Syntheses and Crystal Structures of Cuprate Complexes of Europium and Ytterbium, {[(PhC≡C)₃Cu][Eu(Py)(THF)₂]}₂ and {[(PhC≡C)₃Cu][Yb(THF)₂]}₂

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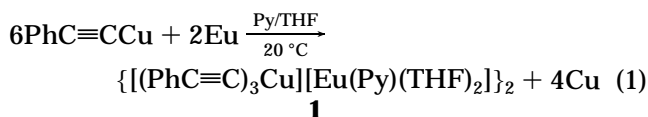Alexander I. Yanovsky,[§] and Yuri T. Struchkov[§,‖]

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Summary: The (Phenylethynyl)cuprate europium complex {[(PhC≡C)₃Cu][Eu(Py)(THF)₂]}₂ (**1**) *was synthesized by reaction of Eu with PhC≡CCu in pyridine. The cuprate ytterbium complex* {[(PhC≡C)₃Cu][Yb(THF)₂]}₂ (**2**) *was synthesized by reaction of Yb with PhC≡CCu in THF in the presence of a catalytic amount of ytterbium diiodide and also by the reaction of (PhC≡C)₂Yb with PhC≡CCu.*
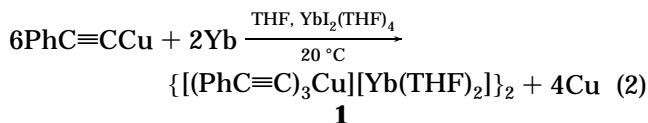
Organocuprates of alkali metals are well-known[1] and widely used in organic synthesis.[2] Among other electropositive metals, similar cuprate complexes have been synthesized only for Mg[3] and Ba.[4] Here we report the synthesis and the molecular structures of (phenylethynyl)cuprate complexes of europium (**1**) and ytterbium (**2**). For the preparation of the title compounds we used the redox transmetalation reactions which are known to be a convenient synthetic pathway to organolanthanoids.[5] Such types of processes depend essentially on the solvent used and the reaction conditions. We recently observed that lanthanoid metals exhibit an increased reactivity in THF toward some organometallic compounds in the presence of lanthanoid halides as catalysts. The catalytic reactions of metallic lanthanoids with Ph₃EEPh₃ (E = Si, Ge, Sn), the dimer of the triphenylmethyl radical, Ph₂Hg, and Ph₃Bi allowed us to obtain and X-ray structurally characterize various types of organolanthanoids: (Ph₃E)₂Yb(THF)₄,[6−8] [Yb(THF)₆]²⁺[Ph₃C]₂⁻,[9] Ph₃Ln(THF)₃ (Ln = Er, Tm).[10] Therefore, we used the catalytic effect of a lanthanoid salt for preparation of complex 2.

While studying the reactions of metallic lanthanoids with organocopper compounds in different solvents, we found that Sm, Eu, and Yb react readily with PhC≡CCu[11] in pyridine at room temperature and form (phenylethynyl)cuprate complexes. In case of europium, the product was isolated as a microcrystalline solid[12] and identified by X-ray diffraction study as complex **1** (eq 1). The reaction is complete in *ca.* 5 h, and

$$6PhC{\equiv}CCu + 2Eu \xrightarrow[20\,°C]{Py/THF}$$
$$\{[(PhC{\equiv}C)_3Cu][Eu(Py)(THF)_2]\}_2 + 4Cu \quad (1)$$
$$\mathbf{1}$$

compound **1** is isolated in 70.4% yield as air-unstable pale yellow-brown crystals, sparingly soluble in THF and insoluble in hexane. It decomposes at 150−155 °C, and μ_{eff} is equal 8.03 μ_B.

In THF, these metallic lanthanoids are unreactive toward PhC≡CCu, while in the presence of YbI₂(THF)₄ (1.7 mol%) metallic Yb reacts with PhC≡CCu at room temperature with the formation of complex **2**[12] (eq 2).

$$6PhC{\equiv}CCu + 2Yb \xrightarrow[20\,°C]{THF,\ YbI_2(THF)_4}$$
$$\{[(PhC{\equiv}C)_3Cu][Yb(THF)_2]\}_2 + 4Cu \quad (2)$$
$$\mathbf{1}$$

If the reagents are allowed to stand for 6 days without stirring, and complex **2** forms as red air-unstable, diamagnetic crystals in 60.0% yield. Compound **2** appears to be an intermediate since further reaction leads to the disappearance of the red crystals and the formation of a black, amorphous substance with enhanced ytterbium content (38.2%), in which, according to the IR data, C≡C bonds are absent. The interaction at this stage probably includes the cleavage of the triple

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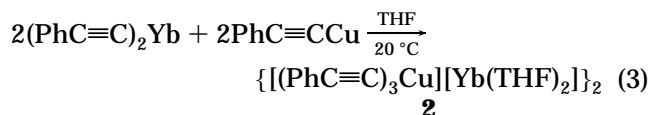(3) (a) Costa, G.; Camus, A.; Gatti, L.; Marsich, N. *J. Organomet. Chem.* **1966**, *5*, 568. (b) Zakharkin, L. I.; Sorokina, L. P. *Z. Org. Khim.* **1970**, *6*, 2470.
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(11) PhC≡CCu was prepared by a reported method: Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, .3313.

bonds of the phenylethynyl fragments and the formation of a polymeric product.

Complex **2** was also synthesized by the reaction of $(PhC\equiv C)_2Yb$[13] with $PhC\equiv CCu$. It was found that the reaction proceeds readily at room temperature and is complete in *ca.* 10 h with the formation of complex **2** in 82% yield (eq 3). Complex **2** is sparingly soluble in THF,

$$2(PhC\equiv C)_2Yb + 2PhC\equiv CCu \xrightarrow[20\,°C]{THF}$$
$$\{[(PhC\equiv C)_3Cu][Yb(THF)_2]\}_2 \quad (3)$$
$$\mathbf{2}$$

insoluble in hexane, and decomposes at 155−160 °C. The IR spectra of **1** and **2** are similar and confirm the presence of phenylethynyl groups and coordinated solvent.[12] The intensity of the $\nu(C\equiv C)$ band (2025 cm^{-1}) in the spectrum of **2** is noticeably decreased in comparison with the intensity of the corresponding band in the spectrum of **1**. Complexes **1** and **2** were found to be weak electrolytes in THF solution.[12]

The structures of **1** and **2** were determined by X-ray diffraction.[14] Both molecules have a similar centrosymmetric structure in which the two Eu(Py)(THF)$_2$ units in **1** and two Yb(THF)$_2$ units in **2** are bonded by two bridging $(PhC\equiv C)_3Cu$ fragments (Figures 1 and 2). In both molecules, all C_α carbon atoms of the alkynyl $C_\alpha\equiv C_\beta Ph$ groups act as μ-bridges forming with the Ln and Cu atoms the central centrosymmetrical four-member Ln(μ-C)$_2$Ln cycle and the four nonplanar four-member Ln(μ-C)$_2$Cu cycles. The environment of the Ln atoms is a distorted pentagonal bipyramid around the Eu atom in **1** and a distorted octahedron around the Yb atom in **2**. In both molecules, the Cu(1)C(9)C(10)C-
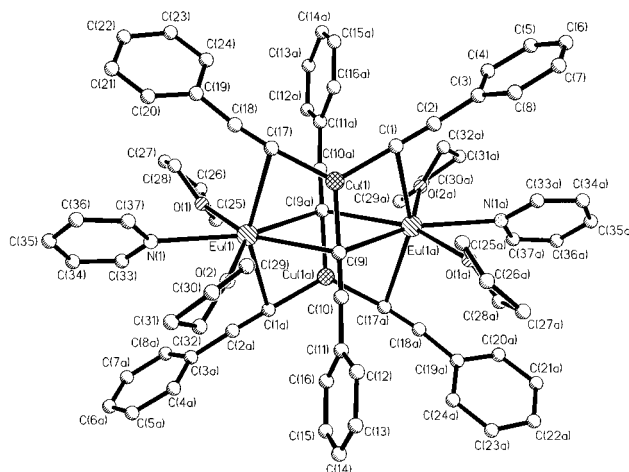
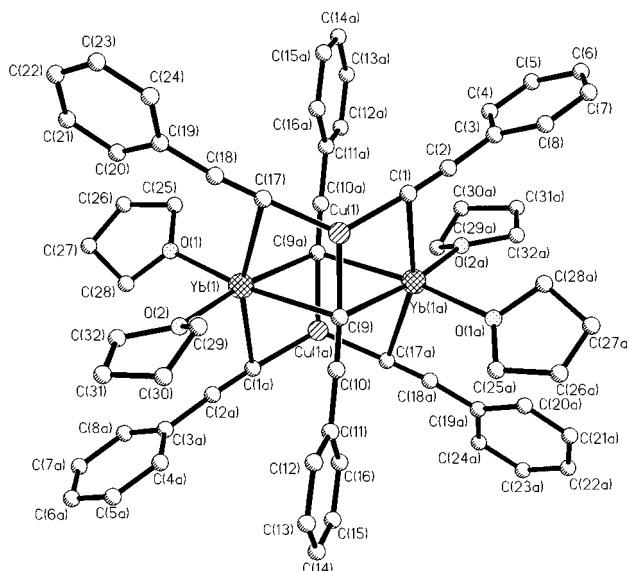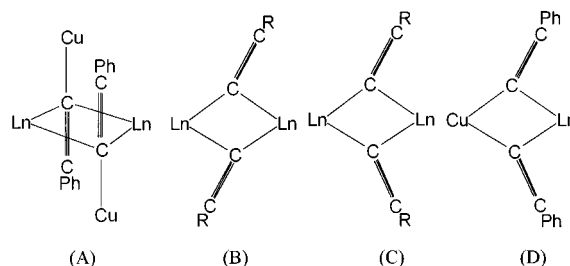

Figure 1. X-ray structure of **1** and atom labeling.

Figure 2. X-ray structure of **2** and atom labeling.

(11) fragment and its centrosymmetric equivalent are approximately in the bisector plane of the molecule. The angles between the triple C(9)≡C(10) bond and the normal to the plane of the Ln$_2$(μ-C)$_2$ cycle are 26.8° in **1** and 26.6° in **2**. Such an arrangement of C≡C groups relative to the central four-member Ln$_2$(μ-C)$_2$ cycle (A) distinguishes the molecules of **1** and **2** from the other X-ray-characterized lanthanoid complexes containing a Ln(μ-C≡CR)$_2$Ln cycle in which the triple C≡C bonds are approximately in the plane of a central four-member cycle (B and C): [(MeC$_5$H$_4$)$_2$SmC≡C^{t}Bu]$_2$,[15] [(tBuC$_5$H$_4$)$_2$-

(A) (B) (C) (D)

SmC≡CPh]$_2$,[16] [(Me$_5$C$_5$)EuC≡CPh(THF)$_2$]$_2$,[17] [Cp$_2$-ErC≡C^{t}Bu]$_2$,[18] and (Me$_5$C$_5$)$_4$Yb$_3$(C≡CPh)$_4$.[17] All four-member Cu(μ-C)$_2$Ln cycles (D) in **1** and **2** are non-planar: the dihedral angles between the Cu(μ-C)$_2$ and (μ-C)$_2$Ln planes are 25.9, 35.7° and 28.5, 35.5° for the Ln(1)C(9)Cu(1)C(17) and Ln(1a)C(9)Cu(1)C(1) cycles in **1** and **2**, respectively.

(12) The synthesis and isolation of **1** and **2** were performed under vacuum in sealed ampules using thoroughly dried solvents. YbI$_2$(THF)$_4$ used as a catalyst was synthesized by reaction of Yb with I$_2$ in THF. Preparation of **1**: A mixture of PhC≡CCu (0.60 g, 3.65 mmol) and Eu filings (1.19 g, 7.83 mmol) in 20 mL of pyridine was stirred for *ca.* 5 h at room temperature. As the solid yellow PhC≡CCu dissolved, the solution became dark-brown. Pyridine was next removed from the reaction mixture, and 20 mL of THF was added. The solid excess Eu, metallic copper, and solid complex **1** were separated by centrifugation and extracted with THF (5 × 15 mL). Metallic copper (0.08 g, 50.0%) was found in the excess Eu. The THF solution and all extractions were combined, the total volume was reduced to 15 mL, and the solution was stored at 0 °C for ca. 20 h to yield pale yellow-brown crystals of **1** (0.63 g, 70.4%), dec pt 150−155 °C. Anal. Calcd for C$_{37}$CuEuH$_{36}$NO$_2$: C, 59.88; Cu, 8.57; H, 4.85; Eu, 20.50. Found: C, 58.93; Cu, 9.25; H, 4.75; Eu, 19.91. IR (Nujol, cm^{-1}): 3030 (w), 1060 (m, br), 900 (m, br), 740 (s), 690 (s), (ν(C≡C)) 2020 (m), (THF) 870 (m, br), 1030 (m) (Py), 1615 (w), 1580 (m). Conductivity (THF, 20 °C): $\lambda_\infty = 32.0$ cm$^2\cdot\Omega^{-1}\cdot$mol^{-1}, $K_D = 1.73 \times 10^{-7}$ mol^{-1}. Preparation of **2**: (a) A mixture of PhC≡CCu (1.00 g, 6.08 mmol), Yb chips (2.28 g, 13.18 mmol), and YbI$_2$(THF)$_4$ (0.09 g, 0.10 mmol) in 20 mL of THF was allowed to stand at room temperature for 6 days. The PhC≡CCu dissolved, the solution became dark-red-brown, and a fine deposit of metallic Cu and red crystals of **2** was formed. The solution, a fine deposit of Cu, and crystals of **2** were then separated from the excess Yb by decantation. Then 15 mL of hexane was added. After the separation of the fine Cu deposit of in the form of a suspension in hexane, the crystals were dried in vacuum to yield 0.83 g (60.0%) of complex **2**, dec pt 155−160 °C. Anal. Calcd for C$_{32}$CuH$_{31}$O$_2$Yb: C, 56.18; Cu, 9.30; H, 4.54; Yb, 25.31. Found: C, 56.36; Cu, 10.15; H, 4.48; Yb, 24.79. IR: (Nujol, cm^{-1}): 3030 (w), 1060 (m, br), 900 (m, br), 740 (s), 690 (s), (ν(C≡C)) 2025 (w), (THF) 870 (m, br), 1030 (m). Conductivity (THF, 20 °C): $\lambda_\infty = 11.2$ cm$^2\cdot\Omega^{-1}\cdot$mol^{-1}, $K_D = 2.6 \times 10^{-7}$ mol^{-1}. (b) A solution of (PhC≡C)$_2$Yb (0.71 g, 1.89 mmol) in 15 mL of THF was added to PhC≡CCu (0.31 g, 1.89 mmol) in 5 mL of THF. After *ca.* 6 h, the yellow PhC≡CCu had dissolved, the solution became dark-brown, and red crystals of **2** were formed. The crystaline product was separated from the solution, washed with THF, and dried in vacuum to yield 1.05 g (81.5%) of **2**, dec pt 155−160 °C. Anal. Calcd for C$_{32}$CuH$_{31}$O$_2$Yb: C, 56.18; Cu, 9.30; H, 4.54; Yb, 25.31. Found: C, 55.34; Cu, 11.19; H, 4.77; Yb, 24.12. The IR spectrum of the isolated compound is identical to the IR spectrum of complex **2** obtained by the reaction of Yb with PhC≡CCu.

(13) (PhC≡C)$_2$Yb was prepared by the reported method: Deacon, G. B.; Koplick, A. J.; Tuong, T. D. *Austral. J. Chem.* **1982**, *35*, 941.

Table 1. Selected Interatomic Distances (Å) and Bond Angles (deg) for 1 (Ln = Er) and 2 (Ln = Yb)

	1	2		1	2
Ln(1)−O(1)	2.628(4)	2.413(4)	Cu(1)−C(9)	1.954(6)	1.969(7)
Ln(1)−O(2)	2.609(4)	2.403(4)	Cu(1)−C(17)	1.941(6)	1.922(6)
Ln(1)−N(1)	2.714(5)		C(1)−C(2)	1.218(8)	1.215(8)
Ln(1)−C(17)	2.800(6)	2.623(6)	C(2)−C(3)	1.438(8)	1.450(9)
Ln(1)−C(18)	3.219(6)	3.038(6)	C(9)−C(10)	1.215(8)	1.224(8)
Ln(1)−C(9)	2.872(6)	2.694(6)	C(10)−C(11)	1.451(9)	1.443(8)
Ln(1)−C(9a)	2.872(6)	2.699(6)	C(17)−C(18)	1.221(8)	1.220(8)
Ln(1)−C(1a)	2.838(6)	2.685(6)	C(18)−C(19)	1.438(8)	1.448(9)
Ln(1)−C(2a)	3.295(6)	3.126(6)	Ln(1)···Cu(1)	3.125(1)	2.968(1)
Cu(1)−C(1)	1.937(6)	1.930(7)	Ln(1)···Cu(1a)	3.139(1)	2.969(1)
O(1)−Ln(1)−O(2)	137.58(14)	98.37(14)	Ln(1)−C(9)−Ln(1a)	110.0(2)	103.2(2)
O(1)−Ln(1)−N(1)	70.07(14)		Ln(1)−C(9)−Cu(1)	78.2(2)	77.4(2)
N(1)−Ln(1)−O(2)	67.78(14)		Ln(1)−C(9)−C(10)	104.0(4)	110.0(4)
O(2)−Ln(1)−C(9)	72.3(2)	91.4(2)	Ln(1a)−C(9)−C(10)	106.0(4)	101.8(4)
C(9)−Ln(1)−C(9a)	70.0(2)	76.8(2)	Ln(1a)−C(9)−Cu(1)	78.6(2)	77.2(2)
O(1)−Ln(1)−C(9a)	80.2(2)	93.4(2)	Ln(1)−C(17)−Cu(1)	80.3(2)	79.9(2)
C(1a)−Ln(1)−O(1)	84.9(2)	86.2(2)	Ln(1)−C(17)−C(18)	98.7(4)	97.8(4)
C(1a)−Ln(1)−O(2)	101.8(2)	104.2(2)	Ln(1)−C(1a)−Cu(1a)	79.7(2)	78.2(2)
C(1a)−Ln(1)−N(1)	105.7(2)		Ln(1)−C(1a)−C(2a)	101.0(4)	99.6(4)
C(1a)−Ln(1)−C(9)	87.9(2)	92.3(2)	C(1)−Cu(1)−C(9)	116.5(2)	115.1(3)
C(1a)−Ln(1)−C(9a)	70.8(2)	75.3(2)	C(1)−Cu(1)−C(17)	122.7(2)	127.3(2)
C(17)−Ln(1)−O(1)	101.4(2)	101.9(2)	C(9)−Cu(1)−C(17)	120.6(2)	116.6(2)
C(17)−Ln(1)−O(2)	91.5(2)	90.1(2)	Cu(1)−C(1)−C(2)	179.1(5)	174.6(5)
C(17)−Ln(1)−N(1)	101.7(2)		C(1)−C(2)−C(3)	176.3(6)	174.2(6)
C(17)−Ln(1)−C(9)	73.2(2)	77.0(2)	Cu(1)−C(9)−C(10)	173.6(5)	172.5(5)
C(17)−Ln(1)−C(9a)	83.7(2)	88.6(2)	C(9)−C(10)−C(11)	173.1(6)	175.4(6)
C(17)−Ln(1)−C(1a)	152.4(2)	162.5(2)	Cu(1)−C(17)−C(18)	167.5(5)	173.0(5)
			C(17)−C(18)−C(19)	172.3(6)	175.3(6)

The Ln−(μ-C) distances are the same, 2.872(6) Å, in the Eu$_2$(μ-C)$_2$ cycle and close to each other in the Yb$_2$-(μ-C)$_2$ cycle, Yb(1)−C(9) 2.694(6) Å and Yb(1)−C(9a) 2.699(6) Å. The Ln−C(17) and Ln−C(1a) distances for the C atoms in the apical positions at the Ln atom are shorter: 2.800(6), 2.838(6) Å and 2.623(6), 2.685(6) Å, respectively for Ln = Eu and Yb. The differences, ca. 0.17 Å, between the Eu−C and Yb−C distances found in **1** and **2** are close to the difference, 0.18 Å, between an ionic radii for seven-coordinate Eu^{2+} (1.20 Å) and six-coordinate Yb^{2+} (1.02 Å).[19] The Ln−C distances in **1** and **2** are also comparable to those in lanthanoid alkynyl complexes containing a central Ln$_2$(μ-C)$_2$ cycle with Ln-(III) atoms (2.709 and 2.702 Å for the Eu−C distances in [(Me$_5$C$_5$)EuC≡CPh(THF)$_2$]$_2$,[17] 2.40 and 2.52 Å for the Yb−C distances in (Me$_5$C$_5$)$_4$Yb$_3$(C≡CPh)$_4$[17] and the average Yb(II)−C η^2-distance, 2.850 Å, in (Me$_5$C$_5$)$_2$Yb-

(η^2-MeC≡CMe)[20] if the differences in metal oxidation state and coordination number are considered.

In both molecules, the Cu(1) atom has a distorted planar trigonal environment (Cu−C 1.937(6)−1.954(6), 1.922(6)−1.969(7) Å and C−Cu−C 116.5(2)−122.7(2), 116.6(2)−127.3(2)°, respectively in **1** and **2** (Table 1)). The deviation of the Cu(1) atom from the C(1)C(9)C-(17) plane is 0.04 Å in **1** and 0.11 Å in **2**. The shortest Cu(1)···C(10a) contacts between the two [Cu(C$_\alpha$≡C$_\beta$Ph)$_3$]$^{2-}$ units (3.244(6) Å in **1** and 3.279(7) Å in **2**) are long for a direct interaction. All CuC≡CPh fragments in **1** and **2** are slightly nonlinear (Table 1). The C≡C bond lengths (1.215(8)−1.221(8) Å in **1** and 1.215(8)−1.224(8) Å in **2**) are somewhat longer than the average length of triple C≡C bonds 1.189 Å in the C≡CC(sp^2, aren) fragments[21] and comparable to that in the above-mentioned lanthanoid complexes with bridging acetylenide groups, 1.188−1.22 Å.[15−18] The large differences between the Cu−C≡C and Ln−C≡C angles in the Cu-(μ-C)$_2$Ln cycles in **1** and **2** (Table 1) seem to be related to the η^2-interaction of the triple-bond π-orbitals with the Ln atom. However, the Ln(1)···C(18) and Ln···C(2a) distances (3.219(6), 3.295(6) Å for Ln = Eu and 3.038-(6), 3.126(6) Å for Ln = Yb) are long for strong π-interactions.

Supporting Information Available: Tables of crystallographic, data collection, solution, and refinement parameters, positional and thermal parameters, and bond distances and bond angles for **1** and **2** (13 pages). Ordering information is given on any current masthead page.

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(14) X-ray data for **1** and **2** were collected on a Siemens P3/PC diffractometer at 193 and 153 K, respectively (Mo Kα radiation, graphite monochromator, $\theta-2\theta$ scan mode, $2 \leq \theta \leq 25$ and $2 \leq \theta \leq 25°$, 5532 and 5132 independent reflections measured, 3799 ($F > 3\sigma$-(F)) and 3276 ($F > 3\sigma(F)$) reflections observed for **1** and **2**, respectively). Crystal data at 193 K for **1**: C$_{37}$H$_{36}$O$_2$NCuEu, fw 742.17, space group $P2_1/n$, $a = 14.105(4)$ Å, $b = 15.056(4)$ Å, $c = 15.315(6)$ Å, $\beta = 102.54$-(2)°, $V = 3175(2)$ Å^3, $Z = 4$, $D_{calc} = 1.553$ g/cm^3, $\mu = 2.660$ mm^{-1}. Crystal data at 153 K for **2**: C$_{32}$H$_{31}$O$_2$CuYb, fw 684.15, space group $P\bar{1}$, $a = 10.127(3)$ Å, $b = 11.732(3)$ Å, $c = 12.918(4)$ Å, $\alpha = 102.61(2)°$, $\beta = 109.54(2)°$, $\gamma = 99.26(2)°$, $V = 1365.1(7)$ Å^3, $Z = 2$, $D_{calc} = 1.664$ g/cm^3, $\mu = 4.210$ mm^{-1}. The structures of **1** and **2** were solved by the direct methods. In both structures all non-H atoms were refined anisotropically. The H atoms were located in the difference Fourier maps and refined isotropically. Absorption was taken into account by the DIFABS program (Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158). The final refinements converged at $R = 0.037$, $R_w = 0.080$, $S = 1.06$ (**1**) and $R = 0.036$, $R_w = 0.056$, $S = 1.09$ (**2**) for observed reflections. The weight scheme was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ($P = (F_o^2 + 2F_c^2)/3$) with a and b equal to 0.0541 and 2.7206 (**1**) and 0.0220 and 4.3456 (**2**). All calculations were performed using the SHELXTL-Plus (Sheldrick, G. M. *Structure Determination Software Program Package (PC version);* Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1989) and SHELX93 packages.
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