrected.

*4.2. Synthesis of (η^8-C_8H_8)Sm(SC_5H_4N)(thf)$_x$ (**3a**)*

The finely divided samarium metal (364 mg, 2.42 mmol) and 2,2′-dipyridyl disulfide (267 mg, 1.21 mmol) in THF (40 ml) was charged in a Schlenk tube and then 1,3,5,7-cyclooctatetraene (0.28 ml, 2.49 mmol) and a catalytic amount of iodine were added successively. After the reaction mixture was stirred at 50°C for 24 h, a dark reddish purple solution was obtained. Removal of insoluble impurities and cooling to -20°C gave reddish purple crystals of **3a** (146 mg, 16% yield), m.p. > 300°C. ^{1}H-NMR (270 MHz, THF-d_8, 30°C) δ 12.00 (s, 8H, C_8H_8), 14.94, 7.82, 7.42, and 5.32 (br, each of 1H, SPy). Anal. Calcd. for $C_{13}H_{12}NSSm \cdot (C_4H_8O)_{0.5}$: C, 44.96; H, 4.02; N, 3.50. Found: C, 44.74; H, 4.56; N, 3.17.

*4.3. Synthesis of (η^8-C_8H_8)Sm(SC_5H_4N)(hmpa)$_2$ (**3b**).*

To the reaction mixture of samarium metal (267 mg, 1.78 mmol), 1,3,5,7-cyclooctatetraene (0.20 ml, 1.78 mmol), HMPA (0.93 ml, 5.34 mmol) and 2,2′-dipyridyl disulfide (196 mg, 0.890 mmol) in THF (15 ml) was added a catalytic amount of iodine. After the reaction mixture was stirred at 50°C for 24 h, a dark red solution was obtained. Insoluble impurities were removed and then the resulting solution was concentrated. Addition of hexane and cooling to -20°C gave **3b** as red powder (525 mg, 33% yield), mp 185–188.5°C. ^{1}H-NMR (270 MHz, THF-d_8, 30°C) δ 10.87 (s, 8H, C_8H_8), 14.71, 7.66, 7.24, 5.46 (br, each of 1H, SPy), 2.76 (br, 36H, HMPA). Anal. Calcd. for $C_{25}H_{48}O_2N_6P_2SSm$: C, 41.53; H,6.69; N,13.56. Found: C, 42.71; H, 7.27; N, 14.95.

*4.4. Synthesis of (η^8-C_8H_8)Sm($SC_6H_2tPr_3$-2,4,6) (hmpa)$_2$ (**3c**)*

To a mixture of samarium metal (145 mg, 0.967 mmol), 1,3,5,7-cyclooctatetracne (0.11 ml, 0.967 mmol), HMPA (0.34 ml, 1.95 mmol) and bis(2,4,6-triisopropylphenyl) disulfide (228 mg, 0.485 mmol) in THF (20 ml) was added a catalytic amount of iodine. The reaction mixture was stirred at 50°C for 24 h to afford a dark red solution. Removal of insoluble impurities followed by concentration, addition of hexane, and cooling to $-$ 20°C gave red powder of **3c** (286 mg, 35% yield). Further cooling the mother liquid afforded dark red crystals of **3c** (270 mg, 33% yield). The total yield was 68%, mp 180°C (dec.). ^{1}H-NMR (270 MHz, THF-d_8, 30°C) δ 10.3 (s, 8H, C_8H_8), 7.92 (s, 2H, *m*-H), 7.80 (m, 2H, *o*-$CHMe_2$), 3.34 (m, 1H, *p*-$CHMe_2$), 2.64 (br, 36H, HMPA), 2.35 (d, 6H, *p*-$CHMe_2$), 1.03 (d, 12H, *o*-$CHMe_2$). Anal. Calcd. for $C_{35}H_{67}O_2N_6P_2SSm$: C, 49.55; H, 7.96; N, 9.91. Found: C, 48.86; H, 8.09; N, 9.78.

*4.5. Crystallographic data collections and structure determination of **3b** and **3c***

The crystals of **3b** and **3c** suitable for X-ray diffraction sealed in glass capillaries under argon atmosphere were mounted on a Rigaku AFC-7R four-circle diffractometer for data collection using Mo–K_α radiation. Relevant crystal and data statistics are summarized in Table 2. The unit cell parameters at 23°C were determined by a least-squares fit to 20 values of 25 strong higher reflections for these two complexes. Three standard reflections were chosen and monitored every 150 reflections. Measured non-equivalent reflections with $I > 3.0\sigma(I)$ were used for the structure determination. For each complexes, an empirical absorption correction was carried out on the basis of azimuthal scans. Complex **3b** showed significant intensity decay (max $-$ 22.8%) during the data collection, and hence a linear correction factor was applied to the data to account for this decay. Whereas complex **3c** showed no decay. The data for all complexes were corrected for Lorentz and polarization effects.

Based on the systematic absence of **3b**, ($0kl$ with $k =$ odd, ($h0l$) with $l =$ odd, and ($hk0$) with $h =$ odd, the

Table 2
Crystal data and data collection parameters of **3b** and **3c**

Complex	**3b**	**3c**
Formula	$C_{25}H_{48}N_7O_2P_2SSm$	$C_{35}H_{67}N_6O_2P_2SSm$
Formula weight	723.11	848.36
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/a$
a (Å)	21.536(6)	18.491(6)
b (Å)	18.90(1)	20.116(6)
c (Å)	16.562(8)	11.735(3)
β (°)	—	93.64(2)
Z	8	4
V (Å^3)	6741(8)	4356(2)
D_{calcd} (g cm^{-3})	1.425	1.293
F(000)	2968	1772
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$
Crystal size (mm)	$0.2 \times 0.2 \times 0.3$	$0.3 \times 0.3 \times 0.3$
Abs. coeff (cm^{-1})	19.35	15.07
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$
Temp (°C)	23	23
Scan speed, (° min^{-1})	16	16
Scan width, (°)	$1.63 + 0.35 \tan\theta$	$1.89 + 0.35 \tan\theta$
$2\theta_{max}$ (°)	55.0	60.0
Unique data	6877	10 526 ($R_{int} = 0.057$)
Unique data ($I > 3\sigma(I)$)	2583	5537
No. of variables	343	424
R	0.073	0.057
R_w	0.085	0.080
GOF	2.53	2.85
Δ, eÅ^{-3}	1.24, −1.50	1.06, −0.97

space group of **3b** was determined to be *Pbca*. The systematic absence of ($h0l$) with $h =$ odd and ($0k0$) with $k =$ odd in the data collected for the complex **3c** indicated the space group to be $P2_1/a$. The crystal structures of **3b** and **3c** were solved by a direct method (SAPI91 [30]) and refined by the full-matrix least squares method. Measured nonequivalent reflections with $I > 3.0\sigma(I)$ were used for the structure determination. In the subsequent refinement the function $\Sigma\omega(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors amplitudes, respectively. The agreement indices are defined as $R = \Sigma\||F_o| - |F_c|\|/\Sigma|F_o|$ and $R_w = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega(|F_o|)^2]^{1/2}$ where $\omega^{-1} = \sigma^2(F_o) = \sigma^2(F_o^2)/(4F_o^2)$. The positions of all non-hydrogen atoms for all complexes were found from a difference Fourier electron density map and refined anisotropically. In the final refinement cycle (full-matrix), hydrogen atom coordinates were included at idealized positions, and the hydrogen atoms were given the same temperature factor as that of the carbon atom to which they were coordinated. All calculations were performed by using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP.

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