Supramolecular Chemistry

A Trinuclear Eu^{III} Array within a Diastereoselectively Self-Assembled Helix Formed by Chiral Bipyridine-Carboxylate Ligands**

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Owing to their structural, magnetic, and emissive properties, complexes of lanthanide (Ln) ions with chiral ligands have found use as 1) asymmetric catalysts[1] and 2) probes for the characterization of ionic[2] or chiral environments.[3] However, in view of the lability and the weak coordination preferences of the Ln^{III} centers,[4] the synthesis of stable "true" enantiopure lanthanide coordination compounds, in which all the chirality sources (ligand, metal centers, supramolecular chirality) are fixed, represents a difficult goal. Indeed, only in a few cases has the synthesis of configurationally stable, mononuclear lanthanide complexes been achieved with high diastereoselectivity; these complexes were obtained from N-substituted 1,4,7,10-tetraazacyclododecane derivatives[5] or terpyridine-type chiral ligands.[6] With respect to complexes of higher nuclearity, solely the formation of dinuclear f–f helicates (from an enantiomerically pure ligand)[7] or d–f helicates (using a resolved triple-helical Cr^{III} complex, which preorganizes the ligand strands)[8] have been reported.

Bipyridine ligands that are derivatized with chiral pinene units have been found to be strong inductors of chirality for the stereocontrolled synthesis of complexes of transition-metal ions.[9] We sought to extend this range of ligands[10] to the stereoselective synthesis of supramolecular arrays of lanthanide ions. To this end, we designed ligand L^- (see Scheme 1), which features a carboxylate donor group appended to the pinene moiety to take advantage of the

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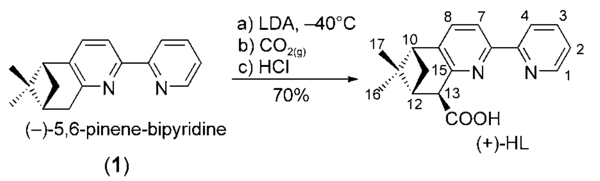
oxophilic character of Ln ions. Besides increasing the stability of the lanthanide complexes, the carboxylate group may also serve to enhance the transmission of the chiral information to the final supramolecular architecture. Herein we report the structure and chiroptical properties of the trinuclear array that results from self-assembly of L$^-$ and Eu^{III} ions with complete diastereoselectivity. This complex displays a very interesting mode of helical chirality that originates from the propeller-like arrangement of the ligands around the trinuclear metal core.



Scheme 1. Synthesis of the ligand (+)-HL, and its numbering scheme for NMR spectral assignments.

The one-pot synthesis of the new carboxylic ligand (+)-HL (Scheme 1) is based on the known regio- and stereoselective deprotonation of (−)-5,6-pinene-2,2′-bipyridine (**1**)[11] by lithium diisopropylamide (LDA).[12] Electrophilic attack of the anion with CO$_2$ generates a further chiral center (*S*). Final treatment of the product with HCl prevents decarboxylation[13] and yields the stable adduct (+)-HL·HCl. Treatment of Eu(ClO$_4$)$_3$ with two or more equivalents of (+)-HL·HCl in methanol in the presence of base (Et$_3$N or LiOH) instantaneously leads to the formation of a white precipitate. Crystals of this product could be grown from a solution in MeCN/MeOH, and X-ray crystallography[14] revealed the trinuclear assembly $[\mathrm{Eu_3}\{(+)\text{-L}\}_6(\mu_3\text{-OH})(\mathrm{H_2O})_3](\mathrm{ClO_4})_2\cdot 3\,\mathrm{H_2O}$, as shown in Figure 1.

The assembly has crystallographically imposed C_3 symmetry (space group: *R*3), which relates the three Eu^{III} centers. The Eu–Eu distance is 3.915(1) Å, and the three metal ions are bridged by a hydroxide ion that lies slightly (0.84 Å) out of the plane defined by these ions. Six L$^-$ ligands are incorporated into the overall array and these may be grouped into two sets of three symmetry-related ligands. The first set of three ligands, depicted in orange in Figure 1 and Figure 2, coordinate solely through their carboxylate groups, which bridge two Eu^{III} centers in a symmetrical μ^2-η^1:η^1 fashion. The uncoordinated bipyridyl units adopt an unusual *cis* conformation (dihedral angle: 4.1(8)°), which appears to be stabilized by hydrogen-bonding interactions with a water molecule of crystallization ($\mathrm{O_{H2O}}\cdots\mathrm{N}$ distance of 2.87(2) Å). These bipyridyl groups adopt a right-handed (*P*) helical arrangement in the solid state (Figure 2). The second set of three ligands, shown in green in Figure 1 and Figure 2, coordinate through both their carboxylate and bipyridyl donor groups. The carboxylate group links two Eu^{III} centers in a μ^2-η^2:η^1 fashion, while the bipyridyl group coordinates to one of the metal ions in a typical bidentate mode. This set of ligands adopts a left-handed (*M*) helical configuration which is manifest in the circular dichroism (CD) spectrum as discussed below. The coordination sphere of the europium ions is completed by a molecule of water, and the geometry at these centers is best described as a distorted, monocapped square antiprism. Preliminary results suggest that the trinu-

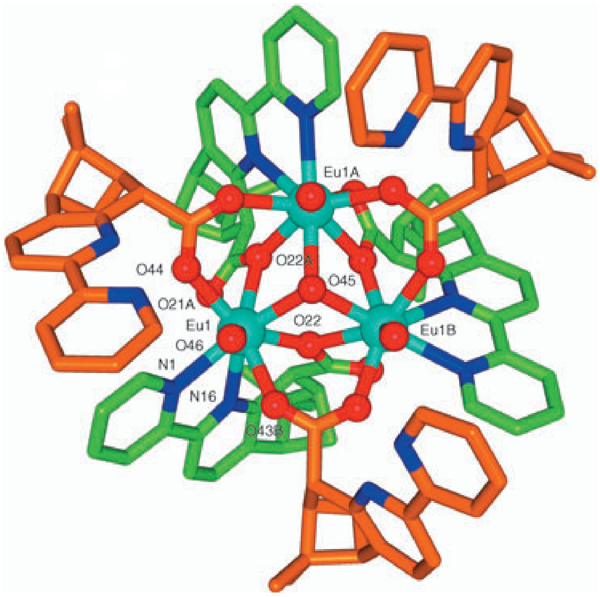


Figure 1. Crystal structure of $[\mathrm{Eu_3}\{(+)\text{-L}\}_6(\mu_3\text{-OH})(\mathrm{H_2O})_3](\mathrm{ClO_4})_2\cdot 3\,\mathrm{H_2O}$ (O red, Eu turquoise, N dark blue; O-coordinated pinene-bipyridyl groups orange, N,O-coordinated pinene-bipyridyl groups green). View parallel to the crystallographic C_3 axis with a simplified labeling scheme. Hydrogen atoms, perchlorate counterions, and water molecules of crystallization have been omitted for clarity. Selected bond lengths [Å]: Eu1–N16 2.767(12), Eu1–O21A 2.667(10), Eu1–O22A 2.451(13), Eu1–O43B 2.333(9), Eu1–N1 2.508(14), Eu1–O22 2.297(11), Eu1–O45 2.411(5), Eu1–O46 2.504(6), Eu1–O44 2.379(9). Symmetry operations: a) $-y, x-y, z$; b) $-x+y, -x, z$.

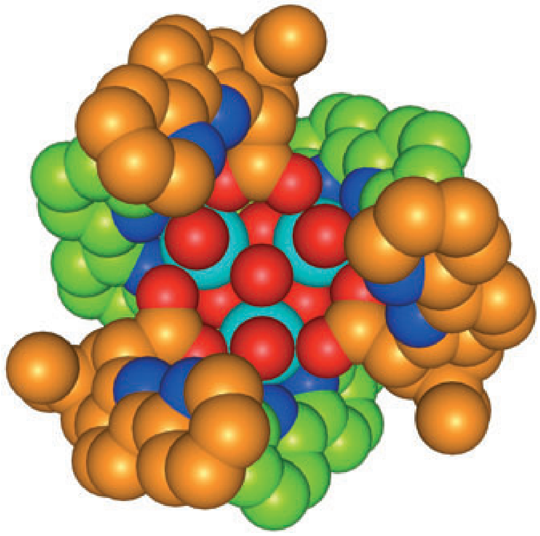


Figure 2. Space-filling representation of $[\mathrm{Eu_3}\{(+)\text{-L}\}_6(\mu_3\text{-OH})(\mathrm{H_2O})_3]^{2+}$ (O red, Eu turquoise, N dark blue). Ligands L$^-$ coordinated only through their carboxylates groups are shown in orange; those coordinated through both the carboxylate and bipyridine moieties are shown in green.

clear assembly persists in the solution state, but further detailed investigations are necessary for a complete characterization of its behavior in solution.

The NMR spectra of the crude precipitate and dissolved crystals of the complexes were found to be identical. In the ^{1}H NMR spectrum, two sets of signals were observed in a 1:1 ratio spread over a range of almost 25 ppm (see Figure 3 and Experimental Section). This observation indicates the existence of two magnetically distinct environments for the ligands in the complex, which may be related to the two distinct sets of ligands observed in the X-ray crystal structure of $[Eu_3\{(+)\text{-}L\}_6(\mu_3\text{-}OH)(H_2O)_3](ClO_4)_2\cdot 3H_2O$, as well as a high diastereoselectivity (d.e. > 95 %) of this self-assembly process.

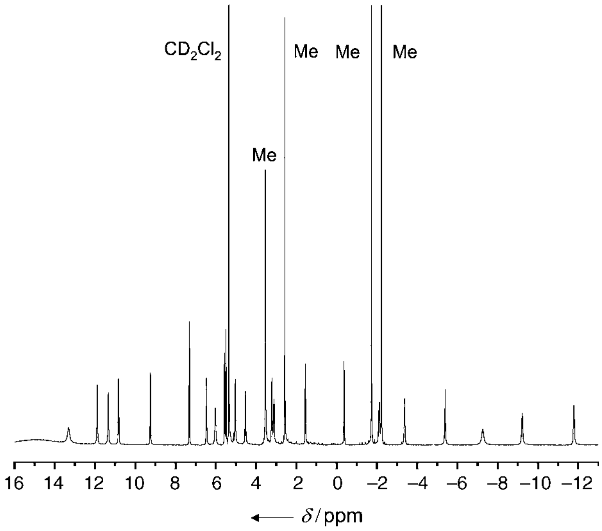


Figure 3. ^{1}H NMR spectrum of $[Eu_3\{(+)\text{-}L\}_6(\mu_3\text{-}OH)(H_2O)_3](ClO_4)_2\cdot 3H_2O$ in CD_2Cl_2 (400 MHz, RT).

The major peaks in the electrospray (ES) mass spectrum may be assigned to the molecular cation with loss of the coordinated water molecules, $[Eu_3L_6(OH)]^{2+}$, and its perchlorate adduct $\{[Eu_3L_6(OH)](ClO_4)\}^+$ (see Supporting Information). A third intense signal is attributed to $[Eu_3L_6(OH)(H_2O)]^{2+}$, which probably arises from the fragmentation processes in the gas phase.

The CD spectrum of $[Eu_3\{(+)\text{-}L\}_6(\mu_3\text{-}OH)(H_2O)_3](ClO_4)_2$ exhibits a bisignate curve centered around 320 nm (Figure 4). From the shape of this curve and the energy at which it appears, it is likely that it arises from the exciton coupling of the long-axis polarized π–π* transitions of the bipyridine-type L$^-$ ligands.[15] Of the two distinct sets of ligands in the overall array, the bipyridyl chromophores of the set that coordinate only through their carboxylate groups will rotate freely in solution, thus the average of their exciton-coupling interactions will be zero. On the other hand, the second set of ligands also coordinate through their bipyridine moieties and therefore will be rigidly held in a helical arrangement similar to that observed by crystallography (see Figure 5). Consequently, it is expected that exciton interactions between this set of chromophores will be entirely responsible for the low-energy exciton couplet. Exciton-coupling theory predicts that the left-handed (Λ) arrangement of these chromophores will give rise to a positive exciton couplet;[16] that is, a bisignate curve which is positive at lower energies. This prediction is in exact accord with the experimentally observed CD spectrum, but in the present case the three bipyridyl chromophores are coordinated to different metal centers, so the curve may be ascribed solely to internuclear exciton coupling.[17] These results underscore the importance of this phenomenon in metallosupramolecular chemistry.

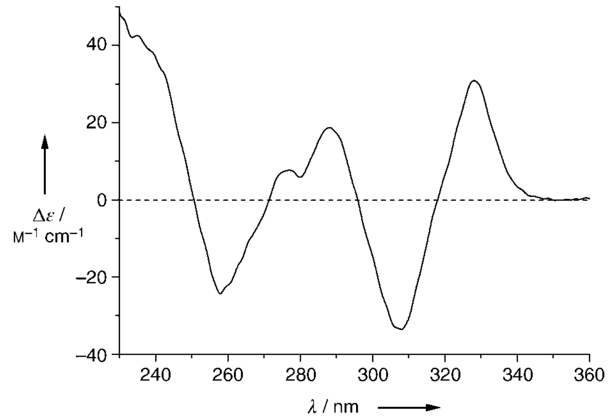


Figure 4. CD spectrum of $[Eu_3\{(+)\text{-}L\}_6(\mu_3\text{-}OH)(H_2O)_3](ClO_4)_2$ (10^{-4} M in CH_3CN).

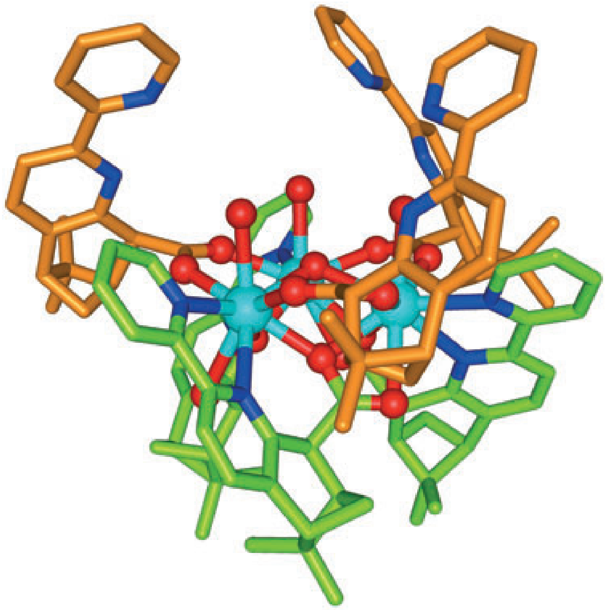


Figure 5. View perpendicular to the C_3 axis of the complex to highlight the ligands in the *M* configuration (green) that are responsible for the exciton coupling (O red, Eu turquoise, N dark blue).

Upon UV irradiation, the Eu^{III} array displays bright red luminescence in both solution (total emission quantum yield: $\phi_{tot}^{Eu} = 6.5\,\%$; lifetime: $\tau = 1.5$ ms in CH_3CN) and the solid state. These properties prompted us to investigate the chiroptical properties in the excited state by circularly polarized luminescence (CPL) spectroscopy. Excitation of the organic chromophore ($\lambda_{ex} = 315$ nm) gives rise to polarized emission bands that correspond to the Eu^{III}-centered $^5D_0 \rightarrow {}^7F_J$ transitions (Figure 6). The largest luminescence dissymmetry factor, defined as $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, in which L and R denote left and right, respectively, is found for the magnetic-dipole allowed transition $^5D_0 \rightarrow {}^7F_1$. Its value of −0.16 ($\lambda = 585$ nm) is comparable to those of some reported mononuclear Eu^{III} complexes,[5c,18] and much higher than others.[5b,6] For the $\Delta J = 2$, 3, and 4 transitions, significantly lower absolute magnitudes of g_{lum} (0.09–0.01) were observed. CPL spectroscopy of polynuclear lanthanide complexes is still in its infancy, and the correlation of spectroscopic phenomena (transition type and sign sequence) with structural properties such as absolute configuration would require the systematic investigation of other enantiopure C_3-symmetric Ln^{III} complexes.

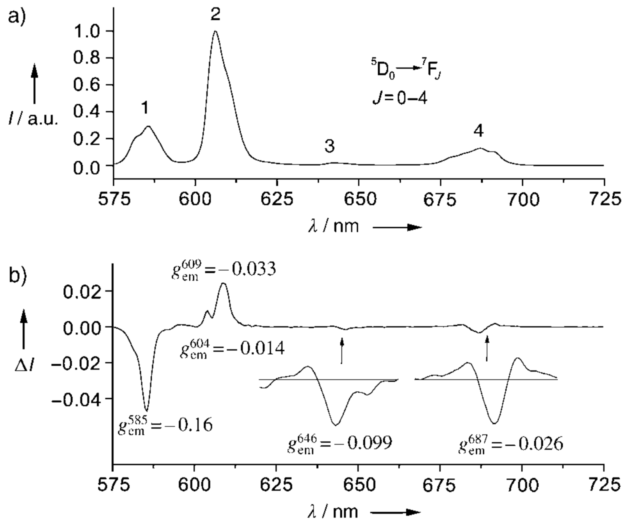


Figure 6. a) Total luminescence ($I_L + I_R$) and b) circularly polarized luminescence ($I_L - I_R$) spectra of the Eu^{III} complex (1.27×10^{-4} м in CH_3CN, 298 K).

In summary, we have presented the diastereoselective self-assembly, structure, and chiroptical properties of a trinuclear Eu^{III} array, which exhibits an interesting mode of supramolecular helical chirality related to the arrangement of the ligands around the metallic core. This chirality is manifest in the CD spectrum of the trinuclear complex and lends strong support to a recently proposed internuclear exciton coupling model.[17] The new chiral bipyridine-carboxylate ligand discussed here successfully extends the family of pinene-derivatized bipyridine ligands to incorporate those capable of forming stable complexes with lanthanide ions. Preliminary investigations have shown that this ligand leads to similar trinuclear arrays with other lanthanide cations, including La^{III}, Gd^{III}, and Pr^{III}, through high-yielding self-assembly processes. Furthermore, the availability of both enantiomers of the ligand enables investigations of chiral discrimination phenomena in various energy-transfer processes.[19]

Experimental Section

Caution! Perchlorate salts are potentially explosive.[20] Tetramethylsilane (TMS) was used as internal reference for ^{1}H NMR experiments. The CPL spectrum was measured using a Jasco CPL-200 spectrophotometer (bandwidth: 2 nm).

(+)-HL·HCl·H_2O: ^{1}H NMR (400 MHz, CD_2Cl_2, TMS, 25 °C): δ = 8.97 (d, $^3J_{1,2} = 5.8$ Hz, 1H; H1), 8.40 (m, 2H; H3,H4), 8.13 (d, $^3J_{7,8} = 7.9$ Hz, 1H; H7), 7.85 (dd, $^3J_{2,1} = 6.0$ Hz, $^3J_{2,3} = 6.0$ Hz, 1H; H2), 7.63 (d, $^3J_{8,7} = 7.9$ Hz, 1H; H8), 4.34 (d, $^3J_{13,12} = 2.5$ Hz, 1H; H13), 2.99 (dd, $^3J_{10,15a} = 5.6$ Hz; $^3J_{10,15b} = 5.6$ Hz, 1H; H10), 2.91 (ddd, $^2J_{15b,15a} = 9.6$ Hz, $^3J_{15b,10} = 5.8$ Hz, $^3J_{15b,12} = 5.8$ Hz, 1H; H15b), 2.74 (ddd, $^3J_{12,15b} = 5.8$ Hz, $^4J_{12,10} = 5.8$ Hz, $^3J_{12,13} = 2.8$ Hz, 1H; H12), 1.60 (d, $^2J_{15a,15b} = 9.6$ Hz, 1H; H15a), 1.52 (s, 3H; Me17), 0.72 ppm (s, 3H, Me16); UV/Vis (CH_3CN): λ_{max} (ε): 305 (10600), 250 nm (7500 $м^{-1}cm^{-1}$); CD (CH_3CN): λ ($\Delta\varepsilon$): 220 nm (5 $м^{-1}cm^{-1}$); $[\alpha]_D^{20} = +13.1$ deg dm^2 mol^{-1} ($c = 6.9 \times 10^{-3}$ м in CH_3CN); HR-MS: m/z calcd for $C_{18}H_{19}N_20_2$: 295.1442 $[M+H^+]^+$; found: 295.1441.

$[Eu_3\{(+)\text{-}L\}_6(OH)(H_2O)_3](ClO_4)_2$: Triethylamine (77 µL, 0.53 mmol, 2.3 equiv) was added to a solution of (+)-HL·HCl·H_2O (80 mg, 0.23 mmol) in MeOH (3 mL). A solution of $Eu(ClO_4)_3 \cdot 9H_2O$ (0.115 mmol, 0.5 equiv) in methanol (1.2 mL, 0.0487 м) was then dropped onto the stirring mixture. The white precipitate formed was collected by filtration, washed with cold MeOH, and dried (82 mg, 83 % based on $[Eu_3\{(+)\text{-}L\}_6(OH)(H_2O)_3](ClO_4)_2 \cdot 5H_2O$). ^{1}H NMR (400 MHz, CD_2Cl_2, TMS, 25 °C): δ = 13.31 (1H), 11.89 (1H), 11.33 (d, $J = 6.0$ Hz, 1H), 10.83 (dd, $J = 6.6$ Hz, $J = 6.6$ Hz, 1H), 9.25 (dd, $J = 6.9$ Hz, $J = 5.0$, 1H), 7.31 (d, $J = 7.5$ Hz, 1H), 6.47 (dd, $J = 6.7$ Hz, $J = 6.7$ Hz, 1H), 6.02 (1H), 5.58 (d, $J = 7.6$ Hz, 1H), 5.49 (d, $J = 7.6$ Hz, 1H), 5.03 (d, $J = 7.3$ Hz, 1H), 4.53 (d, $J = 6.7$ Hz, 1H), 3.53 (3H, Me), 3.23 (d, $J = 6.8$ Hz, 1H), 3.11 (1H), 2.57 (3H, Me), 1.55 (1H), −0.39 (1H), −1.69 (3H, Me), −2.15 (3H, Me), −2.11 (d, $J = 10.3$ Hz, 1H), −3.37 (1H), −5.38 (1H), −7.25 (1H), −9.21 (1H), −11.78 ppm (1H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 228.9, 190.1, 169.5, 160.7, 156.8, 154.4, 152.9, 152.2, 151.0, 147.4, 146.5, 141.9, 140.3, 136.0, 132.0, 128.3, 126.3, 124.9, 117.8, 105.4, 104.3, 93.1, 45.5, 43.3, 42.7, 41.9, 35.8, 30.1, 26.5, 23.3, 23.0, 21.2, 18.0, 1.1, −8.9, −40.5 ppm; IR: $\tilde{\nu} = 2935$w, 1618s (COO^-), 1567m, 1454w, 1421s (COO^-), 1238w, 1094s (Cl–O), 860w, 792m, 753m; UV/Vis (CH_3CN, 1.8×10^{-6} м): λ_{max} (ε): 306 (67000), 278 (52500), 255 nm (48500 $м^{-1}cm^{-1}$); $[\alpha]_D^{20} = -97.3$ deg dm^2 mol^{-1} ($c = 1.1 \times 10^{-3}$ м in CH_3CN); ES-MS (10^{-4} м in CH_3CN): m/z (%): 1116.3 (100) $[Eu_3L_6(OH)]^{2+}$, 1107.3 (75) $[Eu_3L_6(OH)-H_2O]^{2+}$, 2331.4 (34) $[Eu_3L_6(OH)(ClO_4)]^+$, 1254.3 (15) $[Eu_3L_7]^{2+}$; Elemental analysis: calcd for $C_{108}H_{109}Eu_3N_{12}O_{23}Cl_2 \cdot 5H_2O$ (%): C 50.36, H 4.66, N 6.52; found: C 50.36, H 4.49, N 6.24.

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[14] X-ray data for $[\mathrm{Eu_3\{(+)\text{-}L\}_6(\mu_3\text{-}OH)(H_2O)_3](ClO_4)_2 \cdot 3\,H_2O}$: $M_r = 2539.90$, rhombohedral, space group $R3$, $a = b = 17.3468(11)$, $c = 30.846(4)$ Å, $V = 8038.3(13)$ Å^3, $Z = 3$, $\rho_{\mathrm{calcd}} = 1.574\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 1.865\ \mathrm{mm^{-1}}$, $T = 140(2)$ K, $F(000) = 3858$, $2\theta_{\max} = 50.1°$; 16262 reflections collected of which 6240 unique ($R_{\mathrm{int}} = 0.1147$). Final R indices (3080 observed reflections, $I > 2\sigma I$): $R_1 = 0.0535$, $wR_2 = 0.0915$; final R indices (all data): $R_1 = 0.1049$, $wR_2 = 0.1189$. Highest residual electron density 1.242 e Å^{-3}. The structure was solved by direct methods using SIR97 ("SIR97, A new tool for crystal structure determination and refinement": A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115); refinement was performed using SHELXL-97 (G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany), **1997**) by the full-matrix least-squares technique. Hydrogen atoms were included in calculated positions and treated as riding atoms. No absorption correction was applied. CCDC-259970 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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