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Synthesis, X-ray structure and magnetic properties of a unusual transition Co(II) complex with polychlorotriphenylmethyl radicals

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Abstract

A new cobalt(II) complex with a polychlorotriphenylmethyl radical ligand properly functionalized with a carboxylate group ($PTMMC^-$), $[Co(PTMMC)_2(py)_2(H_2O)_2]\cdot[Co(PTMMC)\ (py)_3(H_2O)(Cl)]_2\cdot 2py\cdot 2THF$ (**3**), has been synthesized and characterized including single-crystal X-ray diffraction. The structure of **3** consists of two different Co(II) units, $[Co(PTMMC)_2(py)_2(H_2O)_2]$ (**3A**) and $[Co(PTMMC)\ (py)_3(H_2O)(Cl)]$ (**3B**), which cocrystallize together with two molecules of pyridine and two molecules of THF. Its magnetic behaviour shows the presence of antiferromagnetic interactions between the PTMMC radicals and the Co(II) ions. The experimental data was fitted to a magnetic model based on the sum of a linear trimer ($S_{R1}\ldots S_{Co}\ldots S_{R2}$) and a dimer ($S_{Co}\ldots S_{R3}$) to give a Co(II)-radical exchange coupling of $J/K_B = -16.0$ K for both complexes.

Keywords: Molecular magnetism; Supramolecular; Carboxylate; Radical; Co(II) complexes; Hydrogen-bond

1. Introduction

The design of molecular materials with interesting magnetic properties has been one of the major challenges of the last few decades. More in detail, a great deal of work in molecular magnetism has focused on the so-called metal–radical approach that combines paramagnetic metal ions and pure organic radicals as ligating sites [1]. With this aim, organic free radicals having basic coordinating sites together with magnetic metal ions have been employed to design new complexes containing organic 2p and metal 3d hybrid spins. However, even though a large number of metal–radical systems have been studied, the variety of radical-based ligands used up to know is fairly limited. One of the most extensively used families is that of nitroxide-based radicals, namely nitroxides and α-nitronyl nitroxides radicals. In addition the weakly coordination ability of α-nitronyl nitroxides, new nitroxide radicals bearing different coordinating functionalities or a multi-coordination ability, have also been reported [2]. Besides nitroxide-based radicals, other examples of open-shell ligands used up to now are: (1) derivatives of the verdazyl radical family [3]; (2) *o*-quinone ligands that can be found in different accessible oxidation states, including the radical semiquinones (SQ^-) [4], (3) TCNE and TCNQ radical anions [5] and (4) diphenylcarbenes substituted with chemical function able to coordinate with metal ions [6].

Recently, we described, for the first time, the use of polychlorotriphenylmethyl (PTM) radicals as new ligands to obtain metal complexes following the metal–radical approach [7]. Among others, the main advantages of PTM radicals are their astonishing thermal and chemical stability and their rich redox behaviour. In such previous communication, we used a polychlorinated triphenylmethyl radical properly functionalized with a carboxylic group **1** (PTMMC) to obtain new transition metal complexes. Herein, we describe the synthesis and magnetic characterization of the sodium salt **2** and its use as new ligand to obtain a unusual Co(II) complex.

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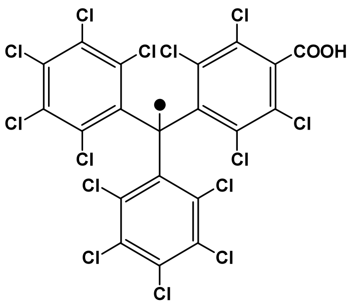
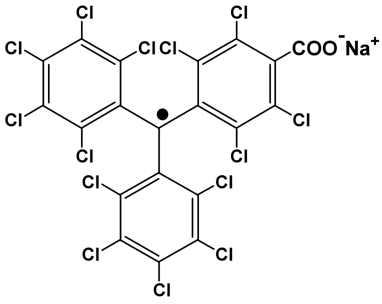


PTMMC (1)



(2)

2. Experimental

2.1. Materials

All the reagents were used as received and they were purchased from Aldrich. Solvents were distilled before use. In particular, THF was dried over sodium/benzophenone, and distilled under Argon. Thin-layer chromatography was performed on aluminum plates coated with Merck Silica gel 60 F_{254}. αH-4-[bis(2,3,4,5,6-pentaclorophenyl)methylene]-2,3,5,6-tetraclorophenylcarboxylic acid was prepared according to literature procedures [8]. All reactions were carried out in dark.

2.2. Physical measurements

Microanalyses were performed by the Servei d'Analisi of the Universitat Autònoma de Barcelona. The FT-IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer using KBr pellet. The UV–Vis spectra were acquired on a VARIAN Cary 5 instrument and the MS spectra on a JEOL JMS-DX 300 instrument. The ESR spectra have been recorded on X-band (9.3 GHz) Bruker spectrometer (ESP-300E). The g values were determined against the DPPH standard ($g = 2.0030$). Magnetic susceptibility measurements were obtained with a Quantum Design SQUID magnetometer.

2.3. Synthesis

2.3.1. $C_{20}Cl_{14}O_2Na$ (**2**)

A mixture of monoacid **1** (2.0 g, 2.6 mmol), powdered NaOH (5.5 g), ether (1200 ml) and DMSO (200 ml) was stirred for 58 h. The red mixture obtained was filtered through a sintered glass funnel over I_2 (2.4 g, 9.5 mmol), and the resulting solution was left undisturbed under argon for 24 h. The red residue was dissolved in ether and treated with aqueous $NaHSO_3$. Radical **2** was formed and extracted with a saturated solution of $NaHCO_3$, and the precipitate formed in the aqueous layer was filtered, cleaned with water and ether and dried under vacuum (Fig. 1).

Yield: 1.4 g (65%). M.p.: > 300 °C. *Anal.* Found: C, 30.48. Calc. for $C_{20}Cl_{14}O_2Na$: C, 30.35%. IR (KBr, cm^{-1}) 3656 (w), 1611 (w), 1389 (m), 1335 (w), 1323 (w), 1260 (m), 1037 (w), 916 (w), 815 (w), 733 (w), 767 (w), 673 (w), 638 (w), 616 (w), 577 (w), 519 (w). UV (THF; λ, nm; ε, $M^{-1}\cdot cm^{-1}$) 222 (70 580), 282 (sh, 4419), 348 (sh, 6955), 373 (sh, 16 830), 387 (30 960), 432 (1428), 526 (1392), 573 (1710). LDI-TOF/MS (*m/z*) 689, 663, 619. ESR (toluene/dichloromethane): g, 2.0029; line width, 1.2 G; hyperfine coupling constants: C^{13}(α), 29.5 G; C^{13}(aromatic, bridge), 13.2 G; C^{13}(aromatic, *ortho*), 10.4 G.

2.3.2. $[Co(PTMMC)_2(py)_2(H_2O)_2]\cdot[Co(PTMMC)(py)_3(H_2O)(Cl)]_2\cdot 2py\cdot 2THF$ (**3**)

An aqueous solution (10 ml) of $CoCl_2\cdot 6H_2O$ (0.015 g, 0.063 mmol) was dropwise added to a methanolic solution (30 ml) of **2** (0.100 g, 0.126 mmol) and stirred for 10 min at room temperature. A red microcrystalline solid (0.068 g) was isolated through filtering and dissolved in THF (10 ml). A solution of hexane (10 ml) containing pyridine (3 drops) was layered onto solution of THF. Slow diffusion over 20 days and slow evaporation of the resulting solution yielded red prism crystals of **3**.

Yield: 0.033 g (37%). M.p.: 271–273 °C. *Anal.* Found: C, 37.88; N, 2.94%; H, 1.45%. *Anal.* Calc. for $C_{138}H_{74}Cl_{58}Co_3N_{10}O_{14}$: C, 38.29%; N, 3.23%; H, 1.71%. IR (KBr, cm^{-1}) 1736 (w), 1634 (m), 1603 (m), 1525 (w), 1506 (w), 1488 (w), 1446 (m), 1398 (m), 1335 (s), 1324 (s), 1259 (m), 1219 (w), 1135 (w), 1120 (w), 1070 (w), 1041 (w), 1021 (w), 843 (w), 820 (w), 754 (m), 732 (m), 702 (m), 674 (w), 638 (w), 617 (w), 580 (w), 549 (w), 521 (w).

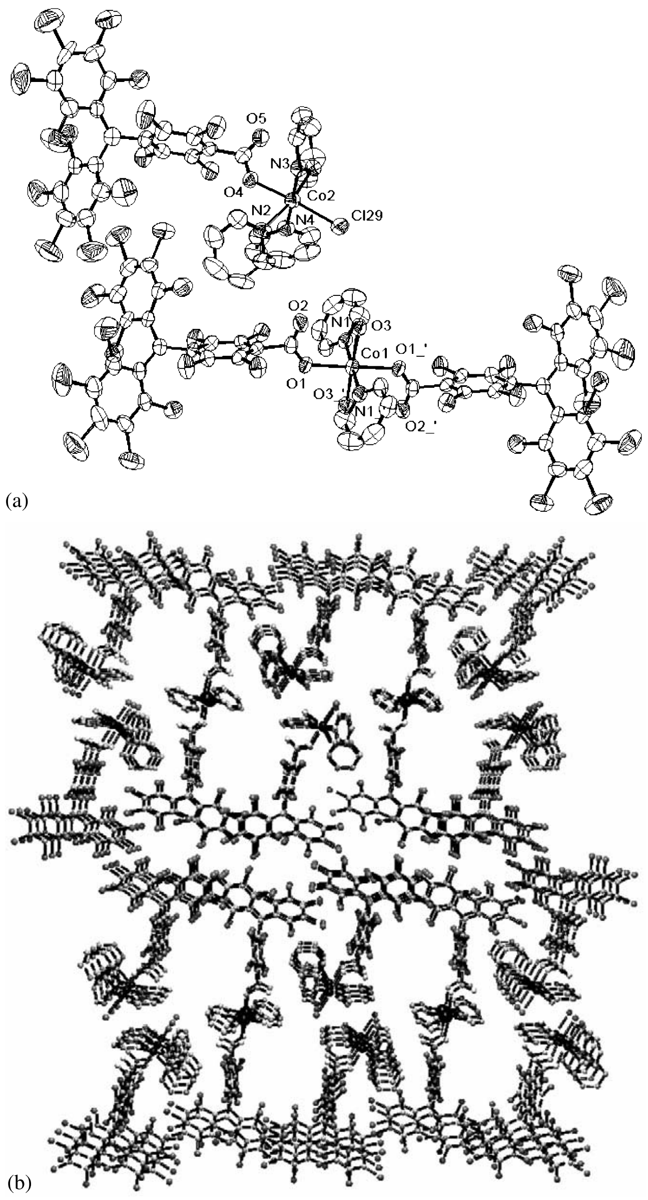


Fig. 1. Crystal structure of $[Co(PTMMC)_2(py)_2(H_2O)_2]\cdot[Co(PTMMC)(py)_3(H_2O)(Cl)]_2$ (**3**). (a) ORTEP drawing of **3** at the 50% probability level; (b) Crystal packing in the direction [1 0 0]. (Hydrogen atoms and THF and pyridine molecules are omitted for clarity.)

2.4. Structure determination

Crystal data of complex **3** were collected on a Nonius KappaCCD diffractometer with an area detector and graphite-monochromized Mo Kα radiation. The structure was solved by direct methods and refined by full-matrix least squares based on $|F_{obs}|$ using the program SHELXL-93. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms isotropically on calculated positions. The relevant crystal data are summarised in Table 1.

Table 1
Crystal data and structural refinement parameters for **3**

	$[Co(PTMMC)_2(py)_2(H_2O)_2]\cdot[Co(PTMMC)(py)_3(H_2O)(Cl)]_2\cdot2py\cdot2THF$ (**3**)
Empirical formula	$C_{138}H_{74}Cl_{58}Co_3N_{10}O_{14}$
Formula weight	4328.96
Temperature (K)	223(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.5863(4)
b (Å)	18.0840(7)
c (Å)	28.164(1)
α (°)	95.962(3)
β (°)	95.450(2)
γ (°)	101.243(3)
V (Å^3)	4236.2(3)
Z	1
D_{calc} (M gm^{-3})	1.697
Absorption coefficient (mm^{-1})	1.266
F(0 0 0)	2151
Crystal size (mm)	0.25 × 0.15 × 0.05
θ Range for data collection (°)	1.0–21.0
Index ranges	$0 \leq h \leq 8$, $-17 \leq k \leq 17$, $-27 \leq l \leq 26$
Reflections collected	13 718
Independent reflections	7807
Absorption correction	none
Observed reflections	7807
Number of parameters	1023
Number of restraints	4
Goodness-of-fit on F^2	1.016
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0548$, $wR_2 = 0.1199$

3. Results and discussion

3.1. Crystal structure

Despite recurrent recrystallization experiments, the obtaining of single crystals of salt **2** was not possible. Otherwise, high-quality crystals of **3**, suitable for single crystal X-ray diffraction analysis, were obtained directly from slow evaporation of the reaction liquors.

3.1.1. $[Co(PTMMC)_2(py)_2(H_2O)_2]\cdot[Co(PTMMC)(py)_3(H_2O)(Cl)]_2\cdot2py\cdot2THF$ (3)

Complex **3** crystallizes in the $P\bar{1}$ triclinic space group with the cell parameters reported in Table 1. The ORTEP plot of **3** including an atom-numbering scheme is shown in Fig. 1(a). The crystal structure analysis showed a cocrystallization of two different units of Co(II), $[Co(PTMMC)_2(py)_2(H_2O)_2]$ (**3A**) and $[Co(PTMMC)(py)_3(H_2O)(Cl)]$ (**3B**) in a proportion of 1:2, respectively. The first complex **3A** consists of a complex of Co(II) ion that adopts a octahedral coordination polyhedron formed by two monodentate carboxylic groups [O(1),

Table 2
Bond distances (Å) and bond angles (°) involving the Co(II) ions

	3A
Bond distances	
Co(1)–O(1), Co(1)–O(1)′	2.118(5)
Co(1)–N(1), Co(1)–N(1)′	2.174(6)
Co(1)–O(3), Co(1)–O(3)′	2.073(5)
Bond angles	
O(1)–Co(1)–O(1)′	180.00(8)
O(3)–Co(1)–O(1), O(3)′–Co(1)–O(1)′	90.1(2)
O(3)–Co(1)–O(1)′, O(3)′–Co(1)–O(1)	89.9(2)
O(3)–Co(1)–O(3)′	180.0(4)
N(1)–Co(1)–O(1), N(1)′–Co(1)–O(1)′	90.7(2)
N(1)–Co(1)–O(1)′, N(1)′–Co(1)–O(1)	89.3(2)
N(1)–Co(1)–O(3), N(1)′–Co(1)–O(3)′	89.2(2)
N(1)–Co(1)–O(3)′, N(1)′–Co(1)–O(3)	90.8(2)
N(1)′–Co(1)–N(1)	180.0(3)
	3B
Bond distances	
Co(2)–O(4)	2.101(5)
Co(2)–O(6)	2.150(5)
Co(2)–N(2)	2.175(7)
Co(2)–N(3)	2.158(6)
Co(2)–N(4)	2.139(6)
Co(2)–Cl(29)	2.403(2)
Bond angles	
O(4)–Co(2)–O(6)	86.6(2)
O(4)–Co(2)–N(2)	82.1(2)
O(4)–Co(2)–N(3)	91.0(2)
O(4)–Co(2)–N(4)	86.9(2)
O(4)–Co(2)–Cl(29)	176.89(16)
O(6)–Co(2)–N(2)	168.4(2)
O(6)–Co(2)–N(3)	90.5(2)
O(6)–Co(2)–N(4)	86.9(2)
O(6)–Co(2)–Cl(29)	96.23(16)
N(2)–Co(2)–N(3)	92.5(2)
N(2)–Co(2)–N(4)	89.7(3)
N(2)–Co(2)–Cl(29)	94.98(19)
N(3)–Co(2)–N(4)	176.7(2)
N(3)–Co(2)–Cl(29)	90.24(17)
N(4)–Co(2)–Cl(29)	92.0(2)

Table 3
Details of hydrogen bonding distances (Å) and angles (°)

D–H···A	D–H	D···A	H···A	D–H···A (°)
Complex 3A				
O(3)–H(3A)···O(2)	0.8973	1.7724	2.6521	166.03
O(3)–H(3B)···N(5)	0.8972	1.8693	2.7445	164.54
C(61)–H(61)···O(1)	0.94	2.5675	3.4077	148.98
C(68)–H(68A)···Cl(5)	0.98	2.7770	3.7223	162.22
Complex 3B				
O(6)–H(6A)···O(5)	0.9009	1.8420	2.7086	160.68
O(6)–H(6B)···Cl(29)	0.8983	2.3241	3.1821	159.75
C(46)–H(46)···O(4)	0.94	2.5721	2.9142	101.86
C(52)–H(52)···O(6)	0.94	2.5553	3.3897	148.06
C(60)–H(60)···Cl(29)	0.94	2.7948	3.3338	117.42
C(64)–H(64)···O(5)	0.94	2.4756	3.3148	148.66
C(66)–H(66A)···Cl(15)	0.98	2.681	3.6333	164.04
C(67)–H(67A)···Cl(23)	0.98	2.3818	3.2846	152.89

O(1)′], two water ligands [O(3), O(3)′] and two pyridine ligands [N(1), N(1)′]. The second unit **3B** is an octahedral Co(II) complex also formed by a monodentate carboxylic group [O(4)], three pyridine ligands [N(2), N(3), N(4)], a water molecule [O(6)] and a chlorine atom [Cl(29)]. Two molecules of pyridine and two molecules of THF are included in the cell.

The bond distances and angles around the Co(II) atoms of both units are shown in Table 2. It is interesting to note that due to the great steric hindrance of the chlorine atoms in *ortho* positions with respect the carboxylic group of PTMMC ligands, the latter groups are twisted by 73° [**3A**] and 79° [**3B**] with respect to the phenyl plane to which it is bonded.

A view down in the [1 0 0] direction (Fig. 1b) shows an alternation of **3A** and two confronted **3B** units along the [0 1 0] direction. This conformation is further stabilized by several intra and intermolecular strong hydrogen bonds and chlorine–chlorine contacts (see Table 3). In complex **3A**, the non-coordinative oxygen atom O(2) of ligand PTMMC is the acceptor in the O–H···O with the oxygen atom O(3) of the water ligand. In complex **3B**, also the non-coordinative oxygen atom O(5) forms a hydrogen bond with the oxygen atom O(6) of the water ligand, while the same oxygen atom O(6), the coordinative oxygen atom O(4) and the chlorine atom Cl(29) are the acceptor in the C–H···O and the C–H···Cl with the C(52), C(46) and C(60) of a pyridine group, respectively. Each confronted **3B** units are connected to each other through an intermolecular hydrogen bond O–H···Cl between coordinated chlorine atom Cl(29) and oxygen atom O(6). This stabilization is completed through other hydrogen bonds, and π–π interactions between pyridine and THF molecules of crystallization (Table 3).

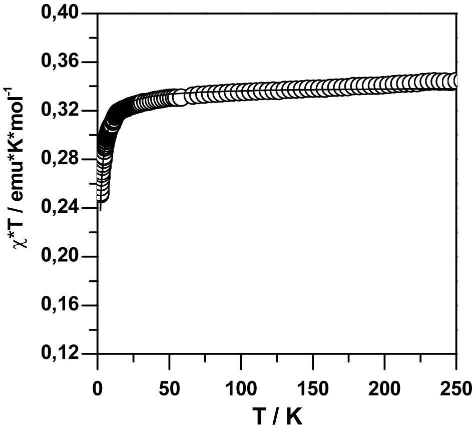


Fig. 2. Plot of $\chi_{\mathrm{mol}}T$ vs. T for PTMMCNa (**2**). The solid line is theoretical one as described in the text.

3.2. Magnetic properties

Magnetic susceptibility data of a polycrystalline sample of radical **2** was measured in the interval of 2–300 K with an external applied field of 1 kG. The $\chi_{\mathrm{mol}}T$ vs. T curve for radical **2** is shown in Fig. 2. At room temperature the $\chi_{\mathrm{mol}}T$ value is 0.34 emu K mol^{-1}, which is close to the theoretical one ($\chi_{\mathrm{mol}}T = 0.375$ emu K mol^{-1}) calculated for an isolated $S = 1/2$ spin. The $\chi_{\mathrm{mol}}T$ value is constant for the whole range of studied temperatures, decreasing at low temperatures due to the presence of weak intermolecular antiferromagnetic interactions. Experimental data was fitted to a Curie–Weiss model to give a molar Curie constant of 0.34 cm^3 K mol^{-1} and a Weiss constant of -0.9 K. In spite of the absence of its crystal structure, Cl···Cl contacts might be responsible for this weak antiferromagnetic interactions, as seen in other chlorinated triphenylmethyl radicals derivatives [8,9].

Magnetic susceptibility of a microcrystalline sample of complex **3** was performed in a temperature range of 2–300 K with an external magnetic field of 1 kG. The $\chi_{\mathrm{mol}}T$ vs. T curve for complex **1** is shown in Fig. 3. The $\chi_{\mathrm{mol}}T$ value at room temperature is 8.40 emu K mol^{-1} and it decreases gradually with decreasing the temperature, which suggests the existence of antiferromagnetic interactions between Co(II) ions and radicals.

In octahedral Co(II) complexes the orbital contribution must generally be included in order to interpret the low-temperature magnetic behaviour. Due to the difficulties to make an analysis with the orbital contribution, the higher temperature magnetic susceptibility data was only fitted above 50 on the basis of the sum of two models: a linear three-spin model ($S_{R1}\ldots S_{Co}\ldots S_{R2}$; $H = -2JS_{Co}(S_{R1}+S_{R2}) - 2J'S\ S_{R1}\cdot S_{R2}$) for **3A** [10] and a dimer model ($S_{Co}\ldots S_{R3}$; $H = -2J''\ S_{Co}\cdot S_{R3}$) for **3B** [11], which were deemed to be appropriate on the basis of the X-ray crystal structure. The least-squares fitting gave $J/K_B = -16.0$ K, $J'/K_B = -2.9$ K and $g_{Co} = 2.437$ for **3A** and $J''/K_B = -16.0$ K and $g = 2.164$ for **3B** and a $\theta = -0.7$ K. Such exchange coupling constants between Co(II) and PTMMC radicals are similar to those previously reported for Cu(II) complexes [7].

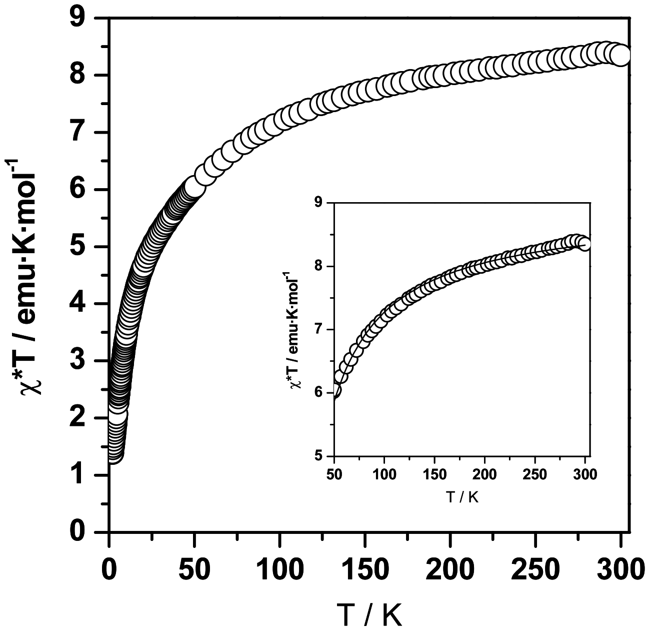


Fig. 3. $\chi_{\mathrm{mol}}T$ vs. T for $[\mathrm{Co(PTMMC)_2(py)_2(H_2O)_2}]\cdot[\mathrm{Co(PTMMC)(py)_3(H_2O)(Cl)}]_2$ (**3**). Insert $\chi_{\mathrm{mol}}T$ vs. T in the range of 50–300 K. The solid line represents the best-fit calculated data.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 194815 for complex **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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