A Polymeric Platinum(II)−Thallium(I) Complex Stabilized by Alkynyl−Thallium and Platinum−Thallium Bonding Interactions

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Received May 9, 1997

Introduction

Polymeric complexes have gradually attracted much attention from synthetic and material chemists, basically because of their novel structural features and perhaps also because of the possibility of their having novel solid state properties.[1] These materials are usually formed by the self-assembly of molecular components held together by weak coordinative bonds or hydrogen bridging bonds.[2] Currently, there is a growing and active investigation into the preparation of polymetallic derivatives based on linear or cross-conjugated σ,σ-bis(alkynyl) and functionalized σ-alkynyl building blocks because of their potential electrical conducting, nonlinear optical, luminescence, and liquid crystalline properties.[3] By contrast, polymeric derivatives involving monoanionic $RC\equiv C^-$ bridging ligands are rather scarce,[4] and only in a few cases have such species been characterized by single-crystal X-ray crystallography.

In the past few years, we have been interested in the synthesis of polynuclear complexes of platinum bearing alkynyl groups as unique bridging ligands.[5] The homoleptic and mixed alkynyl platinates $[PtX_2(C\equiv CR)_2]^{2-}$ ($X = C_6F_5$ *cis*- or *trans*-, $C\equiv CR$) have proved to be valuable precursors for the synthesis of a variety of homo- and heteronuclear complexes with only alkynyl fragments bridging the metal centers.[5] For this reason, we have initiated an investigation into the preparation and structural characterization of heteronuclear platinum−thallium complexes by reacting the above-mentioned platinate substrates with thallium(I) salts. Since little is known about the ability of Tl(I) to interact with acetylenes,[6] this study could provide adequate systems in which such an interaction could occur. On the other hand, the presence of direct Pt−Tl bonds in complexes such as $(NBu_4)_2[Tl\{Pt(C_6F_5)_4\}_2]$,[7] $[Pt(CN)_4Tl_2]$,[8] *cis*-$[(C_6F_5)_2(PPh_3)Pt(\mu\text{-}OOCCH_3)Tl]$,[9] $(NBu_4)_2[\{(C_6F_5)_3Pt\}_2\{\mu_2\text{-}O,\mu_3\text{-}O'CCH_3)Tl\}_2]$,[9] $(NBu_4)_x[Pt(C_6F_5)_4Tl]_x$,[10] $[TlPt_3(CO)_3(PCy_3)_3][Rh(\eta\text{-}C_8H_{12})Cl_2]$,[11a] and $[Pt_6(\mu_6\text{-}Tl)(\mu\text{-}CO)_6(\mu\text{-}dppp)_3][PF_6]$,[11e] usually associated with intense photoluminescence, has also stimulated our interest in the study of these reactions, which will allow us to observe the possible competition between the basic platinum center and the acetylenic fragments to bind the thallium ion and also the possible luminescence properties of the resulting platinum−thallium-containing complexes.

Here we report on the synthesis and X-ray single-crystal characterization of a platinum−thallium-containing polymeric complex, $\{$*trans,trans,trans*-$[PtTl_2(C_6F_5)_2(C\equiv C^tBu)_2](acetone)_2\}_n$, ($\{\mathbf{2}(acetone)_2\}_n$), stabilized by alkynyl bridging ligands and platinum−thallium metal−metal bonding interactions. Its spectroscopic and luminescence properties have also been investigated.

Results and Discussion

Addition of $TlNO_3$ (2 equiv) to an aqueous solution of [*trans*-$Pt(C_6F_5)_2(C\equiv C^tBu)_2]^{2-}$, prepared, as previously reported,[12] from *trans*-$[Pt(C_6F_5)_2(tht)_2]$ (tht = tetrahydrothiophene) and $LiC\equiv C^tBu$, results in the immediate precipitation of $[PtTl_2(C_6F_5)_2(C\equiv C^tBu)_2]$ (**2**) as a deep yellow solid (yield 70%). Complex **2** can also be prepared in moderate yield (43%) by reacting $(NBu_4)_2[$*trans*-$Pt(C_6F_5)_2(C\equiv C^tBu)_2]$ (**1**) and $TlNO_3$ (1:2.5) in

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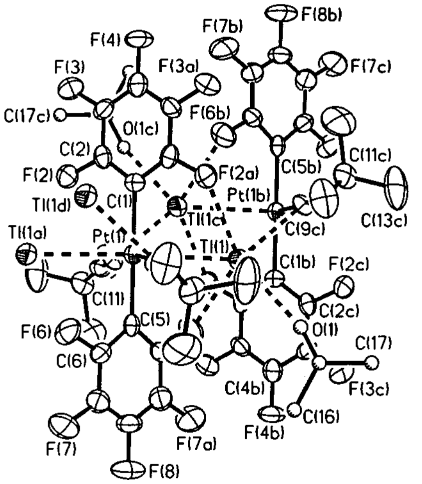

Figure 1. Short section of the chain structure of $\{\mathbf{2}(\text{acetone})_2\}_n$. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted, and acetone molecules have been left isotropic for clarity. Symmetry codes: (a) $-x,y,0.5 - z$; (b) $x,-y,-0.5 + z$; (c) $-x,-y,-z$; (d) $x,-y,0.5 + z$.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for $\{\mathbf{2}(\text{acetone})_2\}_n$[a]

Pt(1)−C(1)	2.11(2)	Pt(1)−C(5)	2.05(2)
Pt(1)−C(9)	2.030(11)	Pt(1)−Tl(1)	3.135(1)
Tl(1)−C(9c)	2.905(10)	Tl(1)−F(2a)	2.887(8)
Tl(1)−F(6a)	2.937(7)	Tl(1)−O(1)	2.83(2)
Tl(1)−Pt(1b)	3.785(1)	Tl(1)−Tl(1c)	3.982(1)
C(1)−Pt(1)−C(9)	94.6(4)	C(5)−Pt(1)−C(9)	85.4(4)
C(9)−Pt(1)−C(9a)	170.8(5)	C(5)−Pt(1)−C(1)	180.0(4)
C(9)−Pt(1)−Tl(1)	107.8(3)	C(9a)−Pt(1)−Tl(1)	72.0(3)
C(1)−Pt(1)−Tl(1)	91.38(2)	C(5)−Pt(1)−Tl(1)	8.62(2)

[a] Symmetry transformations used to generate equivalent atoms: $a = -x,y,0.5 - z$; $b = x,-y,-0.5 + z$; $c = -x,-y,-z$.

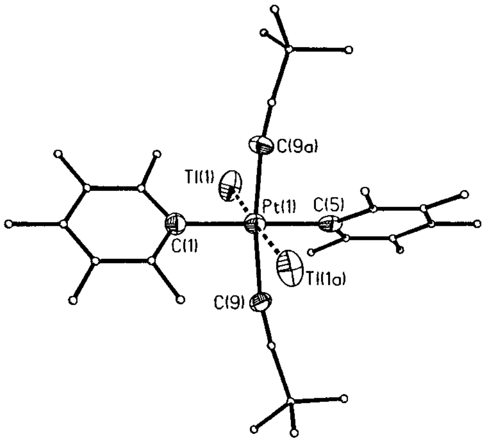

Figure 2. Octahedral-like geometry at the platinum center in $\{\mathbf{2}(\text{acetone})_2\}_n$.

an acetone/H_2O mixture (1:1). This compound was fully characterized spectroscopically (IR and ^1H and ^{19}F NMR) and by elemental analysis. The IR spectrum shows a $\nu(C\equiv C)$ absorption at 2085 cm^{-1}. This value is only slightly lower than that observed in the starting material **1** (2091 cm^{-1}), suggesting that the interaction of the thallium centers with the acetylenic fragments is probably weak. The room temperature ^1H and ^{19}F NMR spectra confirm the expected pairwise chemical equivalence of the alkynyl and pentafluorophenyl ligands (see Experimental Section). Although solvent-free crystals of **2** could not be obtained, crystals of an acetone adduct ($\{\mathbf{2}(\text{acetone})_2\}_n$) were prepared by slow diffusion of *n*-hexane into an acetone solution of **2** at low temperature (−40 °C). The single-crystal X-ray study has revealed a very unusual one-dimensional chain extending along the crystallographic *c* axis of the lattice. A short section of the chain is depicted in Figure 1, and selected interatomic distances and angles are presented in Table 1. The polymeric complex can be regarded as trinuclear octahedral fragments *trans,trans,trans*-$[PtTl_2(C_6F_5)_2(C\equiv C^tBu)_2]$ linked through weak alkynyl−thallium interactions. To our knowledge, this is the second heterometallic polymeric species assembled only by monoanionic alkynyl ligands characterized by X-ray crystallography,[4k] and it also increases the short list of examples containing platinum−thallium bonds.[7−11] The local geometry at the platinum center has some resemblance to that of the deceptively simple molecular compound $[Pt(CN)_4Tl_2]$,[8a,d] which contains a $Pt(CN)_4$ core and two axial Pt−Tl bonds. Thus, in the $\{$*trans,trans,trans*-$[PtTl_2(C_6F_5)_2(C\equiv C^tBu)_2](\text{acetone})_2\}$ building blocks, the thallium atoms sit above and below the square-planar *trans*-$Pt(C_6F_5)_2(C\equiv C^tBu)_2$ unit, completing an octahedral-like geometry at the platinum atom (see Figure 2), with the *cis* bond angles ranging from 72.0(3)° for C(9)−Pt(1)−Tl(1a) to 107.8(3)° for C(9)−Pt(1)−Tl(1) and nearly linear *trans* angles. Both Pt−Tl distances within the octahedral unit are 3.135(1) Å, similar to distances observed in other complexes with Pt(II)−Tl(I) interactions.[11a,b,e,14] It is remarkable to note that the thallium atoms do not bind to the alkynyl functions within the pseudooctahedral unit, as corresponding distances Tl(1)$\cdots$C(9a) = 3.165(13) Å and Tl(1)$\cdots$C(9) = 4.223(8) Å are well beyond a significant bonding interaction.

By contrast, both pentafluorophenyl groups are oriented in such a way that both *o*-F atoms on each ring are close to the Tl atoms. The Tl$\cdots$F distances [2.887(8) and 2.937(7) Å] are comparable to those observed in $[Tl\{Pt(C_6F_5)_4\}_2]^{2-}$ [7] but somewhat shorter than the Tl$\cdots$F distances observed in other related compounds.[9,15] Although the ^{19}F NMR spectrum of **2** at room temperature does not show coupling of the *o*-F resonance to the ^{203}Tl nuclei, this signal became very broad on cooling, suggesting that the Tl$\cdots$F interactions are partially lost in solution, even at low temperature. Nevertheless, these Tl$\cdots$F weak interactions contribute to the stability of the complex and clearly have an influence on the conformation of the C_6F_5 rings, as in other pentafluorophenyl Pt→M-containing complexes.[16] The dihedral angle between both rings is 71.5(5)°, and their respective angles to the C(1)C(5)C(9)C(9a)Pt(1) plane are 39.9(4)° [C(1)−C(4) ring] and 68.6(4)° [C(5)−C(8) ring]. In addition, an acetone molecule is weakly bonded to each thallium atom, the Tl−O distance [2.83(2) Å] being comparable to those found in other complexes[11b,13a,b] but clearly longer than the sum of the covalent radii (2.21 Å). This longer distance indicates a very weak Tl−O bond.

The resulting $\{$*trans,trans,trans*-$[PtTl_2(C_6F_5)_2(C\equiv C^tBu)_2](\text{acetone})_2\}$ units are assembled in such a way that the Tl atoms of each unit make a short secondary contact with the C_α atom of one of the alkynyl functions [Tl(1)−C(9c) = 2.905(10) Å]

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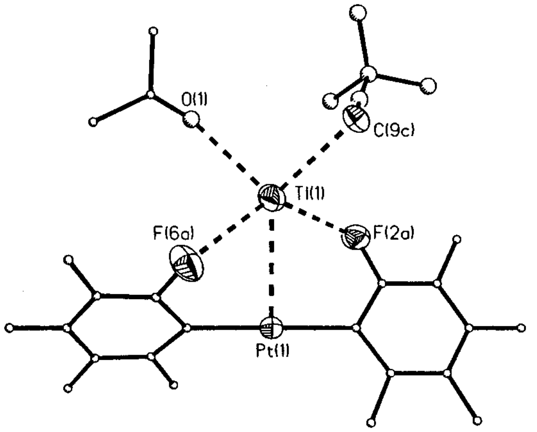

Figure 3. Thallium environment in $\{\mathbf{2}(\text{acetone})_2\}_n$.

of the next unit, which results in six-membered metallacycles ($Pt-Tl-C_\alpha-Pt-Tl-C_\alpha$) which run along the *c* axis. The $Tl-C_\alpha$ distance of 2.90(1) Å is much longer than $Ag-C_\alpha$ distances found in platinum−silver alkynyl complexes but comparable to Tl−C distances reported for cyclopentadienyl thallium arene complexes[17] and shorter than distances reported in thallium arene complexes (3.00−3.36 Å).[6] The Pt···Tl [3.785(1) Å] and Tl···Tl [3.982(1) Å] distances between units exclude any bonding interaction.

Figure 3 shows the thallium environment. From the crystallographic data it seems reasonable to assume that the bonding system between the Pt and Tl centers is similar to the one found in $[Pt(CN)_4Tl_2]$, for which theoretical analysis recently carried out supports a mainly ionic bonding between the Tl^+ and $[Pt(CN)_4]^{2-}$ ions with some covalent character and in which the correlation and the crystal field contributions are also important.[8b,d] In addition, the thallium centers establish weak interactions with F, O, and C atoms which are similar in strength to the Tl···N interactions observed in $[Pt(CN)_4Tl_2]$.[8d]

In acetone solution, **2** shows a significant electrical conductivity ($\Lambda_M = 20$ S cm^2 mol^{-1}), suggesting a partial Pt−Tl dissociation.

The optical properties of **2** show evidence of Tl−Pt bonding. The absorption spectrum of the starting precursor **1** in benzene solution ($\sim 5 \times 10^{-5}$ M) exhibits two intense bands at 278 and 300 nm, respectively. Increasing the concentration of **1** does not lead to a notable change of the spectrum; presumably, the absorptions at lower frequencies, if any, are too weak to reflect any change. It should be noted that bands at $\lambda > 300$ nm have been previously assigned to metal-to-ligand charge-transfer (MLCT) transitions.[18] The intense, high-energy bands observed are probably due to intraligand transitions. The absorption spectrum of thallium−platinum derivative **2** (benzene, $\sim 10^{-4}$ M) is significantly different and also shows two moderately red-shifted, prominent bands at 286 and 310 nm and an intense absorption at lower frequencies (386 nm), thus reflecting the presence of thallium centers. Upon photoexcitation, both **1** and **2** exhibit luminescence in the solid state.[13,18] For **2**, no emission was detected in solution at room temperature. The dotted line in Figure 3 shows the excitation spectrum obtained by monitoring the light intensity emitted at 640 nm. The luminescence of **1** upon excitation at 315 nm consists of a very broad band with its maximum at 620 nm (16 130 cm^{-1}) and full width at half-maximum (fwhm) of 4650 cm^{-1}. It shows an excitation maximum at 420 nm (23810 cm^{-1}) and another, more efficient, excitation at higher energies. According to previous spectroscopic reports,[18] the lowest energy excitation may be due to metal (d)→ligand (π^*) transitions (mlct) (ligand $C{\equiv}C^tBu$).

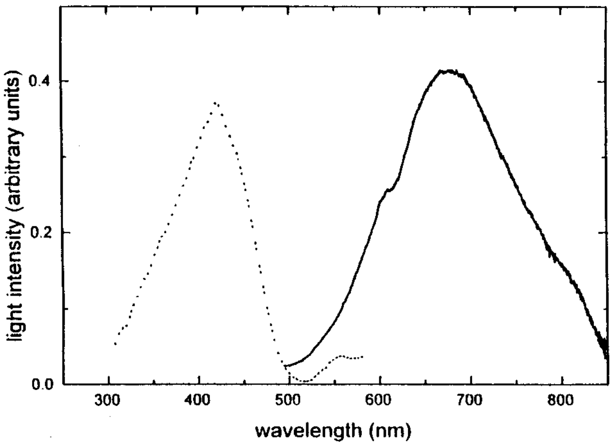

Figure 4. Luminescence spectrum of a solid sample of **2** upon excitation at 441 nm (solid line) and excitation spectrum monitoring the emission at 640 nm (dotted line).

Upon excitation ($\lambda = 441$ nm), **2** (Figure 4) exhibits a much more intense yellow luminescence, giving a broad emission band with a maximum at 678 nm (14 750 cm^{-1}) and fwhm of 3900 cm^{-1}. Excitation maxima for this band are observed at 555 (18 005 cm^{-1}) and 420 nm (23 700 cm^{-1}). In the solid state, two absorption features are observed at *ca.* 430 and 300 nm; the lower energy absorption matches well with the 420 nm excitation maximum. Although both complexes exhibit wide luminescence bands, as well as large Stokes shifts (7680 (**1**) and 3255 cm^{-1} (**2**), **2** shows a stronger luminescence, red-shifted with respect to that of **1**, which can be obviously related to the presence of Pt−Tl bonds. Tl^+ is luminescent, but its absorption and emission bands lie at higher energies. Consequently, as in **1**, luminescence may be ascribed to MLCT transitions, where the Pt metal and the ligand orbitals probably also have a contribution from the thallium orbitals. As in the related $[Pt(CN)_4Tl_2]$ complex,[8b] the two thallium centers in **2** probably stabilize the $[Pt(C_6F_5)_2(C{\equiv}C^tBu)_2]^{2-}$ fragment and lower the energy of the first empty orbitals, which could explain the observed shift to the red of the optical absorptions. Furthermore, the smaller Stokes shift in **2** indicates less modification of the electronic distribution upon optical excitation and, consequently, less relaxation to produce the luminescence. The presence of Tl orbitals in the initial and final states would diminish the Pt MLCT character of the transition. Further luminescence and structural studies of new platinum−thallium alkynyl complexes are in development.

Experimental Section

All manipulations were carried out in N_2 atmosphere using distilled solvents. The bidistilled H_2O used was routinely deoxygenated. The instruments and procedures used have been previously reported.[12] The optical absorption spectra have been registered in U-3400 Hitachi (solid) and Hewlett Packard 8452 A (benzene solution) spectrophotometers in the visible and near-UV ranges. Luminescence as well as excitation spectra have been corrected for instrumental response of the equipment using a standard calibrated tungsten−halogen lamp. The complexes *trans*-$[Pt(C_6F_5)_2(tht)_2]$[19] and **1**[12] were prepared as described elsewhere.

Preparation of $[PtTl_2(C_6F_5)_2(C{\equiv}C^tBu)_2]$ (2). (a) *trans*-$[Pt(C_6F_5)_2(tht)_2]$ (0.320 g, 0.454 mmol) was added at low temperature (−20 °C)

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Table 2. Crystallographic Data and Structure Refinement Parameters for $\{\mathbf{2}(\text{acetone})_2\}_n$

empirical formula	$C_{28}H_{30}F_{10}O_2PtTl_2$
formula weight	1192.35
crystal system	monoclinic
space group	$C2/c$
unit cell dimensions	$a = 16.197(3)$ Å
	$b = 23.537(3)$ Å
	$c = 11.002(1)$ Å
	$\alpha = 90°$
	$\beta = 122.88(1)°$
	$\gamma = 90°$
volume	3522.4(9) $Å^3$
Z	4
density (calcd)	2.248 Mg/m^3
absorption coeff	13.164 mm^{-1}
$F(000)$	2176
temp	200(1) K
radiation (graphite monochromator)	Mo Kα, $\lambda = 0.710\,73$ Å
R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0390$, $wR_2 = 0.0798$
R indices (all data)^a	$R_1 = 0.0741$, $wR_2 = 0.0958$

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2]^{1/2}$. $w = [\sigma^2(F_o) + (0.0479P)^2]^{-1}$; $P = [\max(F_o^2;0) + 2F_c^2]/3$.

to a freshly prepared solution of $LiC{\equiv}C^tBu$ (3.632 mmol) in diethyl ether (30 mL), prepared from $^tBuC{\equiv}CH$ and Li^nBu, and the mixture was stirred at room temperature for 24 h. The resulting white suspension was evaporated to dryness, and the residue was treated with water (~50 mL). The aqueous solution was filtered and added dropwise to a stirred solution of $TlNO_3$ (0.242 g, 0.908 mmol) in water (15 mL), causing the precipitation of **2** as a yellow solid. The resulting yellow suspension was stirred for 2 h and then filtered off, washed repeatedly with deoxygenated water, and finally air-dried (0.350 g, 70% yield).

(b) A solution of $TlNO_3$ (0.110 g, 0.413 mmol) in water (10 mL) was added to an acetone solution (10 mL) of $(NBu_4)_2[\textit{trans}\text{-}Pt(C_6F_5)_2(C{\equiv}C^tBu)_2]$ (**1**) (0.200 g, 0.170 mmol), and the mixture was stirred at room temperature for 3 h. The yellow solid formed was then filtered off and washed with water (0.08 g, 43% yield).

Anal. Calcd for $C_{24}H_{18}F_{10}PtTl_2$: C, 26.20; H, 1.65. Found: C, 27.19; H, 1.99. FAB(+) mass spectrum: m/z (relative intensity) 933 $[M - C_6F_5]^+$ (47), 1305 $[M + Tl]^+$ (33), other peaks 358 (92), 429 (100), 685 (42). IR(cm^{-1}): $\nu(C{\equiv}C)$ 2085(w); $\nu(C_6F_5)_{x-\text{sensitive}}$ 774(s). ^1H NMR ($CDCl_3$): at 15 °C, δ 1.10 (s, ^tBu). ^{19}F NMR ($CDCl_3$): at 15 °C, δ −113.59 (d, *o*-F, $^3J_{Pt-o-F} = 230$ Hz, coupling to thallium is not observed), −160.93 (tt, *p*-F), −162.61 (m, *m*-F); at −35 °C, δ −113.3 (vbr, *o*-F, ^{195}Pt satellites are not observed), −160.44 (tt, *p*-F), −162,67 (br, *m*-F). Λ_M (in acetone) = 20 S cm^2 mol^{-1}. Due to the low solubility of the complex, the ^{13}C NMR spectrum could not be registered.

X-ray Crystal Structure determination of $\{\textit{trans,trans,trans}\text{-}[PtTl_2(C_6F_5)_2(C{\equiv}C^tBu)_2](\text{acetone})_2\}$. A representative crystal of **2**(acetone)$_2$ of dimensions 0.50 × 0.18 × 0.10 mm was selected and mounted on a Siemens P4 four circle diffractometer. The basic crystallographic parameters for this complex are listed in Table 2. Data were collected at 200 K by the $\omega-2\theta$ scan technique. Three standard reflections measured at regular intervals showed no decay during data collection. Data reduction included an empirical correction (ψ scan method, 12 reflections, transmission factors = 1.000, 0.377). The structure was solved by the Patterson heavy atom method, which revealed the positions of the Pt and Tl atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses and refined with anisotropic thermal parameters. Hydrogen atoms were constrained to ride on their C atoms and located at fixed positions with the isotropic equivalent thermal parameter taken as $1.5U_{eq}(C)$. One acetone molecule was found to be present per asymmetric unit. A total of 2756 independent reflections were used to refine 207 parameters. Final residuals were $R_1 = 0.0390$ and $wR_2 = 0.0958$, with a quality of fit indicator of 1.028. The peaks above 1 e/$Å^3$ in the final difference map (three peaks of 1.40, 1.28, and 1.10 e/$Å^3$) are close to those of the Pt or Tl atoms and have no chemical significance.

All calculations were performed on a local area VAX cluster (VAX/VMS V5.5) with the Siemens SHELXTL PLUS[20] and SHELX 93[21] software packages.

Acknowledgment. We thank the Comisión Interministerial de Ciencia y Tecnología (Spain, Project PB 95-0003-CO2-01,-02) and the Universidad de La Rioja (Project 96PYB30ELP and a grant to J.G.) for financial support.

Supporting Information Available: Luminescence spectrum of **1** and skeleton diagram of the polymeric structure of **2** (2 pages). An X-ray crystallographic file, in CIF format, for **2** is available on the Internet only. Ordering and access information is given on any current masthead page.

IC970546V

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